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## 35 Abstract

Strict air pollution restrictions have increased the need for effective low-temperature selective 36 37 catalytic reduction (LT-SCR) of NO<sub>x</sub> with hydrocarbons (HC), and as such, mixed metal oxides and clay minerals supported catalysts have received significant attention. Pillared interlayered 38 clay (PILC) materials use clay mineral as a raw material for catalyst support coupled with metal 39 40 oxide particles to provide a porous structure between clay mineral layers through ion exchange. PILC has been widely used in catalysis and adsorption applications, due to its meso-microporous 41 structure, good surface acidity, large specific surface area, adjustable pore size, interlayer ion-42 exchange nature, and good thermal stability. It is a widely used catalyst carrier material with 43 44 excellent performance for LT-SCR of NO<sub>x</sub> with HC. Notably, the montmorillonite (Mt) based Cu- and Fe-PILC catalysts exhibited a high LT-SCR activity, which can be assigned to the 45 excellent redox capability of the co-existing Fe<sup>III</sup>/Fe<sup>II</sup> and Cu<sup>II</sup>/Cu<sup>I</sup>. In addition, the presence of 46 47 Cu<sup>II</sup> isolated species, as well as the strong interaction between Fe, Cu, and PILC support is believed to increase the SCR activity. This review study is primarily focused on the clay mineral 48 importance and Mt-based PILC-supported catalysts for LT-SCR of NO<sub>x</sub> with HC. In addition, the 49 SCR performances of various metals-supported PILC-based catalysts were compiled, in order to 50 study their proposed reaction mechanisms, the influence of metal loading, effects of O<sub>2</sub>, H<sub>2</sub>O, 51 52 and SO<sub>2</sub> poisoning for HC-SCR of NO<sub>x</sub> conversion. This study provides a detailed review of Mt-53 based PILC catalysts for LT-SCR technology, including recent challenges and future prospects. 54 Keywords: Montmorillonite; Pillared interlayered clay; Low-temperature selective catalytic 55 reduction; NO<sub>x</sub>; Hydrocarbons

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#### 58 1. Introduction

Air pollution has become a serious environmental issue in recent years and is continuously 59 affecting the natural characteristics of the atmosphere such as environment temperature, gaseous 60 contents, humidity level, and the ozone layer, etc. Motor vehicles and coal-fired power plants are 61 62 the two main sources to emit pollutants (e.g.,  $NO_x$ ,  $SO_x$ , and  $CO_2$ ) into the atmosphere. Nitrogen 63 oxides (NO<sub>x</sub>) are one of the major atmospheric pollutants, mainly composed of NO (>90%), NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O, and N<sub>2</sub>O<sub>5</sub>, which cause detrimental impacts on the environment and human 64 health. NO<sub>x</sub> is not only the reason for nitric acid rain but also the formation of ground ozone ad 65 photochemical smog via reacting with volatile organic compounds (VOC) through a series of 66 reactions (Peng et al., 2014; Liu et al., 2017; Xu et al., 2017; Alzaky et al., 2021). Further, NO<sub>x</sub> 67 could also react with ozone in the stratosphere, leading to the destruction of the ozone layer 68 (Wang et al., 2021; Zhang et al., 2021). Medical studies have proved that NO<sub>x</sub> can easily combine 69 70 with the hemoglobin in the human blood to cause methemoglobinemia, which can lead to the symptoms, such as shock and respiratory failure, while NO<sub>2</sub> can stimulate the lungs and cause 71 respiratory diseases such as asthma (Li et al., 2021; Zhang et al., 2021). NO<sub>x</sub> sources, chemical 72 73 transformations, and their effects on the environment and the human body are presented in Fig. 74 Error! Not a valid bookmark self-reference.<sup>1</sup>.

Very recently, the selective catalytic reduction with hydrocarbons (HC-SCR) over clay mineral catalysts has become a new research focus (Dong et al., 2018; Yuan et al., 2019; Kashif et al., 2020, 2022). The sources of hydrocarbon compounds are very abundant and cost-efficient. For instance, methane, and ethane are the main components of natural gas, and their corresponding application cost is very low (Pels and Verhaak, 2000; Zhao et al., 2020; Yedala and Aghalayam, 2022). Generally, flue gases from stationary gas-fired boilers and exhaust gas from vehicles

81	contain a small amount of incompletely combusted hydrocarbon compounds, which can react
82	with $NO_x$ to form $O_3$ and cause secondary pollution. Therefore, HC-SCR technology can
83	simultaneously eliminate both the $NO_x$ and the unburned HC. The critical point in this
84	technology focuses on the design and synthesis of effective catalysts for HC-SCR. In the past
85	years, many studies have reported on the synthesis methods of different catalysts, types of
86	carriers, catalyst stability, and $NO_x$ conversion rate under different reaction conditions (Mrad et
87	al., 2015; Yuan et al., 2018, 2019; Halepoto et al., 2020; Kashif et al., 2020, 2022; Khan et al.,
88	2020; Wen et al., 2020; Tang et al., 2022; Vignesh and Ashok, 2022; Xu et al., 2022; Yedala and
89	Aghalayam, 2022). Metal oxide-supported catalysts have been found to be easy to prepare and
90	have good hydrothermal stability at high temperatures (above 400 °C) under high space velocity
91	conditions (Miyahara et al., 2008; Mrad et al., 2015; More, 2017). Precious metal catalysts such
92	as platinum, silver, rhodium, gold, and palladium supported on Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , TiO <sub>2</sub> , and ZrO <sub>2</sub> ,
93	showed good NO <sub>x</sub> reduction and better resistance to SO <sub>2</sub> and water vapor above 400 °C (Zhou et
94	al., 2018; Jia et al., 2021; Yedala and Aghalayam, 2022) but they usually have a relatively low $N_2$
95	selectivity and they may produce N2O as an undesired by-product. In this respect, three-way
96	catalysts (TWC) were prepared to carry out multiple oxidation reactions and reduction reactions
97	simultaneously to convert air pollutants (NO <sub>x</sub> , CO, and unburned HC) in the exhaust into
98	harmless gases such as N2 and H2O (Obuchi et al., 1993; Kobayashi et al., 2001). However,
99	under the condition of excessive oxygen, the TWC cannot effectively reduce $NO_x$ into $N_2$ and it
100	is difficult to meet the exhaust emission requirements. The main disadvantages of precious metal
101	catalysts lie in the facts, e.g., high cost, limited reserves, and a narrow temperature activity
102	window (Mrad et al., 2015). Therefore, they are not suitable for the treatment of large-scale
103	stationary sources of $NO_x$ .

104	Clay and clay mineral-based materials play a significant role in the everyday life and industrial
105	activities of modern society. The development and utilization of raw clays and clay minerals can
106	be traced back to the distant Neolithic age (Zhou and Keeling, 2013; Singh, 2022). Nowadays,
107	these clay and clay minerals play an important role in absorption (e.g., methylene blue),
108	adsorption (e.g., heavy metals removal and organic contamination), sorption (e.g., water and oil),
109	and catalysis (e.g., CO <sub>2</sub> capture, NO <sub>x</sub> reduction, and organic reactions). Clay mineral-based
110	catalysts have generated interest in the pharmaceutical, chemical industries, and petroleum
111	refineries (Bergaya et al., 2006; Zhou and Keeling, 2013; Kumar Dutta et al., 2015; Kurian and
112	Kavitha, 2016).
113	The long history of pillared interlayered clay (PILC) started in the 1950s, but the first extensive
114	studies appeared from the 1970s (Barrer and MacLeod, 1954; Brindley and Sempels, 1977;
115	Yamanaka and Brindley, 1979; Vaughan, 1988; Maes et al., 1997; Cool and Vansant, 1998).
116	Porous clay mineral modified by polyoxocations was successfully prepared for the first time,
117	which uses clay minerals, e.g., montmorillonite (Mt), saponite (Sep), hectorite (Ht), and
118	beidellite (Bd) as raw material and metal oxide as pillars to build a porous structure between the
119	clay mineral layers through cation exchange after calcination. PILC has micro-mesoporous
120	formation, large specific surface area, strong surface acidity, and thermal stability (Su et al.,
121	2020; Wen et al., 2020; Macías-Quiroga et al., 2022). Clay mineral-based catalysts also naturally
122	function as Brønsted and Lewis acids or both (Kashif et al., 2019, 2020, 2022; Su et al., 2020;
123	Wen et al., 2020). PILC catalysts have been used as a green environmental catalytic material
124	(Kumar et al., 2014) and have been studied for biosensor development (An et al., 2015),
125	pollution remediation (Pandey and Saini, 2018), enzyme immobilization (Cheng et al., 2006),
126	wastewater treatment (Najafi et al., 2021), and NO oxidation and reduction reactions (Fernandes

127	et al., 2013). In addition, PILC catalysts have been applied as active solid materials in
128	photocatalysis, catalytic wet air oxidation (CWAO) (Zhou et al., 2014), catalytic wet peroxide
129	oxidation (CWPO), fenton processes for toxic organic pollutants in waste water (Baloyi et al.,
130	2018) and the combustion of toluene (Torres et al., 2021). Therefore, PILC has a broad variety of
131	types and applications (Bergaya et al., 2006; Vicente et al., 2013; Kumar Dutta et al., 2015).
132	PILC catalysts modified with transition metals, precious metals, and rare earth metal ions can be
133	more effective for the NO <sub>x</sub> conversion with HC (Yang and Li, 1995; Belver et al., 2004a, b;
134	Sadykov et al., 2005; Li et al., 2011; Lu et al., 2011). The cations-exchange nature of clay
135	minerals and the interlayer oxide pillars support effectively improve the thermal stability of this
136	type of catalyst. Changing the metal species between the interlayered clay minerals via cation
137	exchange can improve the $NO_x$ conversion at low temperatures and a series of experimental
138	studies broadly investigated the reactivity of PILC-based catalysts for the HC-SCR of $NO_x$ and
139	the SCR reaction mechanism by in-situ diffuse reflectance infrared Fourier transform (DRIFT)
140	spectroscopic study (Qian et al., 2017; Dong et al., 2018; Su et al., 2020; Wen et al., 2020). All
141	the results demonstrated that the PILC-based catalysts were active for HC-SCR and it was
142	possible to lower the reaction temperature by introducing a second metal to modify the catalysts
143	(Qian et al., 2017; Dong et al., 2018; Su et al., 2020). Therefore, the design and preparation of
144	innovative and suitable catalysts based on clay minerals for $NO_x$ conversion with HC have
145	become a key concern.
146	The current study represents a review of PILC materials, with a special focus on the LT-SCR of
147	$NO_x$ with HC as reductants. Herein, the emphasis is placed on SCR performance, possible
148	reaction mechanisms, types of active sites, the effect of metal loading, the influence of the

carrier, the effect of reaction conditions, and the influence of O<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>O over metal-149

### 150 supported Mt-based PILC catalysts.

# 151 **2. Pillared interlayered clay (PILC)**

PILC is a porous material with great research interest and application prospects in different 152 environmental and chemical processes (Macías-Quiroga et al., 2022). This type of clay is 153 typically prepared by introducing different multivalent cations, such as Fe<sup>III</sup>, Al<sup>III</sup>, Ti<sup>IV</sup>, Zr<sup>IV</sup>, 154 155 Ga<sup>III</sup>, and many others, which can form polycations and later on, the oxide pillars formed inside the interlayer space after calcination. The typical method for the preparation of PILC involves (1) 156 157 the preparation of a clay mineral suspension solution and a pillaring polyoxocations solution; (2) the cation exchange between interlayer inorganic cations of the clay mineral and polyoxocations 158 (dilute solution of the single or mixed metal precursors) in the clay suspension solution; and (3) 159 the treated clay is calcined to anchor the pillars and to covert the polyoxycations to its oxide 160 form at the same time, typically with calcination temperatures ranging from 350 to 600 °C (Gil et 161 al., 2008, 2011; Su et al., 2020; Wen et al., 2020), leading to stable materials with a higher basal 162 163 spacing, compared to the host clay mineral.

- Natural interlayered clay materials have a wide range of sources and abundant reserves in a
  broad variety of types, including the most common Mt for LT-SCR of NO<sub>x</sub> with HC. These clays
- 166 have stable pillars by metal oxide in the interlayer of clay structure to improve stability and their
- 167 unique interlayer cation exchange characteristics can be used in the synthesis and modification of
- 168 different materials (Kloprogge, 1998). They have excellent chemical and physical properties,
- 169 e.g., large specific surface area, porosity, and acidity that make them attractive for use in solid
- 170 material, chemical, and electrochemical industries (Gil et al., 2008; Stagnaro et al., 2012;
- 171 Macías-Quiroga et al., 2022).
- 172 Specifically, PILC prepared using Mt as a raw material has good hydrothermal stability, strong

surface acidity, a large specific surface area, and adjustable pore size (Su et al., 2020; Wen et al., 173 2020). Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> are typically present in the interlayer space between the layers of Mt 174 as compensatory cations for the charge imbalance. The cations are only partially located in the 175 hexagonal cavity in the case of complete dehydration. Normally though the hydrated interlayer 176 177 cations are located near the negative charge locations on the siloxane surfaces. After being treated with water, these cations move to the interlayer space where they can be exchanged with 178 a variety of organic/inorganic cations, such as Al<sup>3+</sup>, Fe<sup>3+</sup>, H<sub>3</sub>O<sup>+</sup>, alkylammonium (R<sub>4</sub>N<sup>+</sup>), 179 phosphonium  $(R_4P^+)$ , ammonium  $(NH_4^+)$  and tetramethylammonium (TMA). This is one of the 180 most useful properties of the Mt. Mt-based catalysts also function as Lewis acid sites, Brønsted 181 acid sites, or both. Al<sup>III</sup> and Fe<sup>III</sup> at the crystal edges are sources of the Lewis acidity in the Mt 182 and it can be enhanced by exchanging the interlayer space cations Na<sup>+</sup> and Ca<sup>2+</sup> by treating the 183 clay minerals with Al<sup>3+</sup> in dilute pillaring solutions (e.g., AlCl<sub>3</sub> or Al(NO<sub>3</sub>)<sub>3</sub>). The primary source 184 of the Brønsted acidity of clay minerals is intercalated water molecules which are coordinated to 185 interlayer cations between the clay mineral layers (Yotsuji et al., 2021). 186 In the very early research stage, Barrer and McLeod prepared PILC materials with Mt for the 187 188 sorption of polar and non-polar gases. Since then, over the last five decades, extensive and intensive research has been conducted on this material including synthesis methods, 189 190 physicochemical properties by different characterization methods, and application in catalytic 191 reactions and removal of various pollutants (Chae et al., 2001; Ding et al., 2001; Hart and Brown, 2004; Reddy et al., 2007; Gil et al., 2008; Vicente et al., 2013). In general, the synthesis 192 of this type of material is to introduce a target cation into the interlayer space of clay minerals 193 through cation exchange. After calcination (350 to 600 °C), these groups undergo 194 195 dehydroxylation to form stable oxide "pillars", which are anchored on the clay mineral layers

196 surfaces inside interlayer spaces, keeping them separated.

197 In more detail, the synthesis steps for PILC generally include (1) pretreatment of Mt with NaCl and the exchange of Na<sup>+</sup> ions with a large hydration radius into the clay mineral layers, which 198 supports the full exchange of cations between the clay mineral layers; (2) making an appropriate 199 200 dilute pillaring polyoxocations solution for the full exchange process by adjusting the precursor 201 concentration, and pH value and (3) drying and producing the final PILC material after calcination (350 to 600 °C). At certain conditions (e.g., temperature, time, pH, and addition of 202 203 the polyoxocations pillaring solution to the clay suspension), interlayer cations of sodium Mt and 204 pillaring cations are exchanged between the interlayer space of the clay mineral layers. The target cations are exchanged into the interlayer space between the clay mineral layers at specific 205 conditions and finally, the treated clay mineral is calcined at the exact temperature (350 to 206 600 °C) as shown in Fig. 2a. In other words, cationic clay interacts with an inorganic pillaring 207 208 solution in the cation exchange process, and after the maximum level of cation exchange reaction, it compensates the clay mineral layers by the negative charge. Finally, a calcination 209 process (350 to 600 °C) converts the metal cations into stable oxide pillars. These specific 210 211 conditions (e.g., temperature, time, pH, and addition of the polyoxocations pillaring solution to 212 the clay suspension) play a significant role in the formation of PILC and rigid oxide pillars. 213 Different types of PILC materials, such as titanium dioxide (TiO<sub>2</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and 214 iron oxide ( $Fe_2O_3$ ) can be prepared by changing the types of interlayer exchange ion groups (Yang and Li, 1995; Ding et al., 2001; Yang and Cheng, 2002; Bergaya et al., 2006; Manohar et 215 al., 2006; Vicente et al., 2013; Bahranowski et al., 2015; Torres et al., 2021). The PILC material 216 is a group of micro-mesoporous solid formations with a good porosity and a high specific surface 217 218 area. Mt-based-PILC catalysts reveal disordered flaky external surfaces and a layered structure,

to form a chaotic porous structure by adhering together with different angles as observed in Fig. 219 220 2b. In general, the surface morphology of all PILC depends on the drying conditions (e.g., temperature, surrounding environment). A slow-drying condition (air drying) generates a more 221 ordered arrangement of the crystalline phases, while a fast-drying method (frozen drying) fixes 222 223 the crystalline phases in random orientation in the slurry stage, which is known as a 'house of 224 cards' structure (Maes et al., 1996, 1997). Further, the surface morphology of PILC catalysts is observed as irregular and distributed with different-sized particles, which could be a reason for 225 the different particle sizes of metal oxides (Fig. 2b). In addition, the PILC catalyst displays 226 227 mainly slit-like pore shapes with a layered structure. However, as also observed from TEM images, there were no larger particles on the surface of the PILC catalyst (Su et al., 2020). It is 228 believed that oxides were intercalated into the interlayer of the clay mineral or supported (using 229 the impregnation method) on the surface in the form of nanoparticles. Furthermore, as can be 230 observed in Fig. 2b (E) the Pd-consisted particles were exhibited as dots and they can be 231 determined from the less dense support (Mt-based PILC) material. In other words, the images 232 show that impregnation results in the formation of nanoparticles, spread across the external 233 234 surface of the support. As observed in the HRTEM image of Mt-based Pd-Zr-PILC catalyst (Fig. 235 **2b**, **F**), according to analysis with the corresponding selected area electron diffraction (SAED) 236 patterns, Pd is existing in the catalysts in the form of PdO nanocrystals. In addition, the presence of PdO nanoparticles suggests that a hydrolytic transformation of Pd<sup>II</sup> occurs upon impregnation, 237 238 and polymeric species rather than monomeric Pd species become anchored to the PILC support (Michalik-Zym et al., 2015). On the other hand, mixed metal PILC-based catalysts exhibit high 239 acidity, tunable pore size, and the nature of bimodal pore size distribution with pore size larger 240 241 than zeolites-based catalysts. However, the pore distribution often shows two peaks due to a

242 mixture of different species in the resulting mixed oxide pillars, which is referred to as the

243 bimodal distribution (Seefeld et al., 1995), which is more beneficial for the catalytic reaction

244 (Carriazo et al., 2008; Rejeb et al., 2016). Further details on the active sites and reaction

245 mechanism will be discussed in sections **3.1** and **3.6**.

## 246 **3. PILC-based catalysts**

247 As green and eco-friendly catalytic materials, PILC-based catalysts have attracted much attention with great potential in different applications. For example, the PILC structure and the properties 248 of the oxide pillars are adjustable and suitable for use as a carrier, so it can be used in several 249 250 fields such as the chemical industry and environmental pollutant removal (Gil and Vicente, 2020; Chmielarz and Dziembaj, 2021; Nagendrappa and Chowreddy, 2021; Serwicka, 2021; Li et al., 251 2022; Macías-Quiroga et al., 2022; Tesfay Reda et al., 2022). To date, Mt has been widely used 252 253 as a host material in the preparation of several types of PILC for NO<sub>x</sub> reduction with HC (Table 254 1). The PILC prepared with Mt have a large pore diameter (~8 to 12 nm), specific surface area  $(\sim 150 \text{ to } 270 \text{ m}^2/\text{g})$ , and a regular pore structure, and it can simultaneously function as Brønsted 255 acid and Lewis acid sites for catalytic reactions (Reddy et al., 2009; Su et al., 2020; Wen et al., 256 257 2020). As reported in previous studies (Maes et al., 1997; Konin et al., 2001; Yang and Cheng, 258 2002; Carriazo et al., 2008; Kumar et al., 2014; Lu et al., 2015; Asgari et al., 2021; Yotsuji et al., 259 2021), the pore size or interlayer free spacing of a PILC can be altered by changing the pillaring 260 species (Al, Zr, Fe, Ti). Considering the cation exchange capacity (CEC) of the Mt, the height 261 distance within the interlayer space can primarily be altered by changing the metal cations in the pillar. However, the lateral distance between pillars can also be changed (smaller or larger) by 262 changing the pillaring agents. Not only the interlayer free spacing will be affected, but at the 263 264 same time, the number of oxide pillars and their homogeneity in size and distribution is also

changed. Maes et al. (1997) prepared Mt-based PILC by using different pillaring species, among 265 different pillaring species (Al, Zr, Fe, Ti), due to higher crystallinity, a narrow pore size 266 distribution was reported for the Al-PILC as compared to Zr-PILC. The BET-specific surface 267 area was in order: Al-PILC (341 m<sup>2</sup>/g) > Ti-PILC (282 m<sup>2</sup>/g) > Zr-PILC (271 m<sup>2</sup>/g) > Fe-PILC 268 (134 m<sup>2</sup>/g), the basal spacing was in order: Ti-PILC (23-27 Å) > Zr-PILC (19.6 Å) > Al-PILC 269 (18.6 Å) > Fe-PILC (12.1 Å) and the micropore volume was in order: Ti-PILC  $(0.1540 \text{ cm}^3/\text{g}) >$ 270 Al-PILC  $(0.1320 \text{ cm}^3/\text{g}) > \text{Zr-PILC} (0.0935 \text{ cm}^3/\text{g}) > \text{Fe-PILC} (0.0366 \text{ cm}^3/\text{g})$ . It was concluded 271 that small changes during synthesis will simultaneously affect BET-specific surface area, and the 272 273 basal spacing of the PILC layers. These changes in the properties stem from the distribution of charge density and the pillaring nature of precursors. In addition, the characteristics of the PILC 274 do not only depend on the pillars, but also the stacking nature of the clay mineral layers into 275 aggregates was shown to have a big impact on the physical and chemical properties (Maes et al., 276 277 1996; Gil et al., 2008; Gil and Vicente, 2020). However, the number of pillars, pore size distribution, and their homogeneity in size and distribution are also crucial for the pore volume 278 and adsorption strength, which can also influence the interlayer free spacing. In conclusion, it 279 280 was demonstrated that the introduction of different pillars leads to PILC with specific properties 281 such as different interlayer free spacings, specific surface area, defined adsorption strength, and 282 corresponding changes in the SCR activity. 283 The acidity of PILC is a crucial characteristic of catalytic reactions. Lewis and Brønsted acidities

are primarily present in PILC, and their ratio varies depending on the clay mineral type and pillaring agents. The primary source of the Brønsted acidity of PILC is the dissociation of the intercalated water molecules coordinated to cations, while the oxide pillars are the main sources of Lewis acidity. Higher levels of acidity could be achieved when highly polarizing ions (Cr<sup>3+</sup>)



on catalyst conversion ability resulting in the divergent catalyst's performance order. In this 311 respect, Valverde et al. (2003b) also studied the effects of Ce<sup>III</sup> on the SCR of NO with C<sub>3</sub>H<sub>6</sub> over 312 Cu-Ti-PILC catalyst and found that the highest catalytic efficiency of Ce/Cu-Ti-PILC belongs to 313 Cu-Ti-PILC. The small addition (1 wt.%) of Ce<sup>III</sup> in the Cu-Ti-PILC catalyst slightly increased 314 the NO conversion (45 to 56%) at 235 °C. However, the further doping of Ce<sup>III</sup> (2 wt.%) to the 315 316 Cu-Ti-PILC catalyst decreased the specific surface area (283 to 256  $m^2/g$ ) and NO conversion by 45% at 235 °C. The Ce-Cu-Ti-PILC showed better catalyst stability than the Cu-Ti-PILC 317 catalyst, and it was proposed that the Ce species can prevent the agglomeration of Cu<sup>II</sup> species 318 and stabilize the catalyst performance in presence of O<sub>2</sub> and H<sub>2</sub>O feed conditions. Lin et al. 319 (2007) prepared the Al-Ce-PILC with Mt as a host material, and the Cu and  $SO_4^{2-}$  were 320 introduced with the impregnation method by using the solution of cupric nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>) or 321 ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). The Cu/Al-Ce-PILC catalyst only showed 20% NO conversion 322 at 350 °C with C<sub>3</sub>H<sub>6</sub>. After modification of the Al-Ce-PILC catalyst with SO<sub>4</sub><sup>2-</sup>, the Brønsted 323 acidity and corresponding catalytic efficiency increased. They reported a maximum 58% NO 324 conversion at 350 °C with C<sub>3</sub>H<sub>6</sub> under normal conditions. Based on characterizations (e.g., XPS 325 and H<sub>2</sub>-TPR) and SCR results, they suggested that Cu<sup>I</sup> and Cu<sup>II</sup> species were present on the 326 327 external surface of the catalyst, and by increasing the Cu loading in the catalyst, other CuO 328 aggregates were observed which enhanced the combustion of C<sub>3</sub>H<sub>6</sub>. Further, Lu et al. (2011) used 329 the ion-exchange method to prepare the Cu-Ti-PILC catalyst to explore the effect of pH in catalyst synthesis for the SCR activity and discovered that the catalyst prepared at pH 6 had the 330 maximum NO conversion (42%). Based on the XPS results and quantitative analysis of the H<sub>2</sub>-331 TPR profile, these authors proposed that new Cu<sup>II</sup> species were formed when the pH value of the 332 solution increased to 5, and with a further increase in pH value to 6, the isolated Cu<sup>II</sup>, Cu<sup>I</sup>, and 333

CuO species were also increased. It was observed that Cu<sup>II</sup> sites had a strong connection with the 334 conversion of NO at low temperatures. However, on further increase in pH value, the Cu<sup>II</sup> species 335 rate decreased slightly. Only a 10% NO conversion at 240 °C was achieved with the catalyst 336 prepared at pH-9 and the specific surface area also decreased from 159.5 to 143.1 m<sup>2</sup>/g. It was 337 reported in previous studies (Kim et al., 2001; Li et al., 2011) that isolated Cu<sup>II</sup> species can be 338 reduced to Cu<sup>0</sup> with H<sub>2</sub> in two steps: Cu<sup>II</sup> to Cu<sup>I</sup>, Cu<sup>I</sup> to CuO; while CuO is reduced to Cu<sup>0</sup> in one 339 step, CuO to Cu<sup>0</sup>. This shows that the redox behavior of Cu species plays a direct role in the 340 reaction mechanism of NO reduction over copper catalyst and further details will be discussed in 341 Section 3.6 (reaction mechanism). In addition, SCR activity completely depends on the nature of 342 the species and the reducing environment for the catalytic reaction. It can be concluded that, by 343 considering the LT-SCR activity of PILC catalysts, the Cu-Ti/PILC catalyst showed the high 344 activity at below 300 °C, whereas the Cu-Al/PILC catalyst was active at a high temperature 345 above 300 °C (Table 1). Generally, an increase in the metal content in both catalysts enhances 346 the SCR activity up to its maximum value, thereafter further increasing the metal content leads to 347 a decrease in the SCR activity (section 3.2). As a result, metal species and pillars play a crucial 348 349 part in the PILC catalysts for the SCR process. Meanwhile, it is also important to note that the 350 catalytic activity increased with increasing temperature (kinetic regime, for example, 50 to 351 300 °C for Mt based PILC catalysts), leading to maximum NO conversion, and then decreases at 352 higher temperatures (equilibrium regime). Broad studies have been conducted on the SCR of NO<sub>x</sub> with HC over Mt-based PILC catalysts. 353

- Table 1 summarizes the results of catalytic activities in LT-SCR of  $NO_x$  with HC for several
- 355 metal-modified Mt-based PILC catalysts. Overall, these PILC catalysts were reported to have
- 356 good catalytic activity at low temperatures (100 to 300 °C), but their denitration efficiency is

357 generally low at high temperatures (300 to 600 °C).

## 358 **3.1. Active sites**

In typical heterogeneous catalysis terms, the active site of catalytic reaction refers to the 359 structural region in which the reactants can be adsorbed on the catalyst surface and at this site, 360 361 the overall reaction activation energy can be reduced to make the reaction proceed faster. For 362 metal-modified PILC clay catalysts, the supported metal, the type of support, and the preparation method can all affect the properties of the active sites on the surface. According to existing 363 literature reports (Dong et al., 2018; Su et al., 2020; Wen et al., 2020), the active sites of HC-364 365 SCR on the surface of metal-modified PILC catalysts can be divided into metal ion active sites and acid sites according to the catalytic mechanism. 366 The active sites of metal ions on the surface of the metal-modified PILC catalyst are mainly 367 produced by the active components of supported metals. It is generally believed that metal active 368 369 components mainly exist in the form of isolated metal or metal oxide  $(M_xO_y)$  clusters onto the external/edge surfaces of PILC. The interlayer inorganic cations in the clay mineral exchange 370 with the polyoxocations in the pillaring solution by intercalation while catalyst nanoparticles 371 372 could agglomerate at high metal loading or high reaction temperatures (Fatimah et al., 2022). 373 Meanwhile, some protons remain present in the interlayer space of the PILC and they are still 374 available for further ion exchange. It has been reported that the interlayer composition of PILC 375 could be preserved upon calcination, resulting in distinct bonding between Si-O-M or Al-O-M. 376 This has been inferred based on results from methods such as IR and solid-state nuclear magnetic 377 resonance (NMR) spectroscopy. Notably, the clay mineral layers do not tend to react, and

- pillaring is most likely the result of van der Waals interactions or stems from the formation of
- 379 dative bonding among the oxygen in the layer and the coordinatively unsaturated sites on the

oxides pillars (Pinnavaia et al., 1985). Li et al. (1997) prepared the Cu<sup>2+</sup>-PILC catalyst to 380 compare the SCR activity with Cu<sup>2+</sup>-ZSM-5 catalyst. The Cu<sup>2+</sup>-PILC catalyst was highly active 381 than  $Cu^{2+}$ -ZSM-5 for SCR of NO<sub>2</sub> with C<sub>2</sub>H<sub>4</sub>. The high activity of  $Cu^{2+}$ -PILC catalyst was due to 382 a combination of the redox behavior of the Cu<sup>II</sup>-sites and the strong acidity of the PILC support. 383 Based on their results and the proposed mechanism, the Cu<sup>II</sup> anchored on the Al pillar, resulting 384 385 in Cu-O-Al bonding and a corresponding increased acidity in the catalyst. The C<sub>2</sub>H<sub>4</sub> chemisorbs on the Lewis acid sites on the Cu<sup>2+</sup>-PILC, which is then activated and produces the oxygenated 386 species in the presence of O<sub>2</sub> and further details will be discussed in Section 3.6 (reaction 387 mechanism). The Cu<sup>II</sup> sites in this structure is the active site of the C<sub>2</sub>H<sub>4</sub>-SCR reaction. Alkenes 388 are known to interact with alumina through Al-O ionic pairs in the presence of oxygen, this has 389 been concluded based on results from IR spectroscopy (Raval, 1991). Kim et al. (2001) studied 390 the performance of Cu/Ti-PILC catalyzing the reduction of NO by propene and found that 391 isolated Cu<sup>II</sup> sites had higher catalytic performance, and the agglomerated CuO species reduced 392  $C_{3}H_{6}$ -SCR reaction activity. They reported that the state of copper species on the surface of Ti-393 PILC depended on the mass ratio of Cu, TiO2, and PILC dehydration temperature and confirmed 394 395 this by hydrogen-temperature programmed reduction ( $H_2$ -TPR) and X-ray photoelectron 396 spectroscopy (XPS) characterization analysis. Kundakovic et al. (1998) reported a similar study 397 on the redox characteristic of copper species with the function of copper content. Mendioroz et al. (2006) coincidently found that the metal ion  $M^{n+}$  is the main active site for NO oxidation and 398 399 activation, and the metal oxide cluster  $M_x O_y$  could increase the combustion reaction between hydrocarbon compounds and oxygen, resulting in a decrease in the NO conversion rate. 400 However, Dorado et al. (2006) believed that both isolated Cu<sup>II</sup> and CuO clusters can adsorb 401 C<sub>3</sub>H<sub>6</sub>, and CuO clusters could be the main active sites for C<sub>3</sub>H<sub>6</sub> adsorption and activation. They 402

suggested from temperature programmed desorption (TPD) and Fourier transform infrared 403 404 spectroscopy (FTIR) analysis that the amount of desorbed O<sub>2</sub> is directly related to the amount of CuO, thus C<sub>3</sub>H<sub>6</sub> and O<sub>2</sub> are adsorbed via CuO species. They further proposed that C<sub>3</sub>H<sub>6</sub> is 405 oxidized by CuO species, and as a result,  $C_x H_y O_z$  intermediates are now readily available to 406 move on Cu<sup>II</sup>, where NO is anchored, to form additional reaction intermediates (organic nitrite 407 408 and organic nitro compounds), which in turn lead to N<sub>2</sub> and CO<sub>2</sub> as the primary final products of LT-SCR of NO<sub>x</sub>. Therefore, the isolated Cu<sup>II</sup> species and CuO clusters on the surface of the 409 Cu/Fe-PILC catalyst are both effective for the LT-SCR of NO conversion by C<sub>3</sub>H<sub>6</sub>. In this 410 respect, Lu et al. (2011) prepared the Cu-Ti-PILCs catalyst by the ion exchange method at 411 different pH values (4, 5, 6, 7, 8, and 9). They proposed that the isolated  $Cu^{2+}$  ions on the surface 412 of the Cu/Ti-PILC catalyst are beneficial to improving the SCR activity at low-temperature 413 stages, and the Cu<sup>+</sup> ions active site has high catalytic performance at high temperatures. They 414 identified the Cu species on the catalyst by XPS and quantitative analysis of H<sub>2</sub>-TPR profiles, 415 three different Cu species of Cu<sup>I</sup>, Cu<sup>II</sup>, and CuO were observed on the Cu (5) sample, and Cu<sup>II</sup> 416 and CuO were produced over Cu (6, 7 and 9) samples. On the other hand, it was reported that a 417 418 higher pH value of the pillaring solution favors the hydrolysis reaction, which might increase the 419 degree of polymerization. For other types of metal active sites, Sadykov et al. (2005) found that 420 Pt ions can promote the formation of nitrite and nitrate species. Based on this study, Pt atoms 421 strongly interact with Zr nanopillars, compared to bulk zirconia support, which is reflected in 422 stronger bonding and reduced oxygen reactivity when bound to those active components, leading to a high SCR of NO<sub>x</sub> reduction with HC. Further, Valverde et al. (2002) prepared the Fe, Ni, and 423 Cu metal-loaded Ti/PILC-based catalysts via the ion exchange method and investigated the effect 424 of metal content (wt%), catalyst acidity (mmol NH<sub>3</sub>/g), surface area (m<sup>2</sup>/g), micropore area 425

 $(m^2/g)$  and pore volume  $(cm^3/g)$  on the SCR activity. They suggested that metal loading 426 influences the position of the metal onto the pillars or external surface of the clay and observed 427 an increase in LT-SCR activity (up to 20%) and an increase in acidity with higher metal content 428 (5.8 to 8 wt% Fe, 1.6 to 3.6 wt% Ni and 4.6 to 9.0 wt% Cu) in the catalyst. They believed that 429 Ni<sup>II</sup> sites on the surface of Ni/Ti-PILC catalyst surface are the main active sites for the NO 430 431 conversion into N<sub>2</sub>, and the SCR activity on the Fe/Ti-PILC surface is mainly affected by the acid sites, but it has little connection to the Fe<sup>3+</sup> ion contents. Compared to other metals, the Cu-432 Ti/PILC catalyst showed better SCR results with up to 50% NO conversion and high acidity at 433 7.4 mass ratio of Cu, which is probably due to the intrinsic acidity of the Cu<sup>II</sup> sites and redox 434 characteristics of the Cu species. In order to investigate the effect of the pillars on the properties, 435 Guimarães et al. (2010) prepared the PILC by using different pillaring agents (Al, Ti and Zr) to 436 compare the specific surface area, pore size distribution and basal spacing. Their results showed 437 that the order of the surface area  $(m^2/g)$  was Al-PILC (281.7) > Zr-PILC (217.9) > Ti-PILC 438 (207.2), and the order of the basal spacing (Å) was: Ti-PILC (30.59) > A1-PILC (18.31) > Zr-439 PILC (17.37). It was observed that the Zr-PILC catalyst has more mesopores (65%) formation, 440 441 whereas the Ti-PILC sample was more mesoporous (85%) and the Al-PILC catalyst displayed 442 60% microporous formation. It is suggested that the particle size of the Al-PILC catalyst was 443 smaller than the Ti- and Zr-PILC samples due to the more pronounced delamination formation. 444 Regarding the second type of active sites, the acid sites on the surface of metal-modified PILC 445 catalysts can be divided into Lewis acid sites and Brønsted acid sites, as shown in Fig. 3a. Among them, the Lewis acid sites are electron-pair acceptors, which are mainly located on the 446 metal oxide pillars between the clay mineral layers, formed by the PILC or supported metal ion 447  $M^{n+}$  and could be used to accept lone pairs of electrons or multiple indefinite regions. There are 448

currently two types of opinions on the formation mechanism of Brønsted acid sites on the PILC 449 450 surface. Some scholars (Kloprogge and Frost, 1999; Wen et al., 2019) have observed the formation of Si-OH- linkage of the Al<sub>13</sub>-PILC Bd. It is suggested that these protons may interact 451 with Si-O-Al upon calcination and that they can form a new Si-OH-Al linkage. These protons 452 453 could expose silicon-oxygen-aluminum bridges near aluminum sites of the tetrahedral sheet and 454 subsequently, the reaction of these acidic OH with pillar peripheral OH, bonded to Al, would 455 anchor the pillars to the layer. On the other hand, in the protonated Si-OH-Al structure, bridges and pillars react with one another to produce either Si-O-Al or Al-O-Al linkages. However, the 456 457 catalyst acidity is related to Si-OH groups that are produced by the proton attack of Si-O-Al bonding of the tetrahedral sheet. In addition, during the calcination step, the metal ion groups are 458 thermally decomposed to subsequently produce metal oxides, and at the same time, protons H<sup>+</sup> 459 are generated and they migrate to the catalyst surface to form Brønsted acid sites (Long and 460 Yang, 1999a, b). Meanwhile, it is believed that the Lewis acid and Brønsted acid sites on the 461 462 surface of metal-modified PILC catalysts are effective active sites for NO conversion with HC. Their catalytic mechanism for the reaction on the surface of the catalyst is an acidic catalytic 463 reaction without involving any redox process (Chen et al., 2004). In this respect, Li et al. (1997) 464 suggested that Lewis acidity plays a dominant role in the activation process of HC. In addition, 465 Mendioroz et al. (2006) agreed and proposed that methane adsorption at Lewis acid sites is 466 467 activated to form oxygenated species. This process is affected by the number and strength of acid sites, according to a similar phenomenon reported by Wen et al. (2020). Both studies observed 468 that Lewis concentration was the dominant factor for NO conversion with C3H6 at low 469 temperatures over PILC-based catalysts as shown in Fig. 3b. However, Yang and Li (1995) 470

believed that Brønsted acid sites promote the oxidation and activation of HC for the SCR of NO<sub>x</sub>. 471 It is generally suggested that Brønsted acidity facilitates the catalytic reaction, and it is required 472 in order to bind and disperse the metal ions; however, its direct function is not well defined. In 473 addition, higher acidity may significantly enhance SCR activity by increasing HC concentrations 474 near active sites. Lin et al. (2007) pretreated Cu/Al-Ce-PILC catalyst by using  $SO_4^{2^-}$  to prove 475 476 that Brønsted acid sites could promote the adsorption and activation process of propylene on the catalyst surface. The acidity of the catalyst was determined by FT-IR spectra of chemisorbed 477 pyridine (Py-IR) to investigate the effect of  $SO_4^{2^-}$ , while the insight into the sulfation effect on 478 the SCR reaction mechanism was not revealed, it was shown that the sulfation effects of the Ce-479 PILC catalyst on NO reduction are different at different reaction temperatures. Specific 480 identification of active sites for a catalytic mechanism is complex because the SCR is 481 simultaneously taking place with the oxidation of the reductant gas by the large concentration of 482 oxygen in the flow stream and it is not instantly apparent whether the oxidation of the 483 hydrocarbon by dioxygen takes place on identical sites. On the other hand, contrary to SCR, 484 transition metal ions are required for the activation and oxidation of HC, and one may assume 485 486 that it should occur on any metal active sites which proceed by a surface redox mechanism. On 487 acidic surfaces, it can proceed by the oxidation of the carbonaceous residue formed within the 488 cracking of the reductant gas on the acid sites.

## 489 **3. 2. Effect of metals and their loading**

For the overall understanding of the SCR process, it is very important to examine the influence of active metals on the SCR of NO<sub>x</sub> with HC over PILC catalysts. Yang et al. (1998) examined the C<sub>2</sub>H<sub>4</sub>-SCR of NO conversion performances by using different metals (Fe, Cu, Co, Ce, Ag, and Ga) with Ti-PILC clay catalysts. Their results showed that the order of the maximum NO<sub>x</sub>

494	$conversion \ rate \ on \ the \ surface \ of \ these \ catalysts \ was: \ Cu/Ti-PILC > Ga/Ti-PILC > Ce/Ti-PILC > Ce/Ti-PI$
495	Fe/Ti-PILC > Co/Ti-PILC > Ag/Ti-PILC. Among them, Cu/Ti-PILC has the best catalytic
496	activity at low temperatures, and the NO removal rate was close to $60\%$ at $300$ °C and Ag
497	catalyst was least active for SCR activity up to 15% NO conversion at 300 °C. It was reported
498	that the loading of Cu when it reached 245% ion-exchanged caused an improvement in the SCR
499	activity. However, a further increase in copper loading beyond 245% caused a decline in NO
500	conversion at 300 °C due to the low specific surface area and pore volume of the catalyst. The
501	Ga/Ti-PILC catalyst showed a good NO removal rate at middle and high temperatures. After
502	comparing the SCR results of metal-loaded Ti-PILC-based catalysts with the reductant gas
503	conversion, it is observed that reductant ethylene gas oxidation was a catalyzed reaction and it
504	was not a homogeneous reaction as earlier suggested by Yang et al. (1998). Further, the redox
505	nature of Cu is effective to execute the catalytic reaction for $NO_x$ conversion with $C_3H_6$ , and the
506	redox properties of copper species can be directly related to the LT-SCR reaction. In this respect,
507	the Cu-PILC catalyst appears to be the most active catalyst for HC oxidation and LT-SCR
508	technology. On the other hand, it is generally believed that $NO_x$ is reduced by reacting with
509	intermediates generated from partial oxidation of HC used as reductants and that increased
510	availability of these species either by more C atoms in the reductant, or their easier formation
511	from less saturated HC describes the enhancement of NO <sub>x</sub> reduction (Márquez-Alvarez et al.,
512	1997; Valverde et al., 2003a, b; Dorado et al., 2010; Yuan et al., 2019; Su et al., 2020; Zhao et al.,
513	2020; Goncalves et al., 2021). The C <sub>3</sub> H <sub>6</sub> -SCR performance of Cu, Fe, and Ni-modified Ti-PILC
514	catalysts was explored by Valverde et al. (2003a). The maximum $NO_x$ conversion using the
515	Cu/Ti-PILC catalyst was 55% at 240 °C, 35% at 425 °C of the Ni/Ti-PILC, and 32% NO $$
516	conversion at 225 °C of the Fe/Ti-PILC catalyst. Belver et al. (2008) prepared the Ni-modified

Al-PILC catalyst, and the C<sub>3</sub>H<sub>6</sub>-SCR of NO<sub>x</sub> conversion rate was only 20% at 450 °C. As 517 518 observed in previous studies (Belver, 2010; Asgari et al., 2021), not all metals can be 519 incorporated with co-pillaring procedures due to their acid-base characteristics. This occurs frequently with Ni-based catalysts. A major reason is that Ni is not active to form the optimal 520 521 polycations for intercalation between clay mineral layers and it was also reported to have a low 522 redox characteristic in the SCR reaction (Valverde et al., 2003). Bahamonde et al. (2001) compared the CH<sub>4</sub>-SCR activity of Rh, Pt, and Pd-modified Al-PILC catalysts and found that the 523 Rh catalyst showed the best catalytic performance for NO<sub>x</sub> conversion (60%) at 400 °C, mainly 524 525 due to their high surface acidity and porous structure. However, this again appears to suggest that surface acidity can play a significant role in LT-SCR of NO<sub>x</sub> conversion, although factors such as 526 pore volume, specific surface area or even metal dispersion could also be determinants of the 527 overall activity of Al-PILC catalysts. On the other hand, it is observed that the SCR activity of 528 529 those catalysts is controlled by the loading of metal, synthesis method, textural characteristics, and feed conditions. The promoter of the pillaring solution can change the formation of pores 530 within the clay mineral and the distribution of pore sizes and specific surface area. It is also 531 532 important to remark that several PILC have different types of inorganic polyoxocations that have 533 their own specific characteristics (specific surface area, basal spacing, or pore size distribution) 534 and applicability for SCR catalytic reaction. Single metal Ti/PILC-based catalysts were reported 535 to have a high catalytic effect on the reaction of NO removal at low temperatures, and their catalytic activity at low temperatures follows a general order of Cu > Ce > Fe > Co > Ag > Ga, 536 537 as shown in Fig. 4a. The addition of small concentrations of earth metals or precious metals was found to effectively improve the SCR reaction activity of PILC catalysts. The rare earth metal Ce 538 539 oxide is widely reported to have good oxygen storage capability and transport capacity

(Kundakovic and Flytzani-Stephanopoulos, 1998; Córdoba et al., 2001; Carriazo et al., 2005; Lin 540 et al., 2007; Boxiong et al., 2014), which is beneficial for improving catalytic performance. In 541 this respect, Yang et al. (1995) introduced a small amount of Ce<sub>2</sub>O<sub>3</sub> promoter (0.5 wt.%) into the 542 Cu/Ti-PILC catalyst by the impregnation method, and the maximum  $NO_x$  conversion rate on the 543 catalyst surface was increased from 80% to 90%. Valverde et al. (2003b) added rare earth metal 544 545 Ce and noble metal Ag promoters (1.0 wt.%) to Cu/Ti-PILC and the denitration efficiency of the catalyst was increased by 8% and 7%, respectively. This improvement was related to the oxygen 546 storage capacity and transfer ability of the cation promoter. In addition, the structural function of 547 Ce in Cu/Ti-PILCs catalyst could be to keep Cu<sup>II</sup> species dispersed by controlling their 548 movement and hence, inhibiting the formation of large CuO clusters. Mainly, Cu<sup>II</sup> dispersed 549 species are the active sites for the LT-SCR reaction. The addition of Ag in the Cu/Ti-PILCs 550 551 catalyst resulted in a small shift of the maximum NO conversion (55%) toward higher temperatures. As observed in previous studies (Li and Flytzani-Stephanopoulos, 1999a, b; 552 Furusawa et al., 2002), the redox activity of the catalyst can improve with the addition of noble 553 metals for HC-SCR technology. Additionally, TPR analysis also confirmed that the addition of 554 555 the Ag promotor could shift the reduction peak towards a lower temperature, which can improve 556 the LT-reduction capacity of the PILC catalyst (Zhang et al., 2019). Further, Lin et al. (2003) 557 introduced the rare earth metal La (0.5 wt.%) to Cu/Al-PILC catalyst and found that the La 558 promoter could help to improve the dispersion of Cu species on the catalyst surface and improve 559 the heat resistance of the catalyst. Furthermore, Sadykov et al. (2006) examined the addition of a small amount of noble metal Pt (0.3~0.5 wt.%) in the Cu/Zr-PILC catalyst and noticed that the 560 small addition of Pt (0.5 wt.%) can improve the low-temperature SCR activity of PILC-based 561 562 catalyst. This suggests that Pt is located on zirconia nanopillars that are partially collated with Cu

563 cations. Based on the infrared (IR) spectroscopic study of absorbed CO, they suggested that Pt is 564 in a very partly oxidized state due to interaction with Cu cations. This synergetic interaction between Pt and Cu cations considerably increases the catalytic oxidation and stability of the 565 catalyst. In addition, efficient oxidation of NO into NO<sub>2</sub> caused by Pt in realistic feeds could 566 567 contribute to the high performance of Pt-Cu/Zr-PILC catalyst. Further, Lu et al. (2015) believe 568 that the addition of precious metal Pd is beneficial to increasing the chemisorption performance of NO<sub>x</sub> on the surface of the PILC catalyst. This is generally suggested in previous studies that 569 PdO is the more active phase for hydrocarbon oxidation and Pd existence in the form of Pd<sup>II</sup>, 570 which is beneficial for high SCR activity with HC in the presence of O<sub>2</sub>. In addition, Konin et al. 571 (2001) also reported that the introduction of Ag can inhibit the carbon deposition of HC on the 572 surface of clay mineral catalysts. 573 As stated above and by considering Table 1 data, it can be concluded that high SCR activities 574 and good physicochemical properties (e.g., larger BET-specific surface area, basal spacing, 575 acidity) were the results of successful pillaring agents. The redox behavior and type of cations in 576 SCR catalysts are also important because cations are the main active species in the NO 577 578 conversion with HC. The Cu-Ti/PILC had a larger BET surface area and higher LT-SCR activity 579 as compared to other metal-supported onto Al- or Zr-Mt-based PILC catalysts and a large 580 specific surface area could provide more accessible active sites for the catalytic reaction. Among 581 the noble metals, Ag, Pt, Rh, and Pd were broadly studied for HC-SCR, but they are found to be 582 not very active at low temperatures (100 to 300 °C).

- 583 On the other hand, the HC-SCR activity of PILC catalysts is closely connected to the loading of
- active metal components. Previous studies have demonstrated that the loading of metals at a
- 585 certain level can increase the SCR activity of PILC-based materials. However, further increases

in metal loading in the catalyst support may have an impact on SCR activity as shown in Fig. 4b 586 587 (Lin et al., 2005). The main reason is generally believed to be the low loading of active metals so that the appropriate concentration of metal ions  $M^{n+}$  active site catalytic reactant molecules 588 cannot be formed. Conversely, when the metal loading is too high, the metal species can 589 590 agglomerate and block the pores of the catalyst, leading to a decrease in the specific surface area 591 as well as active sites of the catalysts. These conditions are known to be unfavorable for the overall SCR reaction (Kashif et al., 2020; Su et al., 2020; Wen et al., 2020). Hence, the LT-SCR 592 activity of a metal-supported PILC catalyst is highly dependent on its metal characteristics, 593 594 nature, and its loading in the catalyst.

## 595 **3.3. Effect of carriers**

596 The SCR catalyst activity is affected by the type of support, the loading of metal, and the

597 synthesis procedure, for example, impregnation, ion-exchange, and co-precipitation method (He

tal., 2016; Chen et al., 2022). The type of catalyst support can significantly affect the

599 physicochemical properties of the catalyst such as specific surface area, pore diameter, and

600 catalyst acidity, and it can also have a big impact on the SCR activity with HC (Zhou et al., 2018;

- 601 Liu et al., 2020). Metal oxide catalysts are mainly prepared by using  $Al_2O_3$ ,  $ZrO_2$ ,  $TiO_2$ , and  $SiO_2$
- as carriers and supporting different metal oxides. The SCR performances of metal oxide catalysts
- are higher at medium and high temperatures. However, the main drawback of metal oxide-
- supported catalysts is their low denitration efficiency at low temperatures and poor resistance to
- 605 SO<sub>2</sub> (Sohn and Bae, 2000; Worch et al., 2011; Liu et al., 2013).
- 606 PILC is an attractive material with a sufficient porous structure, large interlayer spacing, and
- 607 good thermal stability. Due to these features with simple synthesis, PILC is an excellent catalyst
- 608 carrier for SCR application and has also been applied for several organic reactions, due to its

609	easy structural modification and activation, low cost, abundant availability, and ability to act as
610	acidic and basic material without being corrosive. Previous studies compared PILC with
611	molecular sieves and metal oxide catalysts that were prepared with the same active metal and
612	found that the catalysts with PILC as the support have high activity at low temperatures and good
613	resistance to H <sub>2</sub> O and SO <sub>2</sub> (Li et al., 1997; Bahamonde et al., 2001; Belver et al., 2004a). As
614	stated above in previous sections, the physicochemical properties of the PILC support can
615	change with the pillaring agents, which can also affect the SCR activity of the prepared catalyst.
616	In this respect, it was found that the basal spacing of Ti-PILC (~30.59 Å) is greater than that of
617	Al-PILC (~18.31 Å) and Zr-PILC (~17.37 Å), and BET-specific surface area order was: Al-PILC
618	$(281.7 \text{ m}^2/\text{g}) > \text{Zr-PILC} (219.9 \text{ m}^2/\text{g}) > \text{Ti-PILC} (207.2 \text{ m}^2/\text{g}) (Yamanaka and Brindley, 1979;$
619	Guimarães et al., 2010). This is believed to be beneficial to increase the gas diffusion rate
620	between clay mineral layers and subsequently facilitate the gas molecule interactions (Yang et
621	al., 1998; J L Valverde et al., 2005). Qi et al. (2004) compared the catalytic activity of Pd-
622	supported Ti-, Al-, Zr-, and Fe-based PILC catalysts, and found that the specific surface area
623	was: Ti-PILC $(336 \text{ m}^2/\text{g}) > \text{Zr-PILC} (236 \text{ m}^2/\text{g}) > \text{Al-PILC} (190 \text{ m}^2/\text{g}) > \text{Fe-PILC} (91 \text{ m}^2/\text{g})$ ,
624	while the pore volume was: Ti-PILC $(0.31 \text{ cm}^3/\text{g}) > \text{Fe-PILC} (0.61 \text{ cm}^3/\text{g}) > \text{Zr-PILC} (0.11 \text{ cm}^3/\text{g}) > \text{Zr-PILC} (0.$
625	$cm^{3}/g$ ) > Al-PILC (0.10 $cm^{3}/g$ ) and the pore diameter was: Fe-PILC (58.87 Å) > Ti-PILC (31.59
626	Å) > Zr-PILC (28.01 Å) > Al-PILC (26.92 Å) and the Ti-PILC catalyst showed large specific
627	surface area, pore volume and highest catalytic activity. However, the maximum SCR of NO
628	removal efficiency at low temperature (140 °C) was: Pd/Ti-PILC (75%) > Pd/Zr-PILC (45%) >
629	Pd/Fe-PILC (38%) > Pd/Al-PILC (32%). It is generally believed that the large specific surface
630	area, pore volume or pore diameter of PILC materials is not only beneficial to more active sites
631	but also improves the dispersion of the loaded active components on the surface of the carrier,

thus also contributing to the form of isolated  $M^{n+}$  metal ions (Valverde et al., 2003; Ye et al., 632 2011). As reported in previous studies (Sterte, 1986; Ming-Yuan et al., 1988; Bahranowski et al., 633 2015), Ti-PILC catalysts are well-known materials with high surface acidity (the Brønsted and 634 Lewis type) as compared to other PILC (Al-PILC or Zr-PILC). On the other hand, Li et al. 635 (2011) found that when the Ti/clay ratio was 10 mmol/g, the largest number of TiO<sub>2</sub> oxide 636 columns could be formed between the layer of Ti-PILC carrier, which is beneficial to the 637 bonding of Cu<sup>II</sup> on the surface of the TiO<sub>2</sub> column to form the active site for SCR activity. 638 By changing clay minerals and pillaring agents, different pore sizes, basal spacing, and specific 639 surface area could be obtained. Different organometal pillaring species could increase thermal 640 stability and introduce active elements in the PILC. In this respect, it also becomes possible to 641 tune the porosity of the PILC catalysts. The pore size of PILC could be varied from 5 to 20 Å, 642 depending on the synthesis conditions such as the host clay minerals, the CEC of the clay 643 mineral, and thermal treatment temperature and type of metal oxide pillars in the sample. This 644 porosity, combined with the properties of both pillar and host clay minerals, is very important for 645 certain applications, such as SCR reactions and selective gas adsorptions. The properties of PILC 646 with different pillar species generally follow this order for specific surface area  $(m^2/g)$ : Al<sub>2</sub>O<sub>3</sub> 647  $(200-400) \ge Cr_2 O_3 (250-350) \ge TiO_2 (250-330) \ge ZrO_2 (200-300) \ge Fe_2O_3 (100-300)$ , and for 648 649 interlayer free spacing (Å);  $TiO_2(16\pm6) > Fe_2O_3(15\pm5) > Cr_2O_3(12\pm3) > ZrO_2(4-14) > Al_2O_3$ (7-10) (Cool and Vansant, 1998). Kloprogge et al. (1994a, b) studied the pillaring process of Bd 650 and Mt with Al and Ga. The pillaring of Mt results in a basal spacing of 17 to 19 Å and an 651 increase in specific surface area from  $35 \text{ m}^2/\text{g}$  to  $350 \text{ m}^2/\text{g}$ . Similarly, pillaring with Al of 652 synthetic Bd resulted in an increase in basal spacing from 12.4 Å to 18.4 Å (Plee et al., 1985, 653 654 1987; Kloprogge et al., 1994a). However, the basal spacing decreased to 16.4 Å after calcination

at 500 °C. Here, once again, an increase of the specific surface area from 65 m<sup>2</sup>/g to 345 m<sup>2</sup>/g 655 was obtained after pillaring (Kloprogge et al., 1994b). Mt is the most investigated member of the 656 clay minerals for NO<sub>x</sub> reduction with HC. Chmierlaz et al. (2004) investigated the effect of 657 pillars on the LT-SCR of NO<sub>x</sub> with C<sub>2</sub>H<sub>4</sub>. They introduced Ag into the Zr-, Al-, and Ti-Mt-PILC 658 659 by using the ion-exchange method. The  $NO_x$  conversion was not so effective at low temperatures 660 and the maximum NO<sub>x</sub> reduction (%) at 400 °C was in order: Ti-PILC (60) > Zr-PILC (20) > Al-PILC (18). The BET-specific surface area  $(m^2/g)$  displayed a similar trend: Ti-PILC (210) > Zr-661 PILC (156) > Al-PILC (151). Overall, these Mt-based Ti-PILC catalysts are well known to have 662 a large specific surface area with high surface acidity (Lewis and Brønsted type), as compared to 663 other Zr- and Al-PILC catalysts (Sterte, 1986; Ming-Yuan et al., 1988; Bahranowski et al., 2015). 664 As previously stated, the large specific surface area with the high acid function is crucial for 665 designing alternative SCR catalysts for LT-SCR of NO<sub>x</sub> with HC. 666

#### 667 **3. 4. Influence of synthesis**

668 In-depth studies are currently being conducted on the loading method, calcination temperature, and pretreatment method of the metal-modified PILC catalyst. The impregnation and the ion-669 670 exchange methods have been widely studied and reported for the loading of active metals on the 671 PILC support. The impregnation method is easy to perform, fast, economical, and can more 672 accurately control the loading of active metals. The ion-exchange method has received more 673 attention due to the exchangeability of ions between the interlamellar space of the clay minerals 674 and active metal ions. The ion exchange sites between PILC layers facilitate the dispersion of active components on the surface of the catalyst support and affect the formation of active 675 centers. However, the distribution of added pillars can be changed by changing the pillars (e.g., 676 677 TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, or Al<sub>2</sub>O<sub>3</sub>) and their mass ratio. This pillar distribution also depends on the specific

synthesis procedure, the type of clay mineral, the CEC, and the calcination conditions to obtain 678 the final product (Wang et al., 2012; Wen et al., 2020; Macías-Quiroga et al., 2022). In this 679 respect, the quantity of pillar precursors, which becomes intercalated, completely depends on the 680 CEC of the clay and the charge of the pillar. Clay minerals have a CEC that allows them to 681 682 acquire the best swelling and alkali or alkaline ions in the interlayer space, which can be easily 683 exchanged. The pillaring cation requires a high positive charge and must be dissolvable in the polar solvent used to swell the clay. Valverde et al. (2003b) compared the Cu/Ti-PILC catalysts 684 prepared by the impregnation method and the ion exchange method and found that the catalyst 685 prepared by the ion exchange method has a higher content of isolated Cu<sup>II</sup> species and Lewis 686 acidity, and it showed higher SCR performance. Strong Lewis acidity was related to the number 687 of Cu<sup>2+</sup>-ions in the ion-exchange sample. Based on their results and H<sub>2</sub>-TPR profiles, they 688 identified three types of Cu species: isolated Cu<sup>II</sup> anchored at the pillars rather than at the surface 689 of the silica layer, Cu<sup>II</sup> clusters as patches of amorphous CuO, and cupric oxide. The presence of 690 Cu<sup>II</sup> clusters increased with the Cu content in the catalyst. As isolated Cu-ions and Cu<sup>II</sup> (patches 691 of amorphous CuO) clusters were located in the interlayer space of the clay mineral, an increase 692 in Cu content resulted in a decrease of the turnover frequency (TOF) from 86 to  $27.5 \times 10^4 \, h^{-1}$  and 693 pore volume (0.236 to 0.217  $\text{cm}^3/\text{g}$ ) due to the filling of the interlayer space. Based on the XPS 694 analysis results, Mendioroz et al. (2006) posited that Rh<sup>III</sup> species and Rh<sub>2</sub>O<sub>3</sub> oxide clusters exist 695 696 on the sample, either on the external/edge surfaces or in the pillars of the interlayer of the Rh/Al-PILC catalyst that was prepared with the impregnation method, while the Rh ions on the surface 697 of the ion-exchange series' samples can form a strong interaction with charge-compensating 698 cations (e.g., Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>) in the Al-PILC carrier before the calcination of the catalyst. A 699 longer contact time resulted in a higher incorporation Rh species, which is beneficial to improve 700

the reaction activity of the catalyst. Further, the authors suggested from the reaction mechanism study that exchanged  $Rh^{3+}$  in the Al-PILC matrix and oxidized  $Rh_2O_x$  in combination with the acidity of support contribute to forming oxygenated species as the key step for SCR of NO<sub>x</sub> with CH<sub>4</sub>.

705 The pH value of the metal ion solution has a specific effect on the loading of the active components. For example, a high solution acidity can promote the formation of polymeric 706 species, which can improve active sites in the catalyst but can reduce the activation energy 707 during the LT-SCR reaction. In other words, the highly acidic nature of the catalyst could reduce 708 709 the redox capability, and the physiochemical properties and significantly decrease the LT-SCR catalytic activity. Additionally, the high solution acidity (during the exchange of the interlayer 710 inorganic cations of the clay mineral with polyoxocations) can also lead to the leaching of atoms 711 712 from the clay structure. Dorado et al. (2006) reported that the Fe<sub>2</sub>O<sub>3</sub> column structure of the Fe-713 PILC support was easily destroyed under strongly acidic conditions (pH = 1.0), and the specific surface area, pore volume, and acid sites content of the catalysts also decreased, while under 714 715 alkaline conditions (pH = 10.5), Cu/Fe-PILC easily generates agglomerated CuO species, which 716 blocks the catalyst pores and reduces the reaction activity. Further, Lu et al. (2011) investigated 717 the effect of pH with copper acetate solution on the morphology of Cu species over the catalyst 718 surface. When the pH value increased from 4 to 6, the number of isolated Cu<sup>II</sup> species increased, 719 which was useful to increase the NO conversion rate and low-temperature reaction activity, yet when the pH value continued to increase up to 9, at that moment, the isolated Cu<sup>II</sup> species 720 decreased while the CuO species increased, resulting in a significant decrease in catalyst activity. 721 722 In general, the stability of clay mineral structure is affected at low pH because acid attacks the 723 edges of the clay mineral structure and releases atoms. Acidic treatment can have a significant

impact on the crystal structure and morphology of clay minerals, it may cause the release of

structural atoms and changes in the properties (e.g., specific surface area, pore volume, acidity)

of the PILC catalysts (Dorado et al., 2006; Hao et al., 2019).

728

727 The Ti, Fe, Zr, or Al precursors are changed into rigid metal oxide pillars during a calcination

stage at 350-600 °C. The calcination temperature in the catalyst preparation process can also

729 affect the SCR activity (Choo et al., 2003; Wang et al., 2012; Li et al., 2017). Studies have shown that high calcination temperature ( $\geq 700$  °C) can give rise to a strong dehydroxylation reaction of 730 the oxide pillars between the PILC layers as well as the clay mineral structure itself. This reduces 731 732 the number of active sites on the surface of the interlayer columns that can fix metal ions and therefore, the catalytic activity of the catalyst will decrease (Valverde et al., 2002, 2003; Wang et 733 al., 2012). In other words, depending on the clay mineral used, such high temperatures may 734 735 result in the start of the dehydroxylation of the clay mineral layers, where the octahedral sheet starts to lose its hydroxyl groups, and the layer structure changes as a result. It is believed that 736 the layer characteristics of the host clay play a very significant role in determining the layer 737 reactivity upon heating. In this respect, Plee et al. (1985) proposed that the layer reactivity is 738 solely related to the origin of the layer charge, and it only occurs in the case of tetrahedrally 739 740 charged smectites. Further, they proved that the mechanism of layer crosslinking was also 741 possible for the octahedrally substituted fluorohectorite clay. Furthermore, Wang et al. (2012) 742 found that when the calcination temperature reaches 700 °C, it strongly affects the interlayer 743 structure of the Ti-PILC catalyst, which reduces the specific surface area and pore volume and also decreases the denitrification performance of the catalyst. However, an excessively high 744 calcination temperature ( $\geq$  700 °C) can cause the collapse of the interlayer structure of PILC 745 746 (Baloyi et al., 2018). In other words, it will destroy the clay structure, reduce the active centers of the reaction, and also decrease the SCR activity of the PILC catalyst. It is also demonstrated in
previous studies (Table 1), the authors widely used 400 to 500 °C calcination temperature for the
Mt-based PILC catalyst.

Further, the pretreatment of the PILC support has also been reported to effectively improve the 750 751 catalyst reaction activity. Sadykov et al. (2006) found that the pre-sulfurization treatment of 752 Cu/Zr-PILC can reduce the combustion of HC on the catalyst surface and slightly influence  $NO_x$ reduction. The sulfated Pt-Cu/Zr-PILC catalyst was observed to suppress the combustion of the 753 hydrocarbon, thus improving NO<sub>x</sub> conversion (58%) at low temperatures (200 °C). Therefore, 754 the effect of Pt in the complex active component can be attributed to a faster rate of decane 755 oxidation for sulfated Pt-Cu/Zr-PILC catalyst. Another factor that could be considered is the 756 efficient NO oxidation to NO<sub>2</sub> by Pt even in wet conditions. Finally, it was reported that the 757 presence of Pt in sulfated bulk zirconia with supported transition metal cations catalyst is at least 758 759 one of the leading factors for low-temperature activity in decane-SCR. Meanwhile, Lin et al. (2007) reported that the catalytic efficiency of the Cu/Al-Ce-PILC catalyst could be increased up 760 to 36% after SO<sub>4</sub><sup>2-</sup> pretreatment. They found that SO<sub>4</sub><sup>2-</sup> pretreatment can increase the ratio of 761 762 Brønsted acid sites on the catalyst surface, and it contributes to the activation and oxidation 763 process of propylene. However, Brønsted acidity promotes the adsorption of propylene to 764 produce intermediates that are beneficial for the conversion of NO to N<sub>2</sub>. A similar phenomenon 765 was reported by Yang et al. (1995).

## 766 **3.5. Influence of reaction conditions, and presence of SO<sub>2</sub> and H<sub>2</sub>O**

The type and concentration of HC as reductants are important aspects to be considered in the
 reaction system for LT-SCR technology. In order to improve the performance of LT-SCR with

HC, many HC has been investigated, such as  $CH_4$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_8H_{18}$ , and  $C_{10}H_{22}$  are the

most generally tested HC. Recently, among several HC as reductants, the C<sub>3</sub>H<sub>6</sub> has been broadly 770 771 studied in LT-SCR with clay minerals-based catalysts due to its relatively strong reactivity (Valverde et al., 2005; Belver, 2010; Dong et al., 2018; Yuan et al., 2018, 2019; Kashif et al., 772 2020, 2022; Su et al., 2020; Wen et al., 2020). Lin et al. (2006) investigated the effect of 773 774 hydrocarbon reductant concentration on the performance of C<sub>3</sub>H<sub>6</sub>-SCR over Cu/Al-Ce-PILC 775 catalyst, and the results showed that the maximum  $NO_x$  conversion rate increased initially and then decreased with the increase of the reducing agent  $C_3H_6$  concentration (~0.24 to 0.28%). 776 When the  $C_3H_6$  concentration is higher than the critical value (~0.24%), HC could burn violently 777 778 on the surface of the catalyst and can release massive heat, which reduces and deactivates the catalyst activity due to coke deposits on the catalyst surface, meanwhile, it can also destroy the 779 PILC structure. Carbon deposition caused by the burning of HC compounds on the surface of the 780 PILC has often been reported as one of the main reasons for the decrease in SCR activity (Konin 781 et al., 2001; Sadykov et al., 2006). 782

The O<sub>2</sub> concentration also has a great influence on the LT-SCR activity of the PILC catalyst. It has been suggested that O<sub>2</sub> could oxidize NO to produce NO<sub>2</sub> or oxidized HC to form oxygencontaining compounds, and it complicates the NO reaction mechanism in SCR catalytic activity (Petunchi and Hall, 1993; Hernández-Huesca et al., 2001; Kashif et al., 2019). It was also reported that O<sub>2</sub> could be adsorbed on the catalyst surface to form O<sub>ads</sub>, and lattice oxygen can be produced through migration to promote the activation of HC (Argyle et al., 2002; Swislocki et al., 2014). Further, Li et al. (1997) reported that the Cu/Al-PILC catalyst had no C<sub>2</sub>H<sub>4</sub>-SCR

reaction activity under oxygen-free conditions. With the gradual increase of  $O_2$  concentration (0

- $\sim 4\%$ ), the SCR activity of the catalyst first increases and then decreases. In addition, Valverde et
- al. (2005) defined the minimum oxygen concentration required for the complete oxidation of HC

on the metal-modified PILC catalyst as the critical oxygen concentration [1%O<sub>2</sub>]<sub>crit</sub>. They found 793 that when the concentration of  $O_2$  was lower than  $[O_2]_{crit}$ , the maximum NO reduction was 42% 794 at 300 °C, and a small increase in O<sub>2</sub> concentration increased the NO conversion from 42% to 795 59% at low temperatures (250 °C). Further increases in O<sub>2</sub> concentration (1.5 to 7.5%) could 796 797 reduce the catalytic reduction efficiency of the Cu/Ti-PILC catalyst, and the reaction temperature window shifts to the low-temperature ranges. This may be related to the activation of Cu<sup>II</sup> in the 798 reaction by O<sub>2</sub>, the oxidation of carbon, and the formation of lattice oxygen species in the 799 reaction; when the oxygen concentration is higher than  $[O_2]_{crit}$ , the maximum NO conversion rate 800 decreases as the O<sub>2</sub> concentration increases. Notably, they suggested that the O<sub>2</sub> concentration of 801 around 1% is sufficient for the complete oxidation of C<sub>3</sub>H<sub>6</sub> at 300 °C, when the O<sub>2</sub> concentration 802 is at a critical point, the reaction system can be in a reducing environment. They reported that 803 this reducing environment is favorable for Cu<sup>II</sup> reduction. The reduced Cu species is recognized 804 to have a significant role in the LT-SCR of  $NO_x$  (Amiridis et al., 1996). However, Belver et al. 805 (2004b) reported that Al-Fe/PILC catalyst displayed significant C<sub>3</sub>H<sub>6</sub>-SCR catalytic performance 806 in the absence of O<sub>2</sub>. They found that once O<sub>2</sub> was introduced into the SCR system, the NO 807 removal efficiency gradually declined, as shown in Fig. 5a. However, it is proposed that there 808 809 was a lower influence of the iron content in the catalytic reaction in the presence of O<sub>2</sub>. They 810 believe that the decrease of reductants involved in NO reduction due to the combustion reaction 811 of the large number of  $C_3H_6$  with  $O_2$  could be the main reason for the decrease in NO conversion. It is also observed that the effect of oxygen concentration on HC-SCR is different on the surface 812 813 of different kinds of metal-modified PILC catalysts. This can be related to the difference in types of active sites and reaction paths. On the other hand, it is reported that  $O_2$  concentration inhibits 814 815 the formation of isocyanates species on the Fe catalyst, thus reducing their SCR activity for LT-

SCR with HC. To date, the specific reaction mechanism needs further detailed investigation. 816 Several relevant studies have been conducted that investigate the effect on the SCR activity of 817 the PILC catalyst, such as NO concentration, reaction space velocity, and pretreatment 818 atmosphere. The research results have reference values for the practical application and 819 820 development of NO<sub>x</sub> reduction with HC over PILC catalysts (Valverde et al., 2005a, b). In general, high SCR operating temperature may cause an increase in  $NO_x$  generation rather than 821  $NO_x$  reductions. 822 823 The LT-SCR technology is a cost-efficient and effective technique for reducing  $NO_x$  emissions 824 from non-power industrial sources (Guo et al., 2021; Zhu et al., 2022). In commercial applications, the resistance for H<sub>2</sub>O and SO<sub>2</sub> is an important factor for SCR catalysts, particularly 825 for diesel engines. Stationary sources of flue gas and mobile exhaust gas might contain water 826 vapor (~3 to 8%) and SO<sub>2</sub> (~300 to 600 ppm) (Lee et al., 2004; Licki et al., 2015). These 827 conditions directly influence the SCR catalytic activity, and catalyst deactivation could happen in 828 this reaction atmosphere. For example, the framework structure of molecular sieve catalysts is 829 easily dealuminated in water vapor conditions at high temperatures and this leads to a decrease in 830 831 SCR activity (Martínez-Hernández and Fuentes, 2005). The metal oxide catalysts in the SO<sub>2</sub> 832 atmosphere could form poison sulfate species (e.g., ammonium sulfate/bisulfate or metal 833 sulfates) on the catalyst surface, which might reduce the life of the catalyst (Liu et al., 2011). 834 Therefore, the water and sulfur resistance on the HC-SCR catalyst is a very important application 835 for NO conversion. It is generally believed that the adsorption of water vapor at the active site of the catalyst surface with the reactant molecules is the main reason for the decrease in catalytic 836 837 SCR activity. Compared with molecular sieve catalysts, pillaring promoters form rigid stable 838 oxide pillars in PILCs after calcination, thus leading to PILC materials with higher specific
surface area, thermal stability, and more acidity. These oxide pillars have a high degree of 839 840 hydrophobicity (Han et al., 1999), which can improve the water vapor resistance of metalmodified PILC catalysts (Kim et al., 2001). Valverde et al. (2003b) examined the Cu/Ti-PILC 841 catalyst under water vapor conditions, and the NO<sub>x</sub> conversion rate declined from 50 to 22% at 842 843 240 °C, as H<sub>2</sub>O molecules were adsorbed on the active sites between the catalyst, inhibiting the adsorption of NO molecules and C<sub>3</sub>H<sub>6</sub> molecules and reducing the rate of reaction. This 844 supported the finding of Chajar et al. (1998). Further, Li et al. (1997) also reported the LT-SCR 845 activity of the Cu/Al-PILC catalyst under H<sub>2</sub>O conditions. A negligible decline was observed in 846 847 SCR activity (80 to 78%) at high temperatures (500 °C) under the same conditions. However, higher deactivation (38 to 4%) was observed at low temperature (350 °C), which may be related 848 to the decline of adsorption capacity of water vapor at high temperatures. 849 850 The results also show that water vapor can promote the HC-SCR reaction to a certain level. 851 Shimizu et al. (2000) investigated the effect of H<sub>2</sub>O on HC-SCR by using a series of *n*-alkanes (C<sub>3</sub>H<sub>8</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>6</sub>H<sub>14</sub>, *n*-C<sub>8</sub>H<sub>18</sub>), and found that the alkanes with higher carbon numbers 852 revealed better water resistance. Meanwhile, a 10% difference in the SCR activity was observed 853 854 for n-C<sub>6</sub>H<sub>14</sub>. Particularly, for n-C<sub>8</sub>H<sub>18</sub>, the presence of H<sub>2</sub>O had not reduced the NO conversion 855 but enhanced the LT-SCR activity by up to 20% for NO<sub>x</sub>. Based on these findings, it is assumed 856 that one of the causes of water vapor's promotive effect on the SCR process is its selective 857 inhibition of the oxidation of n-octane. Further, the promoting effect of H<sub>2</sub>O in the SCR reaction 858 was explained by in-situ infrared experiments, which notably showed that H<sub>2</sub>O reduces the concentration of carboxylate and carbonate species, rather than the surface concentration of 859 nitrates. It is assumed that H<sub>2</sub>O inhibits the formation of carbonaceous deposits and/or promotes 860 861 their removal, as reported in similar studies by Haneda et al. (1998, 2001) and Misono et al.

(1998). Sadykov et al. (2006) found that the higher water vapor content in the reaction 862 atmosphere was beneficial to reduce the carbon deposition on the catalyst surface, thereby 863 increasing the de-NO<sub>x</sub> activity on the Pt-Cu/Zr-PILC catalyst surface, as shown in Fig. 5b. Sato 864 et al. (1997) suggested that water vapor on the surface of the Ag ion-exchange saponite catalyst 865 866 could inhibit the formation of by-product N<sub>2</sub>O, and improve the N<sub>2</sub> selectivity. 867 There are two main reasons for the deactivation of catalysts in the SO<sub>2</sub> atmosphere. The first reason is similar to the deactivation of the catalyst in the steam gas, which is due to the 868 competitive adsorption of SO<sub>2</sub> molecules with the reactant molecules at the active site of the 869 catalyst (Chen et al., 2011). Another reason is that SO<sub>2</sub> is oxidized on the surface of the catalyst 870 to form sulfate compounds. The poisoning effect of SO<sub>2</sub> gas can decrease the reaction activity of 871 the catalyst (Liu et al., 2014). Sadykov et al. (2006) also studied ultra-microporous zirconia PILC 872 catalyst by NO-TPD for  $NO_x$  SCR with decane and propylene and reported that the number of 873 nitrate species formed on the surface of the catalyst after the SO<sub>2</sub> atmosphere reaction was 874 significantly decreased, indicating that the metal ions could not activate between PILC, which 875 could be covered by sulfate compounds and can also affect the active sites of the catalyst. It also 876 877 found that SO<sub>2</sub> closely interacts with metal oxides to produce metal bisulfite species, which 878 could block the catalyst pores (Qian et al., 2017; Dong et al., 2018; Jiang et al., 2020). 879 Meanwhile, the resistance of H<sub>2</sub>O and SO<sub>2</sub> was examined for the Fe/Al-PILC and Ag/Fe/Al-880 PILC catalysts by Zhang et al. (2019). A 7% to 9% reduction in the catalytic performance was 881 observed after introducing SO<sub>2</sub> and H<sub>2</sub>O in the feed conditions; however, after stopping the SO<sub>2</sub> and H<sub>2</sub>O feeds, the NO conversion values quickly recovered for both catalysts. Thus, the Fe/Al-882 PILC catalysts with the 2.1 wt% Ag loading performed better than the monometallic Fe. They 883 884 reported that the synergistic effect of Fe and Ag caused by electronic transfer affected the

valence states of metals and improved their SCR performance with C<sub>3</sub>H<sub>6</sub>. The addition of Ag 885 displayed high LT-SCR activity and improved the Brønsted acidity. Recently, Su et al. (2020) 886 investigated the effect of H<sub>2</sub>O and SO<sub>2</sub> on the NO<sub>x</sub> conversion with C<sub>3</sub>H<sub>6</sub> over Cu-Fe/Al-PILC 887 catalyst. They reported that NO conversion decreased by 10 to 15% after introducing 0.02% SO<sub>2</sub> 888 889 and 10% H<sub>2</sub>O in the flow system. It is observed that the influence of H<sub>2</sub>O and SO<sub>2</sub> on the SCR reaction was reversible after removing the H<sub>2</sub>O and SO<sub>2</sub> from the reaction system. To date, 890 solutions for improving SCR activity in the presence of H<sub>2</sub>O and SO<sub>2</sub> are still being researched. 891 In this respect, the primary area of research continues to focus on improving the  $H_2O$  and  $SO_2$ 892 tolerance on the PILC-based catalyst for LT-SCR of NO<sub>x</sub> with HC. 893

## 894 **3.6. Reaction mechanism**

The SCR reaction mechanism of  $NO_x$  conversion with HC is relatively complicated. Many 895 previous studies have investigated and reported a possible mechanism, but there is still no fully 896 defined conclusion. The type of catalyst, surface-active sites, and reaction conditions can affect 897 the intermediate products and reaction pathways of the HC-SCR process. At present, the HC-898 SCR reaction mechanisms are defined over different PILC-based catalysts and are mainly 899 900 divided into two types: redox mechanism and adsorption decomposition mechanism. 901 Typically, the process of HC-SCR redox mechanism is as follows: NO molecules are activated and oxidized on the catalyst surface to form different ad-NO<sub>x</sub> species such as nitrate (NO<sub>3</sub>), and 902 nitrite (NO<sub>2</sub><sup>-</sup>), and adsorb NO<sub>2</sub>, while at the same time, some hydrocarbon compounds are 903 904 partially oxidized on the catalyst surface to form  $C_x H_v O_z$  species, mainly acetate (CH<sub>3</sub>COO<sup>-</sup>). After this, CH<sub>3</sub>COO<sup>-</sup> and other adsorbed  $C_xH_yO_z$  species react with ad-NO<sub>x</sub> on the surface of the 905 catalytic agent to form nitrogen-containing organic intermediates (R-NO<sub>2</sub>) (Burch et al., 2002). 906 907 Although the exact type and form of nitrogen-containing organic intermediates are still unclear,

the formation process of these species is considered to be a significant step in the HC-SCR
reaction (Tanaka et al., 1994). R-NO<sub>2</sub> species quickly transform to R-NCO, R-CN, NH<sub>3</sub>, and
other species on the surface of the catalyst, and react with NO and NO<sub>2</sub> to obtain the final N<sub>2</sub>
product.

As observed in the previous study (Burch et al., 1994), the mechanism of adsorption and
decomposition considers the fact that the hydrocarbon compound first consumes surface oxygen
atoms of the catalyst and converts them into active sites (reduced metal ions). NO molecules
subsequently adsorb on these sites and they dissociatively decompose into N<sub>ad</sub> and O<sub>ad</sub> atoms.
The product N<sub>2</sub> is obtained by the mutual combination of two N<sub>ad</sub> atoms, and at the same time,
when N<sub>ad</sub> and NO<sub>ads</sub> are combined, N<sub>2</sub>O is produced as a by-product.

However, by considering the process of HC-SCR reaction on the surface of some catalysts, the 918 redox mechanism can better explain the experimental phenomena as observed in previous 919 studies. For example, Long et al. (1998) found that the Pt ion-exchange MCM-41 molecular 920 sieve catalyst had almost no catalytic activity for NO conversion with HC in the absence of 921 oxygen. Further, Gruenert et al. (1994) also reported a similar phenomenon over the Cu-ZSM-5 922 923 catalyst, where O<sub>2</sub> plays an important role in promoting the hydrocarbon SCR reaction. These 924 observations prove that NO and HC need to be activated and oxidized first in the redox 925 mechanism. On the other hand, the adsorption decomposition mechanism can better explain the 926 formation of the by-product N<sub>2</sub>O in the reaction process and some catalysts still have good SCR 927 performance for NO under oxygen-free conditions. Therefore, there is debate on there being two 928 HC-SCR reaction paths: one being redox and the other being adsorption decomposition on the surface of the catalyst in the actual HC-SCR process as shown in Fig. 6a. 929 930 As more data became available, particular interest was in the redox process for HC-SCR of NO<sub>x</sub>

over metal-modified PILC catalysts. However, there is still a shortcoming about the intermediate 931 932 products that are involved in the specific reaction path in the SCR of  $NO_x$  with HC. In the very beginning, Li et al. (1997) proposed a reaction mechanism for the NO conversion 933 with C<sub>2</sub>H<sub>4</sub> on the surface of the Cu/Al-PILC catalyst. They reported that C<sub>2</sub>H<sub>4</sub> chemical 934 935 adsorption was activated and oxidized at the active site to form oxygen-containing compounds, 936 and then reacted with adsorbed NO<sub>2</sub> and NO<sub>3</sub> species to form nitrogen-containing organic intermediates, which were further decomposed to produce N2 and CO2. Further, as the reaction 937 activity of C<sub>2</sub>H<sub>4</sub> on the Cu/Al-PILC surface is significantly better than that of CH<sub>4</sub> as a reducing 938 agent, they believe that the coordination between HC and catalyst active sites is more important 939 for the formation of free radicals in the process of  $C_xH_y$  than the formation of free radicals by C-940 H bond breaking. Furthermore, Mendioroz et al. (2006) studied the reaction mechanism of CH<sub>4</sub>-941 SCR of NO conversion on the surface of Rh/Al-PILC catalyst. They believe that NO molecules 942 were mainly activated and oxidized on the surface of Rh<sup>III</sup> sites to form reactive Rh-NO<sub>2</sub> species. 943 At the same time, CH<sub>4</sub> is activated at the Lewis acidic site on the catalyst surface, and then it 944 reacts with the NO<sub>2</sub> species formed on the adjacent Rh<sup>III</sup> active site to form free surface radicals, 945 946 which react with NO and NO<sub>2</sub> molecules to obtain the final product. The difference is that 947 Mendioroz et al. (2006) believe that the presence of oxygen is irrelevant to the activation process 948 of HC but plays a vital role in the oxidation of NO molecules to form Rh-NO<sub>2</sub> species, and this 949 process is the rate-determining step of the entire SCR reaction. Sadykov et al. (2006) have 950 reported that different HC-SCR reaction paths may exist on the surface of the same catalyst at 951 different temperature ranges. For the C<sub>3</sub>H<sub>6</sub>-SCR process on the surface of the Pt-Cu/Zr-PILC catalyst at low-temperature ranges, propylene is activated at acidic bridged hydroxyl sites to 952 953 form isopropanol compounds, and NO molecules are oxidized at the active sites of Pt atoms to

generate NO<sub>2</sub> and the rapid formation of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> species. Next, the bridged or bidentate 954 NO<sub>3</sub> species interacts with isopropanol to produce dinitro propane, which further reacts to 955 produce N<sub>2</sub> and oxidation products. Cu<sup>II</sup> sites can promote the reaction of NO<sub>3</sub><sup>-</sup> species to 956 produce nitrogen-containing organic intermediates. It is believed that the oxidative conversion of 957 958 isopropoxide compounds to acetate and nitromethane conversion to isocyanate species are 959 catalyzed on the active site of Pt and Cu catalysts. However, acetates could efficiently be transformed into nitromethane by acid-catalyzed reaction without any redox activity (Sadykov et 960 al., 2006). In addition, Valverde et al. (2005) used in-situ DRIFTS technology to study the C<sub>3</sub>H<sub>6</sub>-961 962 SCR reaction intermediates on the surface of Cu/Ti-PILC catalyst, and the result showed that the nitrogen-containing organic intermediates (C<sub>3</sub>H<sub>7</sub>-NO<sub>2</sub>), acetate, and nitrate species were the main 963 intermediate products. Dorado et al. (2010) studied reaction mechanisms over Cu/Fe-PILC 964 catalyst surface by in-situ DRIFTS technology as shown in Fig. 6b. The first step of the reaction 965 was that the NO is oxidized on the surface of the catalyst Cu<sup>II</sup> species to produce NO<sub>2</sub> and nitrate 966 species. The formation of nitrate is affected by the distribution of metal active sites and is mainly 967 divided into monodentate nitrate and bidentate nitrate. In the second step of the reaction, 968 hydrocarbon compounds are adsorbed on Cu<sup>II</sup> or CuO cluster sites and are activated to form 969 970  $C_xH_yO_z$  species. In the next step,  $C_xH_yO_z$  species are further oxidized by NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> to 971 acetate species and nitrogen-containing organic compounds (R-NO<sub>2</sub>). Finally, the R-NO<sub>2</sub> species 972 are converted into isocyanate, and the final products (N<sub>2</sub>, CO, and H<sub>2</sub>O) are produced by rapid 973 hydrolysis. Many scholars (Yuan et al., 2018, 2019; Su et al., 2020; Wen et al., 2020) believe that isocyanate 974 species are important intermediates in the HC-SCR reaction. For example, during the C<sub>3</sub>H<sub>6</sub>-SCR 975

976 reaction on the surface of the Cu-ZSM-5 catalyst, the SCR reaction intermediates are nitrogen-

containing organic compounds (R-NO<sub>x</sub>) and cyanide (CN), which are transformed into
isocyanate species (NCO<sup>-</sup>), then NCO<sup>-</sup> is hydrolyzed to form NH and NH<sub>3</sub>, and finally, NH<sub>3</sub>
reacts with NO molecules to form the final product N<sub>2</sub>. The existence of Cu-NCO<sup>-</sup> species was

980 found in DRIFTS spectral data. However, the formation and conversion process of NH<sub>3</sub> could

not yet be proved. This may be caused by the rapid reaction of NH<sub>3</sub> with NO and being

982 consumed after the formation of NH<sub>3</sub>, which is difficult to capture by the existing technology

983 (Gruenert et al., 1994; Liu et al., 2013; Lai et al., 2015).

Meanwhile, Ye et al. (2012) further studied the catalytic cycle of the copper-PILC catalyst for the 984 985 SCR reaction, as shown in Fig. 6c. Based on the previous studies of Valverde et al. (2005) and Dorado et al. (2010), Cu<sup>II</sup> active sites first adsorb NO and form Cu<sup>II</sup> -NO<sup>•</sup>, and then are reduced 986 to  $Cu^{I}$  or  $Cu^{0}$  in the process of reacting with  $C_{x}H_{y}O_{z}$  to generate organic nitro compounds (or 987 organic nitrites), and finally, Cu<sup>I</sup> or Cu<sup>0</sup> can be oxidized by NO or O<sub>2</sub> in the reaction to form Cu<sup>II</sup> 988 species, thus forming a closed catalytic cycle. This cyclic mechanism clearly illustrates the cyclic 989 conversion process of C<sup>II</sup> species as the important reactive sites of copper-based PILC catalysts 990 in HC-SCR. 991

992 Remarkably, Sirilumpen et al. (1999) found that in the absence of reducing agents, NO can be 993 directly decomposed into N2 with a small concentration of N2O on the surface of the Cu/Al-PILC 994 catalyst. They proposed the Eley-Rideal redox mechanism for the decomposition of NO on the copper-functionalized PILC surface. Cu<sup>II</sup> species on the surface of Cu/Al-PILC catalyst form Cu<sup>I</sup> 995 sites under the combined action of surrounding H<sub>2</sub>O molecules and lattice oxygen O\* and NO 996 are adsorbed at this site to form Cu<sup>I</sup>(NO)<sub>2</sub> and decomposed into Cu<sup>II</sup>O<sup>-</sup> and N<sub>2</sub>O. NO molecules 997 can generate monodentate nitrite or bidentate nitrite species on the Cu<sup>II</sup>O<sup>-</sup> active site and are 998 further oxidized to produce monodentate nitrate species by lattice oxygen O\*. Finally, nitrate 999

interacts with NO to form N<sub>2</sub> or a small amount of N<sub>2</sub>O and produces new Cu<sup>II</sup>O<sup>-</sup> sites and 1000 lattice oxygen O\* for the next catalytic cycle. The coupling of the N-N bond is considered to be 1001 an important step in this process. These results show that the addition of external oxygen can 1002 1003 only be used to supplement the lattice oxygen O\* species in Cu/Al-PILC but did not affect the 1004 formation of nitrates species. This mechanism provides a reasonable explanation of the formation 1005 cycle of N<sub>2</sub>O on the surface of copper-based PILC catalyst and complements the NO decomposition in the HC-SCR catalytic reaction. 1006 1007 In summary, although good progress has been made on the HC-SCR reaction mechanism over

the surface of metal-modified PILC catalysts, there are still many challenges that need to be
investigated in detail. For example, the activation mechanism of HC is still not clear, the
structure of nitrogen-containing organic intermediates needs to be analyzed, and the types and
functions of isocyanates need to be explored and analyzed more deeply in order to achieve a full

1012 understanding of the SCR reaction mechanism over PILC-based catalysts.

#### 1013 **4. Summary and future outlook**

1014 Mt-based PILC clay has received considerable attention as a catalyst support material in SCR 1015 catalysts over the last five decades. Metal-supported PILC catalysts have shown good catalytic 1016 activity at low temperatures (150 to 300 °C) with HC as reductants. Among them, the Fe- and 1017 Cu-PILC catalysts have displayed high SCR activity for NO<sub>x</sub> conversion by  $C_3H_6$  at low

1018 temperatures.

1019 At present, although research on the HC-SCR reaction mechanism on the surface of metal-

1020 modified PILC catalysts has made some progress, there are still many shortcomings. For

1021 example, PILC catalysts have low HC-SCR activity under lean-burn conditions and also at high

1022 O<sub>2</sub> concentrations, but their SCR efficiency is generally low at high temperatures (300 to

600 °C). The activation mechanism of HC is still unclear, the structure of nitrogen-containing
organic intermediates needs to be analyzed, and the types and functions of isocyanates require
more in-depth experiments to explore and analyze.

- 1026 In the years ahead, a future research direction for PILC-based catalysts will be further
- 1027 improvement of the catalyst stability at low to high temperatures. Hence, a major challenge will
- 1028 be to improve catalytic activity and N<sub>2</sub> selectivity at high temperatures, as well as to prepare
- 1029 highly stable metal-supported PILC-based catalyst for NO<sub>x</sub> reduction with high H<sub>2</sub>O and SO<sub>2</sub>
- 1030 resistance. Furthermore, PILC catalysts are in the powder state, which can easily transform into
- 1031 the required shape, which is more beneficial for commercial application. In recent advances,
- 1032 research is ongoing in the development of PILC catalysts to convert NO<sub>x</sub> via NH<sub>3</sub> and HC as a
- 1033 reducing agent, pollutant removal, and organic chemical reactions such as condensation,
- 1034 alkylation, isomerization, oxidation, hydrogenation and dehydrogenation, protection-
- 1035 deprotection, hydroboration, iodine capture, and H<sub>2</sub> production.

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Fig. 1 (a) Chemical transformations of  $NO_x$  related to air pollution, copyright (2010) Springer Nature from (Belver, 2010) and (b) illustration of a variety of crucial environmental and biological phenomena and effects induced by  $NO_x$ , copyright (2020) Springer Nature from (Ko et al., 2020).



Fig. 2 (a) Schematic representation of clay pillaring process (Basal spacing;  $d_1 < d_3 > d_2$ ), copyright

(2018) RSC Adv., from (Baloyi et al., 2018) and (b) Mt-based PILC catalysts, A, B (CrCe/Ti) average particle size < 10 nm, copyright (2013) Elsevier from (Zhang et al., 2013), C, D (Cu-Fe/Al), estimated  $d \ge 1.4$  nm, copyright (2020) American Chemical Society from, (Su et al., 2020) and E, F (Pd-Zr) showing a < 5 nm PdO nanocrystal with the corresponding SAED pattern (in the white rectangle), copyright (2015) Elsevier from (Michalik-Zym et al., 2015).



**Fig. 3 (a)** Model for Lewis and Brønsted acid sites on sulfated iron and titanium dioxide Mt-based PILC catalysts, copyright (1999) Elsevier from (Long and Yang, 1999a) and (b) the relationship between NO conversion (%) and Lewis acidity ( $\mu$ mol/g) over Mt-based Fe/Ti-PILC-*x*-500 catalysts (Ti/clay ratio, x = 5, 10 and 30 mmol/g), copyright (2020) Elsevier from (Wen et al., 2020).



**Fig. 4** (a) Maximum NO conversion at low temperature (200 °C) over Mt-based Ti-PILC catalysts, reproduced data with permission from (Yang et al., 1998) (b) effect of the metal loading on SCR of NO<sub>x</sub> over Mt-based PILC catalysts modified with Cu, Fe and Ni, copyright (2003) Elsevier from (Valverde et al., 2003a).



**Fig. 5** (a) Influence of oxygen concentration on SCR performance over Al-Fe/PILC catalysts, copyright (2004) Elsevier from (Belver et al., 2004b) and (b)  $NO_x$  conversion in C<sub>3</sub>H<sub>6</sub>-SCR on Mt-based Pt-Cu/Zr-PILC catalyst (1) without SO<sub>2</sub> and H<sub>2</sub>O (2) with SO<sub>2</sub> and H<sub>2</sub>O, copyright (2006) Elsevier from (Sadykov et al., 2006).



**Fig. 6 (a)** Schematic diagram of adsorption decomposition and redox reaction path on the surface of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, copyright (1999) Elsevier from (Meunier et al., 1999), (b) reaction mechanism scheme for the  $C_3H_6$ -SCR of NO<sub>x</sub> over Mt-based Cu/Fe-PILC, copyright (2010) Elsevier from (Dorado et al., 2010) and (c) catalytic cycle for the SCR reaction over Mt-based Cu-PILC catalysts, reproduced with the permission from (Ye et al., 2012).

Catalysts	Calcination Temp. (°C)/h	Specific Surface Area (m <sup>2</sup> /g)	Reaction Conditions and Catalyst mass	NO Conversion (%)	Temp. (°C)	References
Al-PILC	500/5	180	0.05%NO+0.3%C <sub>3</sub> H <sub>6</sub> +1%O <sub>2</sub> Flow rate=200 ml/min, GHSV=15000h <sup>-1</sup> , 0.4g	15	350	(Qian et al., 2017)
Fe/Al-PILC		186		90		
Rh/Al-PILC	500/2	200		60	400	(Bahamonde et al., 2001)
Pt/Al-PILC		206		5	5 <mark>00</mark>	
Pd/Al-PILC		193		30	400	
Rh/Al-PILC	500/2	190	$\begin{array}{c} 0.1\% \text{NO+} 0.2\% \text{CH}_4 \text{+} 1.2\% \text{O}_2 \\ \text{GHSV} \text{=} 40000 \ \text{h}^{\text{-}1} \end{array}$	24	<mark>4</mark> 50	(Mendioroz et al., 2006)
Pd/Al-PILC		193	0.05%NO+0.5%CH <sub>4</sub> +5%O <sub>2</sub> GHSV= 3600h <sup>-1</sup>	30	400	(Mohino et al., 2005)
Cu/Ti-PILC	400/12		0.1%NO+0.1%C2H4+2%O2 Flow rate=250 ml/min, 0.5g	57	300	(Yang et al., 1998)
Ce/Ti-PILC				30	500	
Fe/Ti-PILC				30	450	
Ga/Ti-PILC				38	450	
Ag/Ti-PILC				20	450	
Ag/Ti-PILC		210	0.25%NO+0.25%C <sub>2</sub> H <sub>4</sub> +2.5%O <sub>2</sub> Flow rate=40ml/min, 0.2g	60	400	(Chmielarz et al., 2004)
Ag/Zr-PILC		156		20		
Ag/Al-PILC		151		18		
Cu/Ti-PILC	400/12	250	0.1%NO+0.1%C <sub>2</sub> H <sub>4</sub> +2%O <sub>2</sub> (0.05%SO <sub>2</sub> or 5%H <sub>2</sub> O), GHSV=15000h <sup>-1</sup> , 0.5g	<mark>60</mark>	300	(Li et al., 1997)
Cu/Ti-PILC	500/5	240	0.1%NO+0.1%C <sub>3</sub> H <sub>6</sub> +4%O <sub>2</sub> (10%H <sub>2</sub> O), Flow rate=250 ml/min, 0.5g	70(58)	300	(Kim et al., 2001)
Cu/Ti-PILC	500/2	234	0.1%NO+0.1%C <sub>3</sub> H <sub>6</sub> +5%O <sub>2</sub> (10%H <sub>2</sub> O) GHSV=15000h <sup>-1</sup> , 0.25g	55(28)	260	(Valverde et al., 2003a)
Fe/Ti-PILC		217		35	325	
Ni/Ti-PILC		236		35	425	
Fe/Ti-PILC	500/2	190	0.1%NO+0.1%C <sub>3</sub> H <sub>6</sub> +1%O <sub>2</sub>	90	375	(Dong et al., 2018)
	700/2	193	Flow rate=100 ml/min, GHSV=12000h <sup>-1</sup> , 0.4g	95	325	(Wen et al., 2020)
Cu/Ti-PILC	350/5	159	$0.1\%NO+0.1\%C_{3}H_{6}+10\%O_{2}$	43	237	(Lu et al., 2011)

# Table 1 Results of HC-SCR of maximum NO<sub>x</sub> conversion over Mt-based PILC catalysts.

			GHSV=25000h <sup>-1</sup> , 0.2g			
			0.1%NO+0.1%C <sub>3</sub> H <sub>6</sub> +10%O <sub>2</sub> Flow rate=100 ml/min, 0.2g	55	280	
Cu/Ti-PILC	400/2	294		50(28)	240 (250)	(Valverde et al., 2003b)
Ag/Cu-Ti-PILC		270		55(35)		
Ce/Cu-Ti-PILC		283		75(65)		
Cu/Ti-PILC	400/4		0.1%NO+0.025%C <sub>2</sub> H <sub>4</sub> +2%O <sub>2</sub> (0.05%SO <sub>2</sub> +5%H <sub>2</sub> O) Flow rate=150 ml/min, 0.5g	80(65)	300	(Yang and Li, 1995; Yang and Cheng, 2002)
Ce-Cu/Ti-PILC			0.1%NO+0.025%C <sub>2</sub> H <sub>4</sub> +2%O <sub>2</sub> Flow rate=150 ml/min, 0.5g	90	300	Tang and Cheng, 2002)
Cu/Fe-PILC	400/2	214	0.1%NO+C <sub>3</sub> H <sub>6</sub> , 5%O <sub>2</sub> , Flow rate=125mL/min, 0.25g	51	260	(Dorado et al., 2010)
Cu/Fe-PILC	400/2	158	$\begin{array}{c} 0.09\%\text{NO+}0.09\%\text{C}_{3}\text{H}_{6}\text{+}10\%\text{O}_{2}\\ \text{GHSV}\text{=}15000\text{h}^{-1}, 0.25\text{g} \end{array}$	34		(García et al., 2007)
Zr/Pt-PILC	400		$\begin{array}{c} 0.2\% \text{NO+} 0.2\% \text{C}_3\text{H}_6\text{+} 2.5\% \text{O}_2, \\ \text{GHSV} = 18000 \text{h}^{-1} \end{array}$	60	- 300	(Sadykov et al., 2005)
Ca/Pt-PILC				<mark>9</mark> 5		
Pt-Cu/Zr-PILC	500	180	$\begin{array}{c} 0.2\% NO {+} 0.2\% C_3 H_6 {+} 2.5\% O_2 {+} \\ 0.02\% SO_2 {+} 3\% H_2 O, \\ GHSV {=} 70000 \ h^{-1} \end{array}$	95	300	(Sadykov et al., 2006)
			$\begin{array}{c} 0.2\% NO{+}0.2\% C_{3}H_{6}{+}2.5\% O_{2} \\ GHSV{=}30000 h^{-1} \end{array}$	78	250	
Cu/Ce-Zr-PILC	600/	200-320	$\begin{array}{c} 0.2\% NO{+}0.2\% C_{3}H_{6}{+}2.5\% O_{2} \\ GHSV{=}18000 \ h^{-1} \end{array}$	50	300	(Sadykov et al., 1999)
Ag-Cu/Ce-Zr-PILC				60	400	
Cu-Ce/Al-PILC	500/6	161	0.22%NO+0.12%C <sub>3</sub> H <sub>6</sub> +2%O <sub>2</sub> GHSV=70000h <sup>-1</sup> , 0.5g	56	350	(Lin et al., 2007)
			$\begin{array}{c} 22\% NO \!\!+\!\! 0.12\% C_3 H_6 \!\!+\! 2\% O_2 \!\!+\! 10\% H_2 O, \\ GHSV \!\!=\! 24000 h^{\text{-}1}, 0.5 g \end{array}$	42	400	
Fe/Al-PILC		61	$\begin{array}{c} 0.05\%\text{NO+0.2\%}\text{C}_3\text{H}_6\text{+}1\%\text{O}_2\\ \text{GHSV=}17,000\text{h}^{-1},0.4\text{g} \end{array}$	65	400	(Su et al., 2020)
Cu-Fe/Al-PILC		81		90	250	
Fe/Al-PILC	500/3.5	184	NO=0.05%, C <sub>3</sub> H <sub>6</sub> =0.2%, O <sub>2</sub> =1%, GHSV=22000h <sup>-1</sup> , 0.4g	85	- 100	(Zhang et al., 2019)
Ag-Fe/Al-PILC		72		95	400	

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