# Benzene Oxidation in Air by an Amine-Functionalized Metal-Organic Framework-Derived Carbon and Nitrogen-loaded Zirconium Dioxide-Supported Platinum Catalyst

Kumar Vikrant<sup>a</sup>, Ki-Hyun Kim<sup>a,\*</sup>, Danil W. Boukhvalov<sup>b, c</sup>, Philippe M. Heynderickx<sup>d, e</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-Ro, Seoul 04763, Republic of Korea

<sup>b</sup> College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, China

<sup>c</sup> Institute of Physics and Technology, Ural Federal University, Mira Street 19, 620002 Yekaterinburg, Russia

<sup>d</sup> Center for Environmental and Energy Research (CEER), Engineering of Materials via Catalysis and Characterization, Ghent University Global Campus, 119-5 Songdo Munhwa-ro, Yeonsu-gu, Incheon 406-840, Republic of Korea

<sup>e</sup> Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

# Abstract

To learn more about the behavior of amine (NH<sub>2</sub>)-functionalized metal-organic framework (MOF)-derived noble metal catalysts in the removal of aromatic volatile organic compounds in air, benzene oxidation at low temperatures has been investigated using 0.2-, 0.8-, and 1.5%-platinum (Pt)/Universitetet i Oslo (UiO)-66-NH<sub>2</sub>. The benzene conversion (X<sub>B</sub>) of x%-Pt/UiO-66-NH<sub>2</sub>-R under dry conditions (175°C) was 23% (x=0.2%) < 52% (x=0.8%) < 100% (x=1.5%): 'R' suffix denotes reduction pre-treatment using hydrogen (10 vol.%) and nitrogen mixture at 300°C for the generation of metallic Pt (Pt<sup>0</sup>) sites and simultaneous partial MOF decomposition into carbon and nitrogen-loaded zirconium dioxide. The prominent role of the reduction pre-treatment was apparent in benzene oxidation as 1.5%-Pt/UiO-66-NH<sub>2</sub> did not exhibit catalytic activity below 175°C (dry condition). The promotional role of moisture in benzene oxidation by 1.5%-Pt/UiO-66-NH<sub>2</sub>-R was evident with a rise in the steady-state reaction rate (r) at 110°C (21 kPa molecular oxygen (O<sub>2</sub>)) from 1.3E-03 to 5.0E-03  $\mu$ mol g<sup>-1</sup> s<sup>-1</sup> as the water (H<sub>2</sub>O) partial pressure increased from 0 to 1.88 kPa. In contrast, the activity was lowered with increasing RH due to catalyst poisoning by excess moisture (r (110°C) of 6.6E-04 µmol g<sup>-1</sup> s<sup>-1</sup> at 2.83 kPa H<sub>2</sub>O (21 kPa O<sub>2</sub>)). Kinetic modeling suggests that X<sub>B</sub> proceeds through the Langmuir-Hinshelwood mechanism on the Pt/UiO-66-NH<sub>2</sub>-R surface (dissociative O<sub>2</sub> chemisorption and the involvement of two oxygen species in benzene oxidation). According to the density functional theory simulation, the carbon and nitrogen impurities are to make the first X<sub>B</sub> step (i.e., hydrogen migration from the benzene molecule to the substrate) energetically favorable. The second hydrogen atom from the benzene molecule is also extracted effectively, while the oxygen derived from  $O_2$  facilitates further  $X_B$ . The  $Pt^0$  sites dissociate the  $O_2$  and  $H_2O$  molecules, while the product of the latter, i.e., free hydrogen and hydroxyl, makes the subsequent  $X_B$  steps energetically favorable.

Keywords: Metal-organic frameworks; Benzene; Volatile organic compounds; Air pollution; Catalytic oxidation

\*Corresponding Author: <u>kkim61@hanyang.ac.kr</u> (K.-H. Kim)

# 1. Introduction

Air quality management (AQM) commonly focuses on volatile organic compound (VOC) removal due to their harmful effects on the biosphere and human health. Benzene (carcinogenic aromatic VOC) has been recognized as a critical AQM target due to its presence in both indoor and outdoor air <sup>1</sup>. Benzene emissions are released from various anthropogenic sources such as petroleum refining, organic chemical production, paint spraying, textile dyeing, and electronic equipment manufacturing <sup>1</sup>. In indoor air, benzene is typically liberated from cosmetics, glass wool insulation, varnishes, paints, curtains, garments, carpets, disinfectants, wallcoverings, cigarette smoke, sterilizers, and sources <sup>2</sup>. To adequately manage benzene in indoor environments, the National Institute for Occupational Safety and Health (United States of America (USA)) has set 0.1 ppm as the 10 h time-weighted average exposure limit <sup>3</sup>.

VOC oxidation/mineralization into water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) at low temperatures is recognized as the most effective and reliable option for their abatement since it can be conducted without the generation of hazardous by-products <sup>1</sup>. Among a variety of thermocatalysts implemented to oxidize VOCs, supported noble metal (e.g., platinum (Pt)) catalysts (SNMCs) have been recommended as one of the most feasible tools for complete mineralization of recalcitrant pollutants <sup>1</sup>. Typically, such catalysts can achieve prolonged time-on-stream (TOS) performance without deactivation or by-product generation. As such, attaining high catalytic activities at low temperatures using novel SNMCs has become a primary area in AQM research.

The catalytic activity of SNMCs has commonly been optimized through the effective dispersion of noble metal nanoparticles (NPs), which, in turn, are tightly controlled by the physicochemical characteristics of the support material <sup>3</sup>. Recent years have witnessed the growing research on using metal-organic frameworks (MOFs (highly crystalline and porous materials)) as sacrificial templates for catalyst synthesis <sup>4, 5</sup>. Several articles have demonstrated that controlled decomposition of MOFs (using a simple post-

treatment such as pyrolysis) can generate stable materials that are not usually prepared using conventional routes <sup>6</sup>. The materials prepared using MOFs retain the unique characteristics of the MOF template, such as high specific surface <sup>7</sup>. It is relatively easy to impregnate noble metals into MOF-based structures with high specific surfaces, so they can be favorably adopted to help stimulate catalytic reactions <sup>8</sup>. Pyrolytic post-treatment is expected to be an effective route to generate a unique metal-oxide/carbon matrix with supported noble metal NPs <sup>6</sup>. To date, the potential of MOF-derived catalysts has been explored against target reactions such as carbon monoxide (CO) oxidation, CO<sub>2</sub> conversion, hydrogenation, dehydrogenation, and other organic reactions <sup>5,6</sup>. Their feasibility for the oxidizing gaseous VOCs is yet to be explored in detail.

For complete mineralization of recalcitrant benzene into CO<sub>2</sub> using MOF-derived noble-metal catalysts, porous polyhedron cobalt (II, III) oxide (Co<sub>3</sub>O<sub>4</sub>)-supported palladium (Pd) catalyst was produced through calcination of zeolitic imidazole framework (ZIF)-67<sup>-9</sup>. ZIF-67-derived Pd catalyst (highly porous) outperformed the conventional Co<sub>3</sub>O<sub>4</sub>-supported Pd catalyst for benzene oxidation since more active sites were exposed to the gas stream for enhanced catalytic activity <sup>5, 9</sup>. Given the unique potential of MOF-derived noble metal catalysts for low-temperature VOC oxidation reactions, it is imperative to extend such studies to gain intriguing insights. We propose that amine (NH<sub>2</sub>)-functionalized MOFs can be ideal for generating or modifying advanced catalysts. For instance, the controlled pyrolysis of NH<sub>2</sub>-functionalized MOF-SNMCs would produce metal oxide-SNMCs with carbon and nitrogen impurities. As the carbon and nitrogen sites can help enhance VOC adsorption, metal oxide-SNMCs with such impurities could help increase the overall catalytic activity.

In the present work, Universitetet i Oslo (UiO)-66-NH<sub>2</sub> (zirconium (Zr)-based NH<sub>2</sub>-functionalized MOF) was utilized as the support material for loading various amounts of Pt (0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts). The UiO-66-NH<sub>2</sub>-supported Pt catalysts were subjected to a high-temperature reduction

pre-treatment using an inert carrier gas (nitrogen (N<sub>2</sub>)) to obtain metallic Pt (Pt<sup>0</sup>) NPs on carbon and nitrogen-loaded Zr dioxide (ZrO<sub>2</sub>). The feasibility of the prepared materials for benzene catalytic oxidation in the air was explored in various respects. The impact of the critical process conditions, such as flow rate, relative humidity (RH), catalyst mass (M<sub>cat</sub>), benzene concentration, and TOS, on the catalytic activity was also assessed. Also, the fundamental benzene oxidation aspects were assessed in the context of mechanism and reaction pathway using density functional theory (DFT) calculations and other characterizations (molecular oxygen (O<sub>2</sub>)-temperature programmed desorption (TPD), *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and hydrogen (H<sub>2</sub>)-temperature programmed reduction (TPR)). The present work is believed to be the first on NH<sub>2</sub>-functionalized MOF-derived carbon and nitrogenloaded metal-oxide-supported Pt as the thermocatalyst for oxidative removal of gaseous benzene.

# 2. Experimental

#### 2.1. Chemical Reagents

Reagent-grade zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O; 98%), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O;  $\geq$  37.5% Pt basis), terephthalic acid (BDC (C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>); 98%), N,N-dimethylformamide (DMF (C<sub>3</sub>H<sub>7</sub>NO);  $\geq$  99.8%), 2-aminoterephthalic acid (BDC-NH<sub>2</sub> (C<sub>8</sub>H<sub>7</sub>NO<sub>4</sub>); 99%), quartz sand (SiO<sub>2</sub>;  $\geq$  99.995%), hydrochloric acid (HCl; 37%), and liquid benzene (99.8%) were procured from Sigma-Aldrich (St. Louis, MO, USA). Ethanol (EtOH (C<sub>2</sub>H<sub>5</sub>OH); 99.9%) was obtained from Daejung Chemicals and Metals Co., Ltd. (Siheung, South Korea). H<sub>2</sub> (99.999%), N<sub>2</sub> (99.999%), and air (99.999%) were procured from Union Gas Co., Ltd. (Yongin, South Korea). No further purification was done for the received chemicals.

#### 2.2. Synthesis procedures

Two UiO MOFs were synthesized per the protocol reported previously after slight modifications <sup>10</sup>. In brief, Zr solution was arranged by adding HCl (18 mL) and ZrOCl<sub>2</sub>·8H<sub>2</sub>O (2,250 mg) to DMF (90 mL). The ligand solution was prepared by adding BDC (or BDC-NH<sub>2</sub> in the case of UiO-66-NH<sub>2</sub>) (2,412 mg) to 180 mL DMF. The above-prepared solutions were ultrasonicated at 40 kHz for 30 min. The ligand and metal solutions were mixed and covered with aluminum foil. The above solution was kept in a convection oven for 20 h (85°C). DMF and EtOH were used to wash the obtained precipitate three times. The MOF was then obtained by drying the solid in a convection oven at 85°C (20 h). The 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> synthesis involved the conventional wetness impregnation protocol <sup>11</sup>. In short, deionized (DI) H<sub>2</sub>O (20 mL) at room temperature (RT) was stirred (500 rpm) for 15 min after adding suitable amounts of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (5.3-39.8 mg). UiO-66-NH<sub>2</sub> (1,000 mg) was added to the Pt solution at RT and stirred (500 rpm) for 3 h. The suspension was then transferred to a convection oven (85°C) for 15 h to evaporate the H<sub>2</sub>O, yielding the dry catalyst powder.

#### 2.3. Benzene oxidation experiments

A quartz tube reactor (length and inner diameter of 16 and 0.3 cm, respectively) was utilized to conduct the benzene oxidation reaction at atmospheric pressure <sup>12</sup>. SiO<sub>2</sub> (300 mg) and the powdered catalyst (30-100 mg) were physically mixed, put inside the quartz tube reactor, and held in position using quartz wool (Ohio Valley Specialty Company, Marietta, OH, USA). The packed bed temperature was controlled using a heating block connected to a tube (electric) heater (TC200P (K), Misung Scientific Co., Ltd., Yangju, South Korea). The packed bed was heated at 300°C for 3 h under (i) H<sub>2</sub> (10%) + N<sub>2</sub> or (ii) N<sub>2</sub> flow (50 mL min<sup>-1</sup>) before the beginning of each experiment. The 'R' suffix was used to describe the reduced catalyst. A vacuum pump (DOA-P704-AC, Gast Manufacturing Inc., Fair Plain, MI, USA) was used to control the gas flow through the packed bed. A calibrator (FC-M1, Sibata Scientific Technology Ltd., Saitama, Japan) and a valve were used to set the gas flow rate. The benzene (100-300 ppm) gaseous-working standard (G-WS) was prepared in a 100 L polyester aluminum (PEA) bag (Top Trading Co., Ltd., Seoul, South Korea) containing air by injecting suitable volumes of liquid benzene <sup>13</sup>. The PEA bag injected with liquid benzene was left under ambient conditions for 20 h to completely vaporize and stabilize the benzene inside the PEA bag <sup>14</sup>. The gas-phase recovery of the injected liquid benzene was assumed as ~ 90% based on previously published research results <sup>14</sup>. The RH in the 30-90% range was maintained by injecting DI H<sub>2</sub>O (680-2,000  $\mu$ L) into the 100 L PEA bag filled with benzene G-WS. For the oxidation experiments, benzene G-WS was pulled through the packed bed in the 50-250 mL min<sup>-1</sup> range.

The packed bed temperature was increased incrementally from 100°C (25°C intervals) until 100% benzene conversion (X<sub>B</sub>) was attained (Equation 1). [B]<sub>out</sub> and [B]<sub>in</sub> refer to the benzene in the reactor effluent and influent, respectively. A steady state was established at each temperature point by maintaining it isothermally for appropriate durations (e.g., at least 1 h). Benzene and CO<sub>2</sub> (generated due to benzene mineralization) were analyzed simultaneously by a gas chromatograph (GC) fitted with a methanizer (iGC-7200, DS Science Inc., Gwangju, South Korea) and flame ionization detector (FID). The GC oven, methanizer, and FID temperatures were fixed at 200, 320, and 280°C, respectively. Gas samples (500  $\mu$ L) were injected using a syringe into the GC (Trajan Scientific and Medical, Ringwood, Australia). Although the methanizer-FID system detects carbon oxides (CO<sub>x</sub>) as a whole (no separate quantification of CO and CO<sub>2</sub>), the detected CO<sub>x</sub> was assumed to be comprised solely of CO<sub>2</sub> as excess O<sub>2</sub> (21%) was used in the present work.

Equation 2 was used to calculate the CO<sub>2</sub> yield (Y<sub>CO2</sub>). [CO<sub>2</sub>]<sub>t</sub> and [CO<sub>2</sub>]<sub>e</sub> represent the theoretical CO<sub>2</sub> amount per the carbon balance and the CO<sub>2</sub> concentration observed in the reactor effluent. Equation 3 was used to calculate the steady-state reaction rate (r (mmol g<sup>-1</sup> h<sup>-1</sup>)). V<sub>B</sub> represents the benzene molar flow rate (mol s<sup>-1</sup>). The r derived through Equation 3 holds under the differential conditions, i.e.,  $X_B < 20\%$  <sup>15</sup>. Under differential conditions, the O<sub>2</sub> and benzene concentrations do not change along the catalyst bed. Hence, the rate of benzene disappearance (-r<sub>B</sub>) remains unchanged throughout the catalyst bed <sup>15</sup>. The RT benzene adsorption capacity (q (mg g<sup>-1</sup>)) and breakthrough (BT (%)) level were calculated for the MOF (10 mg) + SiO<sub>2</sub> (100 mg) bed using the equations reported previously <sup>16</sup>. A Spectrum<sup>TM</sup> 3 spectrometer (PerkinElmer, Inc., Waltham, MA, USA) fitted with an *in-situ* diffuse-reflectance cell (DiffusIR<sup>TM</sup>, PIKE Technologies, Madison, WI, USA) was used to conduct the *in-situ* DRIFTS analysis. Three gaseous streams ((i) benzene + air, (ii) benzene + air + H<sub>2</sub>O, and (iii) benzene + N<sub>2</sub>) were used to acquire the *in-situ* DRIFTS spectra at 200°C.

$$X_B(\%) = \left(\frac{[B]_{in} - [B]_{out}}{[B]_{in}}\right) \times \ 100 \tag{1}$$

$$Y_{CO_2}(\%) = \left(\frac{[CO_2]_e}{[CO_2]_t}\right) \times \ 100 \tag{2}$$

$$r = \left(\frac{3,600 \times 10^{6} \times X_{B} \times V_{B} (m \ ols^{-1})}{M_{cat} (m \ g)}\right)$$
(3)

The criteria regarding negligible external and internal mass transfers, external and internal heat transfers, and radial heat transfer gradients were assessed and found insignificant both at the catalyst particle level and on the reactor scale  $^{17}$ , as detailed in the supporting information (SI). Assuming X<sub>B</sub> as zero at the catalyst bed entrance (maximum r) and establishing the fulfillment of the mass and heat transfer criteria enable the extraction of the intrinsic kinetic data. Such an evaluation was made by considering a benzene, O<sub>2</sub>, and N<sub>2</sub> mixture, as detailed in the SI.

# 2.4. DFT simulation

The energetics and mechanism regulating benzene oxidation over the studied catalyst surfaces were investigated using the DFT simulation. The pseudopotential approach-based Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code was utilized for the DFT simulation <sup>18</sup>. Spin-polarization and +vdW (van der Waals) corrected Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) was utilized to describe the weak non-covalent interactions in all calculations accurately <sup>19</sup>. The atomic positions were effectively optimized during model development based on the DFT simulation. Norm-conserving and non-relativistic pseudopotentials were used to simulate the ion cores (the Zr, Pt, oxygen, nitrogen, and hydrogen cut-off radii were 2.25, 2.3, 1.15, 1.14, and 1.25 au, respectively) in the course of model optimization <sup>20</sup>. The wave function for all species (except hydrogen) was expanded on a double- $\zeta$  plus polarization basis of localized orbitals. A double- $\zeta$  basis was utilized for hydrogen.

#### 3. Results and discussion

#### 3.1. Physicochemical characterization

# 3.1.1. Physical characteristics

The UiO-66, UiO-66-NH<sub>2</sub>, 0.2%-Pt/UiO-66-NH<sub>2</sub>, 0.8%-Pt/UiO-66-NH<sub>2</sub>, 1.5%-Pt/UiO-66-NH<sub>2</sub>, and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R physical characteristics were analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), selected area electron diffraction (SAED), particle-size distribution analyses, pore-

size distribution analysis, inductively coupled plasma optical emission spectrometry (ICP-OES), and N<sub>2</sub> adsorption-desorption isotherms. The instrumentation details can be found in the SI.

The UiO-66 SEM image revealed a granular morphology with aggregated particles, as reported previously <sup>10, 21</sup> (Figure S1 (a)). The average UiO-66 particle size was 83 nm (Figure S1 (b)). UiO-66-NH<sub>2</sub>, 0.2%-Pt/UiO-66-NH<sub>2</sub>, 0.8%-Pt/UiO-66-NH<sub>2</sub>, and 1.5%-Pt/UiO-66-NH<sub>2</sub> showed morphologies similar to UiO-66, which suggest that the parent MOF structure should not be altered by the modification for preparation such as NH<sub>2</sub> functionalization and Pt impregnation (Figures S2 (a)-(d)). The UiO-66-NH<sub>2</sub> average particle size was 33 nm (Figure S2 (e)), while those of 0.2%-Pt/UiO-66-NH<sub>2</sub>, 0.8%-Pt/UiO-66-NH<sub>2</sub>, and 1.5%-Pt/UiO-66-NH<sub>2</sub>, and 1.5%-Pt/UiO-66-NH<sub>2</sub>, and 1.5%-Pt/UiO-66-NH<sub>2</sub> varied in the 65-76 nm range. As such, Pt impregnation should lead to increases in particle size, probably through the deposition of Pt oxide (PtO<sub>x</sub>) species (Figures S2 (f)-(h)). The 1.5%-Pt/UiO-66-NH<sub>2</sub>-R particles (size: 48 nm (Figure S3 (b))) displayed a similar morphology to the parent MOF (Figure S3 (a)). The PtO<sub>x</sub> species are likely converted into Pt<sup>0</sup> NPs because their sizes are smaller than those of their non-reduced counterparts.

The TEM image of UiO-66-NH<sub>2</sub> displayed a uniform distribution of particles, as reported previously <sup>22</sup> (Figure S4 (a)). The 1.5%-Pt/UiO-66-NH<sub>2</sub> morphology per the TEM image was comparable to its pristine form with a slightly larger size of particles (in line with the above SEM observations) (Figure S4 (b)). The absence of distinct Pt NPs in the TEM image of 1.5%-Pt/UiO-66-NH<sub>2</sub> may reflect the absence of Pt in the Pt<sup>0</sup> form (Figure S4 (b)). Here, Pt is suspected to be present in the form of PtO<sub>x</sub>. The individual Pt NPs could be clearly visualized in the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R TEM image (Figure S5 (a)). The crystalline nature of Pt NPs was confirmed by the 0.22 nm interplanar spacing (representing the Pt (111) facet) <sup>23</sup> (Figure S5 (b)). The average size of the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R Pt NPs was ~ 7 nm (Figure S6).

Good compliance between the simulated UiO-66 PXRD pattern and the experimentally determined data indicates proper synthesis of the MOF <sup>24-26</sup> (Figure 1). The characteristic UiO-66 PXRD peaks at the 2θ values of 25.7, 12, 8.3, and 7.2° were ascribed to the (006), (022), (002), and (111) lattice planes, respectively <sup>24</sup> (Figure 1). As the UiO-66-NH<sub>2</sub> PXRD pattern matched well with that for UiO-66, the inherent MOF structure is not likely to be altered by NH<sub>2</sub> functionalization <sup>25, 27</sup> (Figure 2 (a)). The 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> PXRD patterns were similar to UiO-66-NH<sub>2</sub>. Hence, the MOF crystal structure was not altered by Pt loading (Figure 2 (a)). Also, the typical Pt (200) (45.7°) and (111) (39.2°) peaks were not observed in the 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> PXRD patterns (Figure 2 (a)). The above observation can be explained by the high Pt NP dispersion and low Pt loading <sup>12, 28</sup>.

The 1.5%-Pt/UiO-66-NH<sub>2</sub>-R PXRD pattern contained the characteristic peaks for tetragonal ZrO<sub>2</sub> and some other (carbon and nitrogen) impurities <sup>25, 29</sup> (Figure 2 (b)). The prominent peaks observed at 20 values of 30.4, 50.7, and 60.5° were ascribed to the (011), (112), and (121) lattice planes of ZrO<sub>2</sub>, respectively <sup>30</sup> (Figure 2 (b)). Reduction pre-treatment at 300°C (N<sub>2</sub> as the carrier gas) should have led to partial pyrolysis of the MOF to be converted into ZrO<sub>2</sub> <sup>30</sup>. The broad peak in the 20-25° 20 range was not observed in the PXRD pattern of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R to indicate that amorphous carbon was limited to low amounts in the material. The above result aligns with the partial MOF conversion into ZrO<sub>2</sub> observation <sup>31</sup> (Figure 2 (b)). A much higher temperature (e.g., 800°C) is needed to completely pyrolyze the Zr-MOF into a ZrO<sub>2</sub>/amorphous carbon composite <sup>30</sup>. As the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R PXRD pattern is not smooth, amorphous carbon is suspected to form in small quantities (Figure 2 (b)).

The SAED patterns of both 1.5%-Pt/UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub> exhibited a diffraction ring typical of UiO-66 <sup>32</sup> (Figures S7 (a) and (b)). The observed similarity in the SAED pattern between the 1.5%-Pt/UiO-66-NH<sub>2</sub> and its pristine MOF form further indicated that its inherent crystal structure is not altered by Pt impregnation. The SAED pattern of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R displayed three diffraction

rings corresponding to the respective (011), (112), and (121) planes of tetragonal ZrO<sub>2</sub> <sup>30</sup> (Figure S8). The SAED patterns further indicated that the parent MOF was pyrolyzed into ZrO<sub>2</sub> by the reduction pretreatment. The TGA profiles of both the MOFs and Pt/UiO-66-NH<sub>2</sub> catalysts displayed three prominent weight loss events: (i) physisorbed moisture removal in the RT-119°C range, (ii) vaporization of the solvent molecules from the MOF structure along with dehydroxylation of the Zr oxo-clusters in the 119-572°C range, and (iii) structural decomposition beyond 572°C <sup>33</sup> (Figure 2 (c)). The superior UiO-66-NH<sub>2</sub> thermal stability over UiO-66 aligns with previous reports <sup>25,34</sup> (Figure 2 (c)). Also, superior thermal stabilities were observed for the Pt/UiO-66-NH<sub>2</sub> catalysts in comparison to the parent MOF (Figure 2 (c)). The TGA profile of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R also displayed three prominent weight loss events: (i) physisorbed moisture removal in the RT-140°C range, (ii) dehydroxylation of ZrO<sub>2</sub> in the 140-580°C range, and (iii) decomposition of the structure beyond 580°C <sup>35</sup> (Figure S9).

The patterns in the N<sub>2</sub> adsorption-desorption isotherms of the tested materials maintained a Type-I-IV hybridized character, indicating the presence of micropores and some mesopores in their structures <sup>13, 36, 37</sup> (Figure 2 (d)). The existence of defects in the tested materials was reflected by the presence of mesopores in their structures <sup>13</sup>. The N<sub>2</sub> adsorption-desorption isotherm pattern for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R was of the typical Type-IV character, indicating the predominance of mesopores in its structure due to the conversion of the parent MOF into ZrO<sub>2</sub> during the high-temperature reduction pre-treatment (Figure 2 (d)). All tested materials displayed a characteristic hysteresis loop at elevated P/P<sub>0</sub> levels as the N<sub>2</sub> molecules are condensed into the mesopores <sup>37</sup> (Figure 2 (d)). Also, the existence of slit-shaped pores due to particle aggregation was reflected by the H3-type hysteresis loop <sup>38</sup> (Figure 2 (d)).

Table 1 summarizes the detailed information regarding Brunauer–Emmett–Teller (BET), external, and micropore surface area and the average pore diameter and pore volume of the tested materials. The BET surface area comparison between UiO-66-NH<sub>2</sub> (752 m<sup>2</sup> g<sup>-1</sup>) and UiO-66 (1,184 m<sup>2</sup> g<sup>-1</sup>) confirmed

the reduction of the MOF-specific surface due to NH<sub>2</sub> functionalization (Table 1). Such lowering of the BET surface (685-726 m<sup>2</sup> g<sup>-1</sup>) may directly reflect the effect of Pt loading (Table 1). The BET surface area of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R was only 30 m<sup>2</sup> g<sup>-1</sup> due to the conversion of the parent MOF into ZrO<sub>2</sub> during the high-temperature reduction pre-treatment (Table 1). The UiO-66 and UiO-66-NH<sub>2</sub> micropore areas were 1,113 and 703 m<sup>2</sup> g<sup>-1</sup>, respectively (Table 1). The Pt/UiO-66-NH<sub>2</sub> micropore areas were 630-678 m<sup>2</sup> g<sup>-1</sup>, indicating the presence of PtO<sub>x</sub> species within the MOF pores (Table 1). The 1.5%-Pt/UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub> and UiO-66 were 49 and 71 m<sup>2</sup> g<sup>-1</sup>, respectively (Table 1). The similarity in UiO-66-NH<sub>2</sub> and 0.2%- and 0.8%-Pt/UiO-66-NH<sub>2</sub> external surface areas of 1.5%-Pt/UiO-66-NH<sub>2</sub> external surface area of 1.5%-Pt/UiO-66-NH<sub>2</sub> increased to 55 m<sup>2</sup> g<sup>-1</sup>, likely reflecting the aggregation of some PtO<sub>x</sub> species on the external MOF surface with the increase in Pt loading (Table 1). The 1.5%-Pt/UiO-66-NH<sub>2</sub>-R external surface area was almost identical to its BET surface area (Table 1).

The UiO-66-NH<sub>2</sub> and Pt/UiO-66-NH<sub>2</sub> pore volumes ranged between 0.3-0.5 m<sup>3</sup> g<sup>-1</sup>, while that of UiO-66 was 0.7 m<sup>3</sup> g<sup>-1</sup> (Table 1). The average pore diameter of the former was 1.5 nm, while those of the latter were between 1.6 and 2 nm (Table 1). The .5%-Pt/UiO-66-NH<sub>2</sub>-R average pore diameter and volume were 3.4 nm and 0.04 cm<sup>3</sup> g<sup>-1</sup>, respectively (Table 1). Micropores with a few mesopores (2-4 nm) were noted in the pore-size distributions of the tested materials (Figure S10). The 1.5%-Pt/UiO-66-NH<sub>2</sub>-R pore-size distribution analysis confirmed the predominance of mesopores with very limited micropores in the 1-2 nm range (Figure S11). The theoretical Pt loading was similar to that determined experimentally (ICP-OES) for the Pt/UiO-66-NH<sub>2</sub> catalysts (Table 1).

#### 3.1.2. Surface chemistry

The surface chemistry of the tested materials was analyzed using energy-dispersive X-ray spectroscopy (EDX) mapping, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), O<sub>2</sub>-TPD, and H<sub>2</sub>-TPR (See the SI for instrument details). The elemental distribution on the MOF and catalyst surfaces was assessed using EDX mapping (Figure S12). Zr, carbon, oxygen, and chlorine (Cl) were observed on the surfaces of all the samples (Figure S12). The use of ZrOCl<sub>2</sub>·8H<sub>2</sub>O and HCl in the MOF synthesis was responsible for the observed Cl in all samples (Figure S12). The Cl observed on the catalyst surfaces may be accounted for by the use of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. In line with general expectation, nitrogen was clearly mapped on the UiO-66-NH<sub>2</sub>, 0.2%-Pt/UiO-66-NH<sub>2</sub>, 0.8%-Pt/UiO-66-NH<sub>2</sub>, 1.5%-Pt/UiO-66-NH<sub>2</sub>, and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R surfaces (Figure S12). Since the samples were Pt coated for the EDX analysis, Pt was not mapped to avoid confusion.

The catalyst and MOF surface functionalities were assessed using FTIR (Figure S13). The characteristic UiO-66 FTIR spectrum bands at 1581 and 1387 cm<sup>-1</sup> were attributed to the asymmetric/symmetric BDC carboxylate (O-C-O) stretching <sup>21</sup> (Figure S13). The bands at 1657 and 1505 cm<sup>-1</sup> were attributed to the C=O and C=C ligand vibrations (stretching) <sup>21</sup> (Figure S13). The characteristic bands at 479, 546, 655, 743, and 819 cm<sup>-1</sup> were attributed to the Zr-O ligand modes and O-H/C-H bonds <sup>21, 39</sup> (Figure S13). The 1093 and 1017 cm<sup>-1</sup> bands were attributed to the residual DMF and Zr-BDC coordination, respectively <sup>40, 41</sup> (Figure S13).

The characteristic bands at 1261 and 1364 cm<sup>-1</sup> in the FTIR spectrum of UiO-66-NH<sub>2</sub> were associated with the C<sub>ar</sub>-N stretching vibrations <sup>40</sup> (Figure S13). The characteristic band beyond 3000 cm<sup>-1</sup> was ascribed to the N-H groups <sup>13</sup> (Figure S13). Loading Pt onto the MOF did not significantly change the surface functional groups of the MOF, as the FTIR spectra of 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts were comparable to that of UiO-66-NH<sub>2</sub> (Figure S13). For 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, the bands associated with the residual solvent, ligand, and Zr-ligand coordination disappeared, likely due to the

conversion of the parent MOF into  $ZrO_2$  during the high-temperature reduction pre-treatment (Figure S13). The characteristic bands at 1413 and 1539 cm<sup>-1</sup> were ascribed to the  $ZrO_2C$ -H vibration (bending) <sup>42</sup> (Figure S13). The prominent bands at 621 and 765 cm<sup>-1</sup> were attributed to the vibrations of Zr-O in  $ZrO_2$  <sup>42</sup> (Figure S13). The minor band at 1262 cm<sup>-1</sup> was attributed to the C<sub>ar</sub>-N stretching vibrations <sup>40</sup> (Figure S13).

XPS was used to assess the surface chemistry of the tested materials. The UiO-66 Zr 3d core-level spectrum showed two peaks at 185.3 eV ( $3d_{3/2}$ ) and 182.9 ( $3d_{5/2}$ ), representing the typical spin-orbit doublets <sup>43</sup> (Figure S14 (a)). The position of the  $3d_{5/2}$  peak suggests the existence of Zr(IV) in Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub> secondary building unit <sup>44</sup>. As the Zr  $3d_{5/2}$  and  $3d_{3/2}$  peak positions of UiO-66-NH<sub>2</sub> were not altered compared to UiO-66, NH<sub>2</sub> incorporation is not likely to significantly alter the electronic states of the metallic centers (Figure S14 (b)). Variations in the Zr  $3d_{5/2}$  and  $3d_{3/2}$  peak positions were not apparent (e.g., below -0.1 eV) for the 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts (Figures S14 (c)-(e)). Hence, the electronic states of the metallic centers were not significantly altered by Pt loading, although some Pt-Zr interactions cannot be ruled out. The  $3d_{5/2}$  and  $3d_{3/2}$  peak positions in the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R core-level Zr 3d spectrum red-shifted (binding energy (BE) decrement) of -0.5 eV each (in comparison to 1.5%-Pt/UiO-66-NH<sub>2</sub>), which may be ascribable to conversion of the parent MOF into ZrO<sub>2</sub> during the reduction pre-treatment <sup>30</sup> (Figure S14 (f)).

The core-level C 1s spectra of both the MOFs revealed two characteristic peaks at low and high BE that correspond to the adventitious (C-C)/aromatic (C=C) carbon species and carboxylate (O-C=O) in the organic ligands, respectively <sup>43, 45</sup> (Figures S15 (a)-(b)). Variations in the O-C=O peak positions for UiO-66-NH<sub>2</sub> were negligible (within -0.1 eV) (Figures S15 (a)-(b)). Such variations were also negligible (within -0.1 eV) for 0.2- and 0.8%-Pt/UiO-66-NH<sub>2</sub> catalysts compared to UiO-66-NH<sub>2</sub> (Figures S15 (c)-(d)). For 1.5%-Pt/UiO-66-NH<sub>2</sub>, a new peak attributable to the C-O group (286.5 eV) was observed in

addition to the C-C/C=C and O-C=O functionalities <sup>46</sup> (Figure S15 (e)). Metal-support interactions became prominent at higher Pt loadings, enhancing charge transfer at the interface to alter the electronic environment locally. The O-C=O peak in 1.5%-Pt/UiO-66-NH<sub>2</sub> blue-shifted (increase in BE) +0.2 eV in comparison to UiO-66-NH<sub>2</sub> (Figure S15 (e)). For 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, the C-O (286.5 eV), C-OH (288.5 eV), and C-C/C=C (284.9 eV) species were identified in the core-level C 1s spectrum <sup>30</sup> (Figure S15 (f)).

The core-level O Is spectra of the MOFs showed two characteristic peaks corresponding to oxygen in coordinated carboxylate (Zr-O-C) groups (peak at the higher BE) and bridged (Zr-O-Zr) species (peak at the lower BE) <sup>43</sup> (Figures S16 (a)-(b)). Specifically, 98.5% oxygen was present as Zr-O-C in both the MOFs (Figures S16 (a)-(b)). The UiO-66-NH<sub>2</sub> Zr-O-C peak in the core-level O Is spectrum displayed a red-shift (-0.2 eV) compared to UiO-66 as electron density increased through incorporation of NH<sub>2</sub> groups into the MOF (Figure S16 (b)). The O Is core-level spectra for 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts indicated the existence of (i) lattice oxygen (O<sub>latt</sub> at 531.9-532 eV) and (ii) adsorbed oxygen (O<sub>ads</sub> (O<sup>-</sup>, O<sub>2</sub><sup>2-</sup>, and O<sub>2</sub><sup>-</sup>) at 534-534.1 eV) <sup>28,47</sup> (Figures S16 (c)-(e)). The O<sub>latt</sub> peaks for 0.2- and 0.8%-Pt/UiO-66-NH<sub>2</sub> appeared at the same BE of 532 eV with no shifts (Figures S16 (c)-(d)). The variation in 1.5%-Pt/UiO-66-NH<sub>2</sub> O<sub>latt</sub> peak position was also negligible (within -0.1 eV) (Figure S16 (e)). The sequential order of decline in the O<sub>ads</sub> peak relative contribution to the core-level O Is spectra was observed as follows: 1.5%-Pt/UiO-66-NH<sub>2</sub> (18.1%) > 0.8%-Pt/UiO-66-NH<sub>2</sub> (14.1%) > 0.2%-Pt/UiO-66-NH<sub>2</sub> (12.5%) (Figures S16 (c)-(e)). For 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, the O<sub>ads</sub> (533.8 eV), ZrO<sub>2</sub> (529.9 eV), and C-O (531.4 eV) species were identified in the core-level O Is spectrum <sup>30,48</sup> (Figure S16 (f)).

The N 1s core-level UiO-66 spectrum exhibited a characteristic  $-N-(C)_3$  peak (401.2 eV), possibly associated with the residual DMF in the MOF <sup>49</sup> (Figure S17 (a)). The N 1s core-level UiO-66-NH<sub>2</sub>

spectrum had two characteristic peaks representing -NH (400.3 eV) and -NH<sub>2</sub> (399.3 eV) groups <sup>50</sup> (Figure S17 (b)). For 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub>, the -NH<sub>2</sub> and -NH peaks displayed red-shifts (compared to UiO-66-NH<sub>2</sub>) in the -0.1 to -0.2 eV and -0.1 to -0.3 eV range, respectively, likely because of their interactions with the loaded Pt <sup>12</sup> (Figures S17 (c)-(e)). Interestingly, the amount of -NH<sub>2</sub> species in the MOF decreased upon Pt loading, as NH<sub>2</sub> groups preferentially interacted with Pt instead of -NH (Figures S17 (c)-(e)). A minor peak for oxidized nitrogen (402.8 eV) was observed in the 1.5%-Pt/UiO-66-NH<sub>2</sub> core-level N 1s spectrum (Figure S17 (e)). The above was attributed to the strong Pt-MOF interactions at a higher noble metal loading <sup>51</sup>. For 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, the pyrrolic (399.8 eV) and pyridinic (398.7 eV) nitrogen were identified in the N 1s core-level spectrum <sup>30</sup> (Figure S17 (f)). Also, 88.9% nitrogen in the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R structure existed in pyrrolic form (Figure S17 (f)).

The deconvoluted Pt 4f core-level spectra for 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub> displayed the presence of Pt<sup>2+</sup> species in the 4f<sub>5/2</sub> (75.9-78.2 eV) and 4f<sub>7/2</sub> (72.6-72.9 eV) peaks <sup>3, 52</sup> (Figures 3 (a)-(c)). The Pt 4f<sub>7/2</sub> peak experienced redshifts within the -0.2 to -0.3 eV range as the Pt loading increased in the Pt/UiO-66-NH<sub>2</sub> catalysts (Figures 3 (a)-(c)). The Pt 4f<sub>5/2</sub> peak showed redshifts in the -2.1 to -2.3 eV range with an increase in Pt loading for the Pt/UiO-66-NH<sub>2</sub> catalysts (Figures 3 (a)-(c)). For 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, only Pt<sup>0</sup> (characteristic peaks at 71.7 and 74.9 eV) was observed as the reduction pre-treatment should have reduced all the oxidized Pt species <sup>3</sup> (Figures 3 (a)-(d)).

Based on the experimental TPR data, the amounts of oxygen lost by H<sub>2</sub> reduction from 1.5%-Pt/UiO-66-NH<sub>2</sub> and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R were 83.1 ± 13.3 and 24.2 ± 4.63  $\mu$ mol<sub>O\*</sub>, respectively (Table S1). The above result indicates that the pre-reduced catalyst had a lower available oxygen concentration than that without pretreatment. Using the values  $\beta = 10$  K min<sup>-1</sup>, S<sub>0</sub> = 83.1  $\mu$ mol<sub>O\*</sub> (highest value), F·C<sub>0</sub> = 2.04 mmol min<sup>-1</sup> × 0.10 = 200  $\mu$ mol min<sup>-1</sup>, and P = 20 K, the right side of Equation S1 is equal to 4.2 K maximally. Hence, the resolution was not lost for further TPR data modeling. The above results corresponded with available oxygen concentrations of  $1.70 \pm 0.27$  and  $0.48 \pm 0.09 \text{ mol}_{0^*} \text{ kg}_{cat}^{-1}$  per the  $H_2 + O^* \rightarrow H_2O + *$  reaction (stoichiometric surface reduction). The overall TPR data modeling results (Equation S2) present a maximum average error ( $e_{av}$ ) of 0.43% (for 1.5%-Pt/UiO-66-NH<sub>2</sub>) in comparison to the maximum signal observed in each TPR experiment, as calculated using Equation 4. Here, S is defined as in Equation S3, n represents the number of data points per experiment, and  $y_{max}$  is the maximum output value (a.u.) for each TPR experiment.

$$e_{av} = \frac{1}{y_{m ax}} \sqrt{\frac{s}{n}} \tag{4}$$

Figure S18 matches the H<sub>2</sub>-TPR data (1.5%-Pt/UiO-66-NH<sub>2</sub>-R and Pt/UiO-66-NH<sub>2</sub>) obtained experimentally and the corresponding values predicted by the Gaussian model. Table S2 contains the estimated parameters for reducing the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts, and the H<sub>2</sub>-TPR peak temperatures for the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R catalyst are more significant than those for 1.5%-Pt/UiO-66-NH<sub>2</sub>. This result is in contrast with the reported activity for total benzene oxidation. Based on that result, we proposed that the oxygen used in total benzene oxidation might not be the chemically bonded O<sub>latt</sub> at the catalyst surface. In other words, it can be assumed that gas-phase oxygen weakly adsorbs under typical oxidation reaction conditions and that such electrophilic oxygen adsorbate species tend to exhibit non-selective oxidation behavior <sup>53, 54</sup>. This prediction will be supported by the O<sub>2</sub>-TPD results (see below).

UiO-66 consists of  $Zr_6O_4(OH)_4$  nodes with octahedrally arranged six  $Zr^{4+}$  ions, with four hydroxyl (OH) groups or oxygen atoms present at the center of each octahedron facet. Coordination occurs between each node and 12 BDC ligands. Also, a square antiprismatic geometry occurs when eight

oxygen atoms coordinate with each Zr atom. The pre-reduction treatment at 573 K (to prepare the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R catalyst) likely resulted in the creation of defects in the  $Zr_6O_4(OH)_4$  nodes or removal of oxygen from the BDC linker. This process generates local electron-deficient regions where  $O_2$ , with its lone electron pair, can interact without chemical integration into the structure. Hence, these electrophilic oxygen species can accelerate the total oxidation reaction <sup>55</sup>. The  $O_2$  can undergo dissociative adsorption on regular metal oxides, i.e., two adjacent reduced surface sites can be reoxidized.  $O_2$  can be subject to associative adsorption since the position of possible defects in the UiO-66 structure accompanies a distance longer than the typical O–O bond distance in the gas phase. Such a process gives rise to electrophilic oxygen species that can produce total oxidation reactions. As a hydrocarbon reactant, benzene has an aromatic ring with appreciable electron density, so it likely adsorbs better onto the defects of the reduced catalyst than does the unreduced benzene. An example is the reported total oxidation of benzene over a copper manganite spinel (CuMn<sub>2</sub>O<sub>4</sub>) catalyst <sup>56</sup>. The existence of surface metal-terminated sites was responsible for the benzene adsorption before surface oxygen insertion.

Experimental TPD data showed that the amounts of  $O_{ads}$  on the 1.5%-Pt/UiO-66-NH<sub>2</sub> and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R surfaces were  $1.54 \pm 0.02$  and  $0.44 \pm 0.01 \text{ mmol}_{O2}$ , respectively (Table S3). The above results correspond to  $O_2$  adsorption capacities (308 K) of  $30.7 \pm 0.8$  and  $8.8 \pm 0.2 \text{ mmol}_{O2} \text{ g}_{cat}^{-1}$ , respectively. The reduction pre-treatment reduced the adsorption capacity by  $3.50 \pm 0.07$ . The reported BET values of  $685 \pm 1.9$  and  $30 \pm 0.2 \text{ m}^2 \text{ g}_{cat}^{-1}$  can be used to express the  $O_2$  adsorption capacity in areal units. This capacity shows opposing trends of  $44.8 \pm 1.2$  and  $293.3 \pm 7.0 \text{ µmol}_{O2} \text{ m}^{-2}$ , respectively. Hence, more oxygen can be adsorbed per unit area on the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R catalyst, which aligns with its excellent oxidation capability (see below). The overall TPD data modeling results with Equation

S2 show an  $e_{av}$  of 1.61% (for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R) (Equation 4). Figure S19 shows a good fit between the experimental TPD profiles for the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts and the modeling results using the Gaussian model: see Equation 5, with N being the number of peaks.

$$y(T) = \mathbb{Z}_{i=1}^{N} \frac{a_i}{\sqrt{2\pi\sigma_i^2}} \cdot \exp\left(-\frac{(x-\mu_i)^2}{2\sigma_i^2}\right)$$
(5)

Table S4 contains the estimated TPD parameters for the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R and 1.5%-Pt/UiO-66-NH<sub>2</sub> catalysts. Four distinct desorption peaks were determined for all catalysts. From the signal percentage results for 1.5%-Pt/UiO-66-NH<sub>2</sub>, we concluded that ~75% of the total O<sub>ads</sub> desorbs at 183.0  $\pm$  0.1°C with a corresponding desorption energy of 23.5  $\pm$  0.1 kJ mol<sup>-1</sup>. The second desorption peak occurs at 238.5  $\pm$  0.3 °C with a corresponding desorption energy of 52.7  $\pm$  0.7 kJ mol<sup>-1</sup>. The above peak corresponds to somewhat tightly bonded oxygen species (weakly reactive under total oxidation conditions). The above results correspond with the absence of any catalytic activity at less than 175°C (see below). On the other hand, ~8% of the total  $O_{ads}$  for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R desorbs at 91.1 ± 0.3°C with a corresponding desorption energy of  $14.7 \pm 0.3$  kJ mol<sup>-1</sup>. The second desorption peak corresponds with ~47% of the total  $O_{ads}$  and occurs at 151.4  $\pm$  0.3°C with a corresponding desorption energy of 12.4  $\pm$  0.1 kJ mol<sup>-1</sup>, as the former peak represents a higher preexponential factor (A). Overall, ~55% of the total O<sub>ads</sub> shows an energetically favorable desorption energy < 15 kJ mol<sup>-1</sup>, which probably corresponds to the active (electrophilic) oxygen related to total oxidation. Overall, the two desorption peaks in the higher-temperature region (> 350°C) show a slight shift (15-30°C) toward lower desorption temperatures for the reduced catalyst. In contrast, the peaks in the lower-temperature region show a considerable shift of ~90°C. Hence, the corresponding electrophilic surface oxygen can lead to a higher total oxidation rate 56

It should be noted that O<sub>2</sub>-TPD quantifies the types of oxygen on the catalyst surface, which can readily desorb under inert conditions. The adsorbates desorbed at low temperatures were assumed to be the loosely bound oxygen (electrophilic) species, i.e., not part of the lattice structure. The adsorbates desorbed at higher temperatures were assumed to be the oxygen atoms embedded in/onto the catalyst surface. Hence, such oxygen species represent Olatt. For H2-TPR, the loosely bound oxygen adsorbates are readily removed in the pre-treatment step (as mentioned in the experimental protocol). Hence,  $H_2$ can be considered to react with O<sub>latt</sub> (or, in general, with the more strongly bound oxygen species). The quantification of maximal Oads (i.e., without any other reactant in the atmosphere that can interact to alter its amount) can be calculated from the O<sub>2</sub>-TPD data. An inspection of the experimental results indicated a visible distinction in the peak occurrences, i.e., two peaks occur before and after 300°C. Given the corresponding low/high-temperature range, it can be assumed that they correspond to the electrophilic and Olatt oxygen, respectively. For the catalysts of 1.5%-Pt/UiO-66-NH2 and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, the fractions of oxygen desorbed before 300°C are computed as 86.9 and 54.9%, respectively. The total oxygen adsorbate concentrations for the two catalysts are estimated as  $30.7 \pm 0.8$  and  $8.8 \pm 0.2$  $mol_{O^*} kg_{cat}$ -1, respectively, while their electrophilic oxygen concentration corresponded to  $26.6 \pm 0.7$  and  $4.8 \pm 0.1 \text{ mol}_{O^*} \text{ kg}_{\text{cat}}^{-1}$ , respectively.

The  $O_{latt}$  can be assumed to represent the amount of oxygen removed in H<sub>2</sub>-TPR. Therefore, the acquired data can be used to estimate the ratio of the surface electrophilic oxygen to  $O_{latt}$  species, i.e.,  $(O_2^{2^-} + O_2^-)/O_2^-$ . The above term for the catalyst 1.5%-Pt/UiO-66-NH<sub>2</sub> can be estimated as  $(26.6 \pm 0.7)/(30.7 \pm 0.8) \approx 0.87 \pm 0.04$  while that of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R is  $(4.8 \pm 0.1)/(8.8 \pm 0.2) \approx 0.55 \pm 0.03$ . As such, the fraction of the assumed electrophilic oxygen on the unreduced catalyst appears higher. However, when the desorption temperature was inspected, it became evident that the latter catalyst exhibited the highest activity.

The fraction of desorbing surface oxygen as a function of desorption temperature is depicted in Figure 4 (a), wherein the fraction of oxygen adsorbate (f) was calculated according to Equation 6. y(T) was the Gaussian curve used to model the complete experimental TPD data (all N peaks together).

The cumulative fraction of oxygen adsorbate desorbed until desorption temperature (T) was calculated according to Equation 6. Figure 4 (b) shows that the total value of oxygen adsorbate concentration was higher over the 1.5%-Pt/UiO-66-NH<sub>2</sub> catalyst than its reduced counterpart until 155°C; the reduced catalyst showed the higher desorption than its non-reduced counterpart. The above-described early desorbing oxygen was considered an oxygen reservoir under actual oxidation conditions, where O<sub>2</sub> is in excess. In other words, O<sub>2</sub> was readily adsorbed and used in the total oxidation reaction to generate a reduced site. Hence, the above type of oxygen is the most readily consumed and replenished to impart superior activity for the reduced catalyst. There are several electrophilic oxygen species <sup>53</sup>, with the following incorporation from the gas phase into the lattice: O<sub>2</sub> (g)  $\rightarrow$  O<sub>2</sub> (ads)  $\rightarrow$  O<sub>2</sub><sup>-</sup> (ads)  $\rightarrow$ 

 $O_2^{2-}$  (ads)  $\rightarrow O^-$  (ads)  $\rightarrow O^{2-}$  (ads)  $\rightarrow O^{2-}$  (lattice). Probably due to the prior reduction treatment, the surface electron availability of the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R catalyst was lower than that for the 1.5%-Pt/UiO-66-NH<sub>2</sub> catalyst. Consequently, the former possessed electrophilic species that were more easily removed, i.e., at lower reduction temperatures. However, it is not straightforward to quantitatively calculate the fraction of electrophilic oxygen adsorbates on the catalyst surfaces.

$$f(T) = \frac{\mathbb{E}_{-\infty}^T y(x) dx}{\mathbb{E}_{-\infty}^{+\infty} y(x) dx} = \frac{\mathbb{E}_{-\infty}^T y(x) dx}{\mathbb{E}_{i=1}^N a_i}$$
(6)

The combination of  $H_2$ -TPR and  $O_2$ -TPD indicates that 1.5%-Pt/UiO-66-NH<sub>2</sub> prereduction results in a higher total oxidation rate because (1) electrophilic oxygen species seem likely to exist and (2) adsorption of benzene can be assumed to increase with the presence of defects. Overall, heterogeneously catalyzed total oxidation reactions proceed through a Langmuir-Hinshelwood (LH) mechanism <sup>57</sup>. First, both reactants are simultaneously adsorbed, and the surface reaction produces the final total oxidation products. We expected that a linear relation between ln A and the corresponding activation energy (E) would be observed for the same class of reactions (or the same reaction over similar materials) <sup>58</sup>. This occurrence is called 'the compensation effect,' and it expresses interrelated kinetic behavior within a group of rate processes <sup>58</sup>. An excellent linear relationship was observed with ln A versus E for oxygen desorption over the used catalysts (Figure S20).

# 3.2. Benzene removal performance evaluation and oxidation kinetics

The two tested MOFs in the current study (i.e., UiO-66 and UiO-66-NH<sub>2</sub>) behaved as adsorbents at RT (in line with general expectation), as the BT level of benzene (100 ppm) increased gradually to 100% in 60 and 80 min of operation, respectively (110 mg total bed mass (MOF (10 mg) + SiO<sub>2</sub> (100 mg)), 50 mL min<sup>-1</sup> flow rate, and 0% RH) (Figure S21). The UiO-66-NH<sub>2</sub> + SiO<sub>2</sub> system displayed a higher q value for benzene than the UiO-66 + SiO<sub>2</sub> system (Figure S21). The higher q and extended time requirement for obtaining 100% BT confirmed the superiority of the NH<sub>2</sub>-functionalized MOF as an adsorbent. The above results support the critical role of nitrogen species in the capture of benzene molecules.

The relative magnitude of  $X_B$  in light-off curves of the tested catalysts is as follows in descending order: 1.5%-Pt/UiO-66-NH<sub>2</sub>-R > 0.8%-Pt/UiO-66-NH<sub>2</sub>-R > 0.2%-Pt/UiO-66-NH<sub>2</sub>-R > 1.5%-Pt/UiO-66-NH<sub>2</sub> (Figure 5 (a)). The reaction temperature corresponding to 50%  $X_B$  (T<sub>50</sub>) for 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R were 194, 173, and 151°C, respectively (Figure 5 (a)). In contrast, 1.5%-Pt/UiO-66-NH<sub>2</sub> displayed an  $X_B$  of only 12% at the maximum tested temperature of 225°C and became inactive below 175°C (Figure 5 (a)). The T<sub>90</sub> values (reaction temperature corresponding to 90%  $X_B$ ) for 0.2-, 0.8-, and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R were 219, 208, and 170°C, respectively (Figure 5 (a)). Consequently, a higher Pt loading enhanced benzene oxidation. Also, the importance of reduction pre-treatment is directly reflected by the more prominent role of Pt<sup>0</sup> sites in the catalytic process (compared to Pt<sup>2+</sup>). The catalyst that exhibited the best performance in the current study, i.e., 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, was subsequently utilized to gauge the impact of reaction condition and parameters on the catalytic activity.

The decrease in M<sub>cat</sub> to 100, 60, and 30 mg led to decreased oxidation performance against benzene (X<sub>B</sub> (at 150°C)) of 48, 43, and 39%, respectively, with a reduction of total active surface sites available for the catalytic reaction (Figure 5 (b)). Nevertheless, 100% X<sub>B</sub> was obtained at 175°C for all the tested  $M_{cat}$  (30-100 mg) (Figure 5 (b)). Benzene oxidation also declined with increasing flow rate (e.g., 50, 150, and 250 mL min<sup>-1</sup>) with X<sub>B</sub> values (at 150°C) of 48, 32, and 27%, respectively), possibly reflecting shorter contact time between the pollutant molecules and the catalyst bed (Figure 5 (c)). Notably, at 150 and 250 mL min<sup>-1</sup>, 100% X<sub>B</sub> was recorded at 200°C (Figure 5 (c)). An increase in pollutant concentration (e.g., 100, 200, and 300 ppm benzene) lowered the VOC oxidation performance (X<sub>B</sub> (at 150°C)) to 48, 46, and 44%, respectively, due to a lowered active surface site-to-pollutant ratio (Figure 5 (d)). Nevertheless, 100% X<sub>B</sub> was observed at 175°C for all tested benzene concentrations (100-300 ppm) (Figure 5 (d)).

The increase in RH (e.g., 0 < 30 < 60%) dramatically enhanced the X<sub>B</sub> (at 150°C) to 48, 73, and 100%, respectively (Figure 5 (e)). A rise in RH to 90% suppressed the X<sub>B</sub> (at 150°C) to 33% due to heightened competition between the H<sub>2</sub>O, O<sub>2</sub>, and benzene for the surface sites <sup>59, 60</sup> (Figure 5 (e)). An H<sub>2</sub>O film may also deposit on the catalyst surface at higher RH levels (e.g., 90% RH) to further restrict access to the active surface sites for the benzene molecules, i.e., lowering VOC oxidation <sup>12</sup>. The thermocatalytic benzene oxidation activity of a Pt single-atom (Pt<sub>1</sub>) catalyst supported on mesoporous iron oxide (meso-

 $Fe_2O_3$ ) was reported to increase upon the introduction of moisture into the feed stream <sup>60</sup>. Further, the thermocatalytic oxidation activity of a Pt<sub>1</sub>/manganese oxide (MnO<sub>x</sub>) catalyst against VOC (a mixture of toluene and *iso*-hexane) increased to a maximum at 25% RH <sup>59</sup>. Likewise, the positive effect of RH was recognized in the thermocatalytic oxidation of toluene by a gold (Au)-Pd alloy catalyst supported on a macroporous three-dimensionally ordered (3DOM) Co<sub>3</sub>O<sub>4</sub> <sup>61</sup> and also by a Pt<sub>1</sub>/magnesium oxide (MgO) nanosheet catalyst <sup>62</sup>.

The increased thermocatalytic VOC oxidation activity of SNMCs observed in the presence of moisture can be attributed to the hydroperoxyl-assisted O<sub>2</sub> activation, i.e.,  $O_2^* + H_2O^* \rightarrow OOH^* + OH^*$  and OOH\*  $\rightarrow O^* + OH^*$  <sup>59, 61</sup>. The promotional role of H<sub>2</sub>O vapor in the benzene oxidation reaction could also stem from enhanced benzene adsorption by the generated OH onto the SNMC surface in a moisture-rich environment <sup>63</sup>. As noted by the enhancement in benzene oxidation in the presence of moisture (up to 60% RH), 1.5%-Pt/UiO-66-NH<sub>2</sub>-R may be regarded as a prospective candidate for practical applications due to the ubiquity of H<sub>2</sub>O vapor in ambient air and industrial effluents. The stability and durability of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R were also assessed for benzene oxidation at 200°C in the presence of H<sub>2</sub>O vapor (60% RH) (Figure 5 (f)). The catalyst stably maintained 100% X<sub>B</sub> to CO<sub>2</sub> (Y<sub>CO2</sub> matching the carbon balance) without deactivation for 50 h TOS (maximum tested duration) under optimal conditions (Figure 5 (f)).

The benzene oxidation kinetics for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R was modeled at  $110^{\circ}$ C using four LH models (LH1-LH4), four Eley-Rideal (ER) models (ER1-ER4), and two Mars-van Krevelen (MvK) models (MvK1 and MvK2)<sup>17</sup> (Table 2). The kinetic model equations and assumptions are also listed in Table 2. p<sub>B</sub> and p<sub>O2</sub> represent the benzene and O<sub>2</sub> partial pressure, respectively. Also, k<sub>s</sub>, K<sub>B</sub>, K<sub>O2</sub>, k<sub>B</sub>, and k<sub>O2</sub> correspond to the surface reaction rate constant, benzene adsorption equilibrium constant, O<sub>2</sub> adsorption equilibrium constant, benzene oxidation rate constant, and catalyst reoxidation rate constant,

respectively. For simplicity, the K<sub>02</sub>.p<sub>02</sub> and k<sub>02</sub>.p<sub>02</sub> terms in the kinetic models were pooled as K<sub>2</sub> and k<sub>2</sub>, respectively. The kinetic parameters were determined through non-linear regression analysis to minimize the sum of squares (SSE ( $\sigma^2$ )) between experimentally found (r<sub>e</sub>) and theoretically calculated r values (r<sub>c</sub>) (Equation 7). The best-fitting kinetic model was determined by assessing the coefficient of determination (R<sup>2</sup>) (Equation 8) and chi-squared ( $\chi^2$ ) values (Equation 9). Note that r<sub>m</sub> indicates the mean of the r<sub>e</sub> values.

$$SSE = \sigma^2 = \mathbb{Z}(r_e - r_c)^2 \tag{7}$$

$$R^{2} = 1 - \frac{\mathbb{E}(r_{e} - r_{c})^{2}}{\mathbb{E}(r_{e} - r_{m})^{2}}$$
(8)

$$\chi^2 = \mathbb{E} \frac{(r_e - r_c)^2}{r_c} \tag{9}$$

The r rose steadily from 1.3E-03 to 2.5E-03  $\mu$ mol g<sup>-1</sup> s<sup>-1</sup> as the p<sub>B</sub> increased from 10 to 30 Pa (Figure 6 (a)). The r displayed a sublinear dependence on the p<sub>B</sub> (positive reaction order of 0.6) (Figure 6 (b)). The kinetic modeling results revealed that benzene oxidation proceeded through the LH mechanism (Table 2). The R<sup>2</sup> values for the LH models ranged from 0.9798 (LH1) to 0.9881 (LH4) (Table 2). The LH4 model also displayed the lowest  $\chi^2$  value (4.5E-06) to support its suitability in describing the benzene oxidation process on the catalyst surface (Table 2). The ER and MvK models showed poor fitting results, i.e., low R<sup>2</sup> and high  $\chi^2$  values. As such, they do not appear feasible to describe the benzene oxidation process for the tested catalyst (Table 2). Hence, the benzene and O<sub>2</sub> molecules first adsorbed on the catalyst surface and then reacted to yield the oxidation products. Also, owing to the best fit of the LH4 model in describing benzene oxidation, it is likely that O<sub>2</sub> chemisorbed dissociatively on the catalyst surface while two oxygen species were involved in the benzene oxidation pathway. Furthermore, the r rose steadily from 1.3E-03 to 5.0E-03 µmol g<sup>-1</sup> s<sup>-1</sup> as the H<sub>2</sub>O partial pressure (p<sub>H2O</sub>) increased from 0

to 1.88 kPa (Figure 6 (c)). A further rise in  $p_{H2O}$  decreased the r (6.6E-04 µmol g<sup>-1</sup> s<sup>-1</sup> at 2.83 kPa), likely due to the competition between the benzene and H<sub>2</sub>O molecules for the active surface sites (Figure 6 (c)). The above result aligns with the experimental observation of performance enhancement in a specific RH range, which could be attributed to the role of H<sub>2</sub>O molecules as a source of hydrogen (assisting in the transformation of the activated benzene molecule) and OH groups (assisting in the adsorption and transformation of benzene molecules) upon decomposition on the supported Pt catalyst surface (see Section 3.3).

# 3.3. Oxidation mechanism and pathway

# 3.3.1. In-situ DRIFTS and physicochemical characterization

The *in-situ* DRIFTS spectra for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R were collected under the following three reaction conditions: (i) benzene +  $O_2$  (Figure 7 (a)), (ii) benzene +  $O_2$  +  $H_2O$  (Figure 7 (b)), and (iii) benzene +  $N_2$  (Figure S22) gaseous streams. The *in-situ* DRIFTS spectrum for benzene oxidation under aerobic conditions displayed the following species: (i) C-H deformation vibrations (800-900 cm<sup>-1</sup>), (ii) carboxylates + carbonates (950-1450 cm<sup>-1</sup>), (iii) benzoquinone + phenolate + catecholate (1550-1750 cm<sup>-1</sup>), (iv) CO adsorbed (bridged) between two Pt<sup>0</sup> sites (2050 cm<sup>-1</sup>), and (v) CO adsorbed (linearly) onto the Pt<sup>2+</sup> sites (2150 cm<sup>-1</sup>), benzene (3050 and 3150 cm<sup>-1</sup>), and surface OH (3300-3700 cm<sup>-1</sup>) <sup>3, 60, 64, 65</sup> (Figure 7 (a)).

The above results indicate that benzene may react with the active oxygen (O\* (surface  $O_{latt}$  and  $O_{ads}$ )) to yield phenolate species <sup>1,3</sup>. The *ortho* (*o*)- and *para* (*p*) phenolate conjugates are suspected to exist concurrently because the oxygen-containing group functions as an electron donor and *o-p* position director <sup>1</sup>. The *o-p* benzoquinone could then be formed by subsequent oxidation of the phenolate species

by O\* <sup>3</sup>. The *o*-benzoquinone could also be generated through the oxidation of catecholate species formed by direct oxidation of adsorbed benzene molecules <sup>65</sup>. The O\* species could react further to form aliphatic carboxylate species through the aromatic ring-opening reaction <sup>64</sup>. The carboxylates may break down to produce formate species that are then converted into carbonate <sup>65</sup>. The formed carbonate species should eventually be converted into CO<sub>2</sub> through the CO intermediate <sup>3, 65</sup>. As described above, the O\* consumption in the benzene oxidation pathway could also contribute to generating oxygen vacancies (O<sub>vac</sub>). The catalytic reaction is sustained as the oxygen supplied by O<sub>2</sub> replenishes the O<sub>vac</sub>.

Interestingly, all reaction intermediates generated during benzene oxidation under dry conditions were observed consistently in the presence of moisture (Figure 7 (b)). Such compatibility between the two contrasting conditions indicates that RH does not affect the type of intermediates formed during benzene oxidation. The peak for adsorbed benzene at 1500 cm<sup>-1</sup> was prominent in the presence of moisture, although it was absent under dry conditions. These contrasting trends indicate enhanced adsorption of benzene by the formed surface OH groups <sup>63</sup> (Figures 7 (a) and (b)). The prominent OH bands in the *in-situ* DRIFTS spectrum acquired under moist conditions further confirmed the enhanced formation of surface OH in the co-presence of H<sub>2</sub>O vapor (Figure 7 (b)). The critical role of moisture in generating surface OH groups and promoting the benzene oxidation reaction was described in Section 3.3.2.

The generation of reaction intermediates in an N<sub>2</sub> atmosphere indicates that the benzene molecules could be oxidized by the highly active  $O_{ads}$  and surface  $O_{latt}$  species (Figure S22). The absence of the carboxylate accumulation bands in the *in-situ* DRIFTS spectrum acquired in an N<sub>2</sub> atmosphere indicates an enhancement in the rate of benzene oxidation (Figure S22). The above observation was further supported by the absence of a CO band at 2100 cm<sup>-1</sup> in the *in-situ* DRIFTS spectrum acquired under an N<sub>2</sub> atmosphere (Figure S22). For the CO band at 2100 cm<sup>-1</sup>, Pt<sup>2+</sup> sites need to be generated through the

oxidation of  $Pt^0$  by  $O_2$ , which cannot occur in an  $N_2$  atmosphere. Thus, the catalytic oxidation reaction of benzene cannot be sustained in the absence of  $O_2$  (i.e., if there is no replenishment of the formed  $O_{vac}$ ).

After the 50 h TOS (benzene + air +  $H_2O$ ) benzene oxidation reaction, various characterization analyses of the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R sample were conducted to examine the associated physicochemical changes. For example, a dramatic shift was observed in the PXRD pattern of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R (Figure S23), with the reduced ZrO<sub>2</sub> peaks indicating alterations in the inherent crystal structure (Figure S23). No new surface functionalities formed after benzene oxidation, as confirmed by the FTIR spectra, although the band intensities in the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R FTIR spectrum were altered as an H<sub>2</sub>O layer was deposited on the catalyst surface (Figure S24).

The peak positions of  $3d_{5/2}$  and  $3d_{3/2}$  in the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R core-level Zr 3d XPS spectrum did not undergo any shifts with benzene oxidation (Figure S25 (a)). An increase in electron density was apparent in the 1.5%-Pt/UiO-66-NH<sub>2</sub>-R XPS spectra after benzene oxidation with the two red-shifted values of -0.2 eV (C-O (core-level C 1s) (Figure S25 (b))) and -1.2 eV (O<sub>ads</sub> (core-level O 1s) (Figure S25 (c))). Furthermore, the relative contribution of the O<sub>ads</sub> species in that spectrum dramatically increased from 7.4 to 41.3% after benzene oxidation due to O<sub>2</sub> adsorption (dissociative) on the Pt NPs (Figure S25 (c)). The 1.5%-Pt/UiO-66-NH<sub>2</sub>-R core level N 1s XPS spectrum indicated that the pyridinic nitrogen species were converted into pyrrolic form after the benzene oxidation reaction (Figure S25 (d)). The Pt 4f core-level XPS spectrum indicated the presence of Pt<sup>0</sup> (72.3 and 75.9 eV) species after the benzene oxidation reaction (Figure S26). The Pt 4f<sub>5/2</sub> and 4f<sub>7/2</sub> peaks blue-shifted by +1 and +0.6 eV, respectively (Figure S26).

# 3.3.2. DFT simulation and modeling

First-principle (theoretical) simulations were performed to learn more about the probable oxidation pathways for benzene. Firstly, two DFT models were simulated: the surface of pure  $ZrO_2$  and the same model with substitutional carbon and nitrogen impurities (Figures 8 and 9). A slab of six ZrO<sub>2</sub> layers was used for surface modeling (Figure 8 (a)). Only carbon and nitrogen impurities were present on the surface layers in the simulation of Pt-free substrates. Pt impurities were simulated using a single Pt atom in the interstitial position and a cluster of seven Pt atoms on the surface of pure and carbon-nitrogendoped ZrO<sub>2</sub>. The calculations indicate successful incorporation of the Pt<sub>7</sub>-cluster into the surface of ZrO<sub>2</sub> without sacrificing the large portion of Pt-Pt bonds (Figure 9). The above result qualitatively agrees with the XPS (Pt) data, where increased Pt-O bond-related peaks were accompanied by increased Pt content. Thus, six possible types of doped and undoped ZrO<sub>2</sub> surfaces were considered for DFT simulations. The first step of the modeling involved the calculation of the single benzene molecule adsorption enthalpy on the considered surfaces (Figure 8 (a)). For all four model surfaces, the adsorption enthalpy was predominantly negative (e.g., < -70 kJ mol<sup>-1</sup>). Hence, all types of surfaces were suitable for capturing benzene molecules from the air. In the next step of the simulation, XB was first considered, i.e., hydrogen atom migration from the benzene ring to the substrate (Figure 8 (b)). In the absence of carbon and nitrogen impurities on the surface of the substrate, the hydrogen abstraction from benzene was energetically unfavorable (enthalpy > +110 kJ mol<sup>-1</sup>), even for the Pt-doped surfaces. Thus, the undoped ZrO<sub>2</sub> surfaces (with and without Pt) were excluded from further consideration.

In the presence of carbon and nitrogen impurities, the migration of hydrogen atoms from benzene to the catalytic substrates was energetically favorable, with enthalpy values of -221, -184, and -173 kJ mol<sup>-1</sup> for the carbon and nitrogen-doped substrates without Pt, with one Pt atom, and with seven Pt impurities, respectively. The observed switch in the sign of enthalpy for the reaction corresponds with dangling bond formation due to the partial substitution of Zr and oxygen by carbon and nitrogen. This type of

migration can lead to saturation of some dangling bonds, which is in line with the exothermic character of the reaction. Benzene-to-substrate hydrogen atom migration can also facilitate covalent bond formation between the Zr atoms and dehydrogenated carbon on the surface (Figures 8 (b)-(g)). Thus, the carbon and nitrogen impurities on the ZrO<sub>2</sub> surface obtained from the NH<sub>2</sub>-functionalized organic linker of the MOF should be essential to enhance the catalytic performance of the tested material. The next step in the benzene oxidation process was the second hydrogen atom migration from benzene to the substrate (Figure 8 (c)). The above was also an energetically favorable step, with an enthalpy higher than 70 kJ mol<sup>-1</sup> for the three considered substrates. However, the third hydrogen atom migration from benzene to the substrate was energetically unfavorable. Thus, other reactants may be needed to control the subsequent benzene oxidation pathway.

One may consider oxygen the most natural candidate for the subsequent steps of benzene oxidation in the air. The adsorption of  $O_2$  was energetically favorable, with enthalpy values in the range of  $-30 \sim -$ 60 kJ mol<sup>-1</sup> for different positions and substrates (not shown in Figure 8 for clarity). Under such conditions, the  $O_2$  molecules can be captured efficiently by the target substrates alongside the partially converted benzene molecules. The following reaction step was simulated as  $O_2$  decomposition in which one of the atoms migrated to the  $C_6H_4$  ring while the other adsorbed to the substrate (Figure 8 (d)). The carbon-oxygen pair from the converted benzene ring was released as CO (Figure 8 (e)). These steps were exothermic with enthalpy values (magnitude) above 90 kJ mol<sup>-1</sup>. The described pathway of CO formation leads to the transformation of the six-membered ring into a five-membered ring (Figures 8 (e)-(g)).

The role of moisture in the benzene oxidation process was investigated by analyzing H<sub>2</sub>O decomposition on the substrates. The decomposition pathways of H<sub>2</sub>O can occur by the following two scenarios: (i) hydrogenation of the carbon ring and migration of OH groups to the substrate (Figure 8

(f)) and (ii) hydrogenation of the substrate with oxidation of the C<sub>6</sub>H<sub>4</sub> ring. The first one is a more realizable scenario based on total energy. Hydrogenation of the C<sub>6</sub>H<sub>4</sub> ring may occur with the transformation of one of the ring members from CH to CH<sub>2</sub>, followed by the energetically favorable hydrogen atom migration from the carbon ring to the substrate (Figure 8 (g)). Thus, the existence of H<sub>2</sub>O vapor may enhance the oxidation of benzene. Finally, the effect of Pt doping was assessed in relation to the catalytic performance of the studied systems. In this regard, the energetics of H<sub>2</sub>O decomposition on both types of Pt<sub>7</sub>-clusters (i.e., in pure and carbon-nitrogen-doped ZrO<sub>2</sub> surfaces) were investigated (Figure 9). Accordingly, H<sub>2</sub>O decomposition for both Pt<sub>7</sub>-clusters was favorable, with corresponding enthalpy values of -116 and -124 kJ mol<sup>-1</sup>, respectively. Thus, the Pt<sup>0</sup> centers in Pt<sub>7</sub> clusters embedded in the doped ZrO<sub>2</sub> matrix can be described as the primary catalytically active sites for H<sub>2</sub>O decomposition of H<sub>2</sub>O molecules can be the source of free hydrogen and OH groups for enhancing the oxidation of benzene molecules. Note that the energy gain from exothermic steps described in the above paragraph was more significant than that for benzene oxidation under dry conditions (discussed in previous paragraphs). Thus, the Pt-H<sub>2</sub>O synergy leads to a visible improvement in the catalytic performance of ZrO<sub>2</sub> containing carbon and nitrogen impurities.

In summary, the carbon and nitrogen dopants on the ZrO<sub>2</sub> surface produced from UiO-66-NH<sub>2</sub> are critical in driving the benzene oxidation reaction. The exact list and ratio of the products formed in the benzene oxidation pathways depend on the supply of oxygen and H<sub>2</sub>O to the reaction site. The presence of Pt atoms does not significantly change the energetics or pathways of benzene decomposition. However, the Pt-centers on the ZrO<sub>2</sub> surface help supply various reactants and critical species (e.g., hydrogen and OH groups obtained by H<sub>2</sub>O decomposition and oxygen obtained from O<sub>2</sub> dissociation) to sustain the catalytic process efficiently. The simulation results also demonstrate that benzene oxidation under humid conditions (i.e., using the H<sub>2</sub>O decomposition products) is more energetically

favorable than that under dry conditions due to the lower energy cost of H<sub>2</sub>O decomposition and higher energy gain from the benzene-OH interaction. A schematic of benzene oxidation on the Pt/UiO-66-NH<sub>2</sub>-R surface has been presented based on the *in-situ* DRIFTS and DFT simulation results in Figure 10.

### 3.4. Benzene removal performance comparison

The r-value calculated at 150°C was employed to compare the benzene oxidation performances of the reported Pt catalysts. The r-value provides a numerical evaluation of the collective impact of critical reaction parameters ( $M_{cat}$ ,  $X_B$ , flow rate, and benzene concentration) on the catalytic activity <sup>3, 66</sup>. As seen in Table 3, 1%-Pt/mesoporous cerium(IV) oxide (CeO<sub>2</sub>-MM) showed the highest activity for benzene oxidation (r-value of 0.74 mmol g<sup>-1</sup> h<sup>-1</sup>) <sup>67</sup>. For other catalysts, the r-values were estimated in the range of 0.046 (0.25%-Pt<sub>1</sub>/meso-Fe<sub>2</sub>O<sub>3</sub>) to 0.2 mmol g<sup>-1</sup> h<sup>-1</sup> (1%-Pt/titanium dioxide (TiO<sub>2</sub>)) <sup>3, 60</sup> (Table 3). The catalyst utilized in the present study, i.e., 1.5%-Pt/UiO-66-NH<sub>2</sub>-R (r-value of 0.086 mmol g<sup>-1</sup> h<sup>-1</sup>), outperformed 0.25%-Pt<sub>1</sub>/meso-Fe<sub>2</sub>O<sub>3</sub> (r-value of 0.046 mmol g<sup>-1</sup> h<sup>-1</sup>) and 0.3%-Pt/diatomite (r-value of 0.052 mmol g<sup>-1</sup> h<sup>-1</sup>) <sup>60, 68</sup> (Table 3). As seen in Table 3, 1%-Pt-0.6%-reduced graphene oxide (rGO)/aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) showed the lowest activation energy (E<sub>a</sub>) for benzene oxidation (8.8 kJ mol<sup>-1</sup>) <sup>69</sup>. For other catalysts, the E<sub>a</sub> values were estimated in the range of 20.7 (0.25%-Pt<sub>1</sub>/meso-Fe<sub>2</sub>O<sub>3</sub>) to 214 kJ mol<sup>-1</sup> (1%-Pt/CeO<sub>2</sub>-MM) <sup>60, 67</sup> (Table 3). The catalyst utilized in the present study, i.e., 1.5%-Pt/UiO-66-NH<sub>2</sub>-R (E<sub>a</sub> value of 105 kJ mol<sup>-1</sup>), outperformed 0.3%-Pt/diatomite (E<sub>a</sub> value of 125 kJ mol<sup>-1</sup>) and 1%-Pt/CeO<sub>2</sub>-MM (E<sub>a</sub> value of 214 kJ mol<sup>-1</sup>) (Table 3).

Pt loading (wt.%) can normalize the r-value to achieve a more meaningful performance comparison between different systems <sup>3, 70</sup>. In this regard, 1%-Pt/CeO<sub>2</sub>-MM was also the best-performing catalyst concerning the normalized r-values (74 mmol  $g^{-1} h^{-1}$ ) <sup>67</sup> (Table 3). The normalized r-values varied in the

17 (1%-Pt-0.6%-rGO/Al<sub>2</sub>O<sub>3</sub> and 0.3%-Pt/diatomite) to 64 mmol g<sup>-1</sup> h<sup>-1</sup> (0.18%-Pt/eggshell) range for other catalysts <sup>28, 68, 69</sup> (Table 3). The catalyst utilized in the present research (i.e., 1.5%-Pt/UiO-66-NH<sub>2</sub>-R) did not outperform the other reported catalysts concerning the normalized r-values (5.8 mmol g<sup>-1</sup> h<sup>-1</sup>) (Table 3). The benzene oxidation performance of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R was reported at 60% RH, while all the other catalysts were tested under dry conditions (Table 3). As moisture is ubiquitous under real-world conditions, the catalytic activity under dry conditions may not reflect the actual performance. The catalytic activity of most supported Pt catalysts (except Pt<sub>1</sub>/meso-Fe<sub>2</sub>O<sub>3</sub>) has been reported to decrease in the presence of H<sub>2</sub>O vapor for the benzene oxidation reaction <sup>28, 68</sup>. Since the presence of H<sub>2</sub>O vapor favorably increases the performance of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R (i.e., up to 60% RH) for the benzene oxidation reaction (see Section 3.2), it could be a better thermocatalyst for real-world applications compared to the other reported materials.

# 4. Conclusions

We explored the potential utility of Pt/UiO-66-NH<sub>2</sub>-R for benzene oxidation at low temperatures in the air. The prominent role of the reduction pre-treatment in benzene oxidation was supported by the absence of catalytic activity below 175°C (dry condition) for 1.5%-Pt/UiO-66-NH<sub>2</sub>. The impact of reaction condition (flow rate, M<sub>cat</sub>, RH, benzene concentration, and time-on-stream) on catalytic activity were also tested using 1.5%-Pt/UiO-66-NH<sub>2</sub>-R. H<sub>2</sub>O vapor dramatically promoted catalytic activity, reaching 100% X<sub>B</sub> to CO<sub>2</sub> at 150°C and 60% RH. The catalytic activity decreased with increasing H<sub>2</sub>O vapor content (after 60% RH) due to catalyst poisoning by excess moisture. Benzene mineralization into CO<sub>2</sub> involved phenolate, catecholate, benzoquinone, carboxylate, formate, carbonate, and CO intermediates per the *in-situ* DRIFTS analysis. DFT calculations were used to elucidate the prevalent reaction pathways and the promotional role of H<sub>2</sub>O vapor (supply of free hydrogen and surface OH groups) in benzene oxidation using the Pt/UiO-66-NH<sub>2</sub>-R catalyst. The current work will likely provide insights into the catalytic application of MOF-derived SNMCs for aromatic VOC oxidation reactions.

# **Supporting Information**

Characterization instrumentation; temperature-programmed experiments (experimental conditions, model description of Gaussian deconvolution and peak analysis, standard deviation calculation, and TPD data modeling); external mass transfer limitation; internal mass transfer limitation; external heat transfer limitation; internal heat transfer limitation; radial heat transfer limitation; supplementary tables; supplementary figures; supplementary references

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# **Tables and Figures**

Order	Sample	BET surface Micropore area <sup>a</sup>		External surface area <sup>a</sup>	Pore volume <sup>b</sup>	BJH adsorption average pore diameter (4V/A)	Actual content (wt.%) <sup>c</sup>
		$m^2 g^{-1}$	$m^2 g^{-1}$	$m^2 g^{-1}$	$cm^3 g^{-1}$	nm	Pt
1	UiO-66	$1,184 \pm 4.4$	1,113	71	0.7	1.5	0
2	UiO-66-NH <sub>2</sub>	$752 \pm 2.2$	703	49	0.5	1.9	0
3	0.2%-Pt/UiO-66-NH <sub>2</sub>	$722 \pm 2.1$	672	49	0.5	1.9	0.19
4	0.8%-Pt/UiO-66-NH2	726 ± 2	678	49	0.3	1.6	0.75
5	1.5%-Pt/UiO-66-NH2	685 ± 1.9	630	55	0.5	2	1.5
6	1.5%-Pt/UiO-66-NH <sub>2</sub> -R	$30 \pm 0.2$	-	31	0.04	3.4	-

# Table 1. Physical properties of the UiO-MOF catalyst and its modified forms.

<sup>a</sup> Derived using the t-plot method.

<sup>b</sup> BJH adsorption cumulative volume of pores between 0.1 nm and 300 nm diameter

<sup>c</sup> Determined by ICP-OES

Order	Model	Equation	Simplified equation	Model assumption	Kientic parameters	<b>R</b> <sup>2</sup>	χ²
1	LH1	$r = k_s \cdot \frac{K_{O_2} K_B p_{O_2} p_B}{\left(1 + K_{O_2} p_{O_2} + K_B p_B\right)^2}$	$r = k_s \cdot \frac{K_2 K_B p_B}{(1 + K_2 + K_B p_B)^2}$	O2 chemisorption. Involvement of one oxygen species.	$k_{s}$ = 0.018 $\mu mol~g^{\text{-1}}~s^{\text{-1}},~K_{2}$ = 1.7, and $K_{B}$ = 0.046 $Pa^{\text{-1}}$	0.9798	8.0E-06
2	LH2	$r = k_{s} \cdot \frac{K_{O_{2}}^{2} K_{B} p_{O_{2}}^{2} p_{B}}{\left(1 + K_{O_{2}} p_{O_{2}} + K_{B} p_{B}\right)^{3}}$	$r = k_s \cdot \frac{K_2^2 K_B p_B}{(1 + K_2 + K_B p_B)^3}$	O <sub>2</sub> chemisorption. Involvement of two oxygen species.	$k_{\rm s}{=}0.268~\mu{mol}~{g^{{\text{-}1}}}{\rm s}^{{\text{-}1}},K_{2}{=}0.35,{\rm and}~K_{\rm B}{=}0.014~{Pa^{{\text{-}1}}}$	0.9877	4.9E-06
3	LH3	$r = k_{s} \cdot \frac{\sqrt{K_{o_2}} K_B \sqrt{p_{o_2}} p_B}{\left(1 + \sqrt{K_{o_2} p_{o_2}} + K_B p_B\right)^2}$	$r = k_s \cdot \frac{\sqrt{K_2} K_B p_B}{\left(1 + \sqrt{K_2} + K_B p_B\right)^2}$	Dissociative oxygen chemisorption. Involvement of one oxygen species.	$k_{\rm s}$ = 0.033 $\mu mol~g^{\text{-1}}~s^{\text{-1}},~K_2$ = 0.26, and $K_{\rm B}$ = 0.026 $Pa^{\text{-1}}$	0.9858	5.4E-06
4	LH4	$r = k_{s} \cdot \frac{K_{O_{2}}K_{B}p_{O_{2}}p_{B}}{\left(1 + \sqrt{K_{O_{2}}p_{O_{2}}} + K_{B}p_{B}\right)^{3}}$	$r = k_s \cdot \frac{K_2 K_B p_B}{\left(1 + \sqrt{K_2} + K_B p_B\right)^3}$	Dissociative oxygen chemisorption. Involvement of two oxygen species.	$k_{\rm s}$ = 0.164 $\mu mol~g^{\text{-1}}~s^{\text{-1}},~K_2$ = 0.25, and $K_{\rm B}$ = 0.015 $Pa^{\text{-1}}$	0.9881	4.5E-06
5	ER1	$r = k_s \cdot \frac{K_{O_2} p_{O_2} p_B}{1 + K_{O_2} p_{O_2}}$	$r = k_s \cdot \frac{K_2 p_B}{1 + K_2}$	O <sub>2</sub> chemisorption. Involvement of one oxygen species.	$k_s$ = 0.001 $\mu mol~g^{\text{-1}}~s^{\text{-1}}$ Pa^{\text{-1}} and $K_2$ = 0.16	0.4709	2.6E-04
6	ER2	$r = k_s \cdot \frac{K_{O_2}^2 p_{O_2}^2 p_B}{\left(1 + K_{O_2} p_{O_2}\right)^2}$	$r = k_s \cdot \frac{K_2^2 p_B}{(1+K_2)^2}$	O2 chemisorption. Involvement of two oxygen species.	$k_{s}{=}0.009~\mu mol~g^{{-}1}~s^{{-}1}Pa^{{-}1}$ and $K_{2}{=}0.12$	0.4709	2.6E-04
7	ER3	$r = k_s \cdot \frac{\sqrt{K_{02} p_{02}} p_B}{1 + \sqrt{K_{02} p_{02}}}$	$r = k_s \cdot \frac{\sqrt{K_2} p_B}{1 + \sqrt{K_2}}$	Dissociative oxygen chemisorption. Involvement of one oxygen species.	$k_{s}$ = 0.0003 $\mu mol~g^{\text{-1}}~s^{\text{-1}}$ Pa^{\text{-1}} and $K_{2}$ = 0.18	0.4709	2.6E-04
8	ER4	$r = k_s \cdot \frac{K_{O_2} p_{O_2} p_B}{\left(1 + \sqrt{K_{O_2} p_{O_2}}\right)^2}$	$r = k_s \cdot \frac{K_2 p_B}{\left(1 + \sqrt{K_2}\right)^2}$	Dissociative oxygen chemisorption. Involvement of two oxygen species.	$k_{s}{=}0.001~\mu{mol}~g^{{-}1}~s^{{-}1}Pa^{{-}1}$ and $K_{2}{=}0.17$	0.4709	2.6E-04
9	MvK1	$r = \frac{k_{O_2}k_B p_{O_2} p_B}{k_{O_2} p_{O_2} + 7.5 k_B p_B}$	$r = \frac{k_2 k_B p_B}{k_2 + 7.5 k_B p_B}$	One active site is involved in the reduction and reoxidation step.	$k_B$ = 0.093 $\mu mol~g^{\text{-1}}~s^{\text{-1}}$ Pa^{\text{-1}} and $k_2$ = 0.015 $\mu mol~g^{\text{-1}}~s^{\text{-1}}$	0.005	3.5E-04
10	MvK2	$r = \frac{7.5k_B p_B}{2k_{O_2} p_{O_2}}$	$r = \frac{7.5k_Bp_B}{2k_2}$	Two reduced surface sites are involved in the reoxidation step.	$k_B$ = 9.3E-06 $\mu mol~g^{\text{-1}}~s^{\text{-1}}$ Pa^{\text{-1}} and $k_2$ = 0.25	0.4709	2.6E-04

Table 2. Benzene oxidation kinetic models and fitting results for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R.

			а н <i>и</i>	X (0/) / 1500C				D.C.
concentration (ppm)	Flow rate (mL min <sup>-1</sup> )	$V_B$ (mol s <sup>-1</sup> )	Space velocity	X <sub>B</sub> (%) at 150°C	r (mmol g <sup>-1</sup> h <sup>-1</sup> ) <sup>a</sup>	Pt normalized r (mmol g <sup>-1</sup> h <sup>-1</sup> )	E <sub>a</sub> (kJ mol <sup>-1</sup> ) <sup>5</sup>	Reference
626	40	1.2E-08	48,000 mL $g^{-1} h^{-1}$	85	0.74	74	214°	67
1,000	67	3.2E-08	80,000 mL g <sup>-1</sup> h <sup>-1</sup>	5	0.12	64	41.9°	28
100	200	9.6E-09	8,696 h <sup>-1</sup>	70	0.20	20	NA	3
1,000	16.6	8.0E-09	20,000 mL $g^{-1} h^{-1}$	8	0.046	18	20.7°	60
100	100	4.8E-09	60,000 mL g <sup>-1</sup> h <sup>-1</sup>	100	0.17	17	8.8°	69
1,000	50	2.4E-08	60,000 h <sup>-1</sup>	3	0.052	17	125°	68
100	50	2.4E-09	14,154 h <sup>-1</sup>	100	0.086	5.8	105	This study

actors operated in integral mode ( $X_B > 20\%$ ), the values calculated using Equation 3 overestimated the true r. Because the governing rate expression, kinetic parameters, and other details for the reported catalysts lated r values should not be treated as the real r under the specified conditions when the reactor operates in integral mode ( $X_B > 20\%$ ).

ture<sup>-1</sup> gives  $-E_a/R$ .  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .



Figure 1. Simulated and experimentally obtained PXRD patterns of UiO-66.



**Figure 2.** Physicochemical characterization results. (a) PXRD patterns of UiO-66-NH<sub>2</sub> and the Pt/UiO-66-NH<sub>2</sub> catalysts. (b) PXRD patterns of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R and ZrO<sub>2</sub> (simulated). (c) TGA profiles of UiO-66, UiO-66-NH<sub>2</sub>, and the Pt/UiO-66-NH<sub>2</sub> catalysts. (d) N<sub>2</sub> adsorption-desorption isotherms of UiO-66, UiO-66-NH<sub>2</sub>, Pt/UiO-66-NH<sub>2</sub> catalysts, and 1.5%-Pt/UiO-66-NH<sub>2</sub>-R.



**Figure 3.** Deconvoluted Pt 4f XPS spectra of the analyzed materials: (a) 0.2%-Pt/UiO-66-NH<sub>2</sub>. (b) 0.8%-Pt/UiO-66-NH<sub>2</sub>. (c) 1.5%-Pt/UiO-66-NH<sub>2</sub>. (d) 1.5%-Pt/UiO-66-NH<sub>2</sub>-R.



Figure 4. O<sub>2</sub>-TPD results for the tested catalysts. (a) Fraction (f) of total desorbed oxygen. (b) Total desorption versus desorption temperature. (-) 1.5%-Pt/UiO-66-NH<sub>2</sub> and (-) 1.5%-Pt/UiO-66-NH<sub>2</sub>-R.



**Figure 5.** Benzene removal performance of the tested catalysts. (a) Light-off curve (benzene: 100 ppm in air, M<sub>cat</sub>: 100 mg, flow rate: 50 mL min<sup>-1</sup>, and RH: 0%). (b) Effect of M<sub>cat</sub> (catalyst: 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, benzene: 100 ppm in air, M<sub>cat</sub>: 30-100 mg, flow rate: 50 mL min<sup>-1</sup>, and RH: 0%). (c) Effect of flow rate (catalyst: 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, benzene: 100 ppm in air, M<sub>cat</sub>: 100 mg, flow rate: 50-250 mL min<sup>-1</sup>, and RH: 0%). (d) Effect of benzene concentration (catalyst: 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, benzene: 100-300 ppm in air, M<sub>cat</sub>: 100 mg, flow rate: 50 mL min<sup>-1</sup>, and RH: 0%). (e) Effect of RH (catalyst: 1.5%-Pt/UiO-66-NH<sub>2</sub>-R, benzene: 100 ppm in air, M<sub>cat</sub>: 100 mg, flow rate: 50 mL min<sup>-1</sup>, and RH: 0%). (f) Time-on-stream performance of 1.5%-Pt/UiO-66-NH<sub>2</sub>-R at 200°C (benzene: 100 ppm in air, M<sub>cat</sub>: 150 mg, flow rate: 50 mL min<sup>-1</sup>, and RH: 60%).



**Figure 6.** Benzene oxidation kinetics for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R. (a) r as a function of  $p_B$ . (b) Benzene reaction order estimation. (c) r as a function of  $p_{H2O}$  ( $p_B = 10$  Pa).  $M_{cat}$ : 100 mg, flow rate: 50 mL min<sup>-1</sup>, RH: 0%,  $p_{O2} = 21$  kPa, and temperature: 110°C.

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Figure 7. In-situ DRIFTS spectra (acquired at 200°C under dark condition) for 1.5%-Pt/UiO-66-NH<sub>2</sub>-R.
(a) benzene + air and (b) benzene + air + H<sub>2</sub>O.

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**Figure 8.** Atomic structures simulated using DFT. (a) Optimized atomic structure of the whole ZrO<sub>2</sub> supercell containing carbon and nitrogen dopants. (b-g) Optimized atomic structures near the surface of the supercell. (a) shows adsorption of a benzene molecule, while the other figures show the initial steps of the benzene oxidation process.



**Figure 9.** Optimized atomic structure of carbon- and nitrogen-doped ZrO<sub>2</sub> with seven Pt impurities (a) with physically adsorbed H<sub>2</sub>O or (b) with decomposed H<sub>2</sub>O.



**Figure 10.** Schematic of benzene oxidation on the Pt/UiO-66-NH<sub>2</sub>-R surface per the *in-situ* DRIFTS and DFT simulation results.