Interplay of metal-acid balance and methylcyclohexane admixture effect on \(n\)-octane hydroconversion over Pt/HUSY

Nebojsa Korica \(^a\), Pedro S.F. Mendes \(^a\), Jeriffa De Clercq \(^b\), and Joris W. Thybaut * \(^a\)

\(^a\) Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium

\(^b\) Industrial Adsorption and Catalysis Technology, Ghent University, Valentin Vaerwyckweg 1, B-9000 Ghent, Belgium

* Corresponding author, e-mail: Joris.Thybaut@ugent.be

Abstract

Hydroconversion feeds are mixtures comprising alkanes and cycloalkanes, for which the binary impact on the respective reaction pathways, is still not completely understood. Methylcyclohexane admixture on \(n\)-octane hydroconversion over Pt/HUSY catalysts has been investigated using the pure compounds and their equimolar mixtures in a wide range of operating conditions. The hydroconversion behavior on catalysts with various Pt loading was examined to investigate the role of the site. No impact of methylcyclohexane admixture to \(n\)-octane was observed over catalysts which ensured ideal hydrocracking (0.5 and 0.1wt.%Pt). In contrast, methylcyclohexane addition decreased the octane isomer yield at iso-conversion over 0.07 wt.%Pt/HUSY. A lower metal loading of 0.04 wt.%Pt led to a pronounced decrease in \(n\)-octane conversion in the mixture. The methylcyclohexane conversion was not affected by \(n\)-octane addition regardless of the metal-acid balance. The negative admixture impact on the \(n\)-octane conversion and isomers yield, combined with the absence of any impact on the methylcyclohexane behavior, was attributed to preferred cycloalkane adsorption on metal sites, resulting in a reduced metal site availability for alkanes. Cycloalkane admixture to an alkane in hydrocracking can, hence induce a regime shift from ideal to non-ideal hydrocracking. Consequently, bifunctional catalysts developed purely for alkane hydroconversion may prove not to be optimal for realistic feed behavior, including cycloalkanes.
**Highlights**

- Methylcyclohexane admixture negatively impacts \( n \)-octane hydroconversion.
- Admixture impact increases with decreasing metal-acid ratio.
- Metal catalyzed steps in alkane hydroconversion are hindered by cycloalkane admixture.
- Alkane admixture does not impact cycloalkane hydroconversion.

**Key words**: hydrocracking; mixture effect; alkanes; cycloalkanes; metal-acid balance

1. **Introduction**

Valorization of hydrocarbon feedstocks into various products, which meet contemporary environmental, techno-economic, and social requirements has been triggering numerous researches. Maximized utilization of fossil-based hydrocarbon sources, full use of biomass, and fulfillment of modern emission and performance standards of fuel engines require effective and reliable refining units. Conventional conversion processes, such as hydroconversion (hydroisomerisation and cracking), catalytic cracking, or thermal cracking, can, in this new context, be used for rearranging and converting hydrocarbon molecules from sustainable carbon sources.

The hydrocarbon feeds converted into more valuable products are, in general, complex mixtures of different types of molecules, including alkanes, cycloalkanes, aromatic and heterocyclic components, dienes, etc. The standard hydroconversion feed is hydrotreated prior to hydrocracking, such that all unsaturated and heterocyclic components are converted into saturated alkanes and cycloalkanes, together with some refractory aromatics.

During hydroconversion, saturated hydrocarbons (alkanes and cycloalkanes) are converted over a bifunctional catalyst, comprising metal and Brønsted acid sites, in the presence of hydrogen. Reacting hydrocarbons are physisorbed within the pores of the bifunctional catalyst. Unsaturated intermediates are formed by dehydrogenation of (cyclo)alkanes on metal sites. Intermediate (cyclo)alkenes move from the metal to the Brønsted acid sites where they are protonated, yielding (cyclo)alkyl-carbenium ions. (Cyclo)alkyl-carbenium ions undergo skeletal rearrangement (hydride shifts, alkyl-shifts, and protonated-cyclopropane (PCP) branching) and cracking (\( \beta \)-scission) reactions.
The reaction mechanism and examples of reaction pathways are schematically shown in Figure 1. Reaction rates are decreasing in the order alkyl-shift, PCP branching, and β-scission. The hydrocracking reaction complexity increases for cycloalkanes as compared to alkanes due to additional reaction families (Figure 1a and 1c). Rearrangement and cracking reactions can occur within the ring and in the aliphatic part of the molecule, resulting in additional reaction families: intra-ring alkyl shifts, cyclic PCP branching, exocyclic (dealkylation), and endocyclic β-scission (ring opening).

The balance between the metal and Brønsted acid site activities determines the overall reaction performance in hydroconversion, for given operating conditions and acid function type (e.g. zeolite). A sufficiently high concentration of active metal sites compared to the Brønsted acid sites ensures that (de)hydrogenation reactions are in quasi-equilibrium (good balance of metal and acid sites). Moreover, apart from the ratio, also the distance between metal and Brønsted acid sites should also be sufficiently small such that transfer of intermediate (cyclo)alkenes does not become limiting.

Recent work from the group of de Jong demonstrated this convincingly by depositing the metal either on the binder or the zeolite support of the zeolite (good intimacy of metal and Brønsted acid sites). As a consequence of the optimal balance between metal and acid sites, product yields only depend on the kinetics of acid-catalyzed elementary reactions. Fast hydrogenation at the metal sites avoids consecutive acid catalyzed transformations per protonated species without intermediate deprotonation and (de)hydrogenation (Figure 1b and 1c), resulting in a maximum isomer yield. This specific situation is denoted as ‘ideal hydrocracking’.

By lowering the metal site concentration, the quasi-equilibration of the (de)hydrogenation reactions (Figure 1a) cannot be guaranteed and, so-called, ‘non-ideal hydrocracking’ occurs. The same effect can be achieved by increasing the acid site concentration. Both (de)hydrogenation and acid-catalyzed reactions are kinetically relevant in such a situation. The catalyst activity is lowered due to the slower (de)hydrogenation step, simultaneously leading to a higher probability for the occurrence of
consecutive reactions of the carbenium ions (Figure 1b and 1c) and, consequently, higher yields of cracking products.

The occurrence of ideal hydrocracking over a metal-acid bifunctional catalyst does not exclusively depend on the catalyst and, more particularly, its metal-acid balance, but also on the reaction conditions – temperature, pressure, and reactant molecule. A higher temperature requires a higher metal site concentration to remain in the ideal hydrocracking regime. A higher total pressure increases the metal activity and favors a shift from non-ideal to ideal hydrocracking. A higher total pressure increases the hydrogen partial pressure and, in that way, the hydrogenation rate. However, in ideal hydrocracking, as the thermodynamics control the (de)hydrogenation, the overall conversion will be lowered with total pressure increase, according to the Le Chatelier principle. Concerning the impact of the reactant, the carbon number of alkane impacts the number of the possible elementary acid catalyzed steps, i.e. the size of the reaction network. Consequently, higher concentration of metal sites is required to achieve ideal hydrocracking for larger alkanes. For cycloalkanes, the effect is not well studied yet and even less for mixtures of reactants. Most likely, the complex composition of a real hydrocarbon feedstock significantly impacts the occurrence of ideal hydrocracking. In short, as various operating conditions do impact on the establishment of quasi-equilibrium for the (de)hydrogenation reactions, c.q. ideal hydrocracking, the corresponding metal to Brønsted acid sites ratio does depend on the operating conditions, including the feedstock composition.

In the particular case of cycloalkane admixture to an alkane, although a systematic analysis has not been reported yet in the literature, certain trends and peculiar phenomena have already been reported. Sanchez and coworkers have found that the addition of cyclohexane lowers the n-alkane conversion over 1 wt.%Pt/beta catalyst compared to the pure n-alkane conversion. Over the same zeolite with different acid strengths, cyclohexane admixture did not change total isomer selectivity of n-alkanes. Guisnet and Fouche have observed that addition of methylcyclohexane as impurity in n-hexane decreases its conversion over 0.3 wt.%Pt/mordenite catalysts and that decrease is more prominent for lower Brønsted acid sites concentrations. Overall, cycloalkane admixture has been
reported to have a negative impact on alkane conversion and no impact on product selectivity [21-25]. Furthermore, the impact of zeolite as the acid sites carrier has been assessed [22, 23, 25]. Over shape selective zeolites, higher cracked products amounts were formed [22, 23, 25]. Hence, for a fundamental evaluation of the admixture effect, a non-shape selective zeolite is used [22]. Using such a catalyst, the observed product distributions will only be a function of metal-acid ratio, process conditions and reactants. With respect to the other reaction steps in hydrocracking, cycloalkanes adsorb more strongly on Brønsted acid sites than alkanes, according to Kriz and coworkers [26]. On the other hand, reports on the competitive adsorption between alkanes and cycloalkanes on metal sites were not found. In conclusion, if and how the presence of cycloalkanes impacts the balance between metal and acid sites of bifunctional catalysts has not been thoroughly studied in literature yet.

The goal of this work is, hence, to investigate the effect of cycloalkane admixture on n-alkane hydroconversion over bifunctional catalysts, paving the way to the identification of the affected reaction steps. HUSY was selected as zeolite support to ensure the absence of shape-selectivity which could complicate the analysis of the admixture impact on the hydrocracking reactions. Model components were selected to address the complex nature of bifunctional catalysis and acquire a fundamental understanding of the admixture impact. To further limit the number of variables impacting the metal-acid balance, the differences in adsorption and reactivity on the acid sites are minimized by selection of n-octane and methylcyclohexane as model reactants for alkane and cycloalkane, respectively. The metal-acid ratio represents the key controlling parameter for bifunctional catalyst performance and, therefore, catalysts with different ratios were tested under various operating conditions. By evaluation of the various kinetic results, the reaction step, which is the most prone to the admixture impact, is assessed.
Figure 1 (a) Schematic description of hydroconversion reaction over bifunctional catalyst with (b) an example of a possible reaction pathways of n-octane and (c) an example of a possible reaction pathways of methylcyclohexane.
2. **Materials and methods**

2.1. **Catalyst synthesis**

The role of metal-acid ratio on mutual impact of alkane and cycloalkane in hydroconversion is investigated on catalysts with Pt as the metal site and with the acid function provided by the zeolite HUSY (CBV712 with SiO$_2$/Al$_2$O$_3$ molar ratio of 12, supplied by Zeolyst). Catalysts with four different Pt loadings were synthetized in-house: 0.5wt.%Pt/HUSY; 0.1wt.%Pt/HUSY; 0.07wt.%Pt/HUSY; and 0.04wt.%Pt/HUSY (Table 1). Platinum was loaded on the zeolite by incipient wetness impregnation.$^{27}$, $^{28}$ The precursor was tetraammineplatinum(II)-nitrate hexahydrate $\text{[Pt(NH}_3)_4\text{NO}_3]\cdot\text{6H}_2\text{O}$ purchased from Sigma Aldrich (purity 99.995%). Catalysts were left to mature overnight in the oven at 393 K after impregnation. Next the catalysts were calcined under a static air atmosphere in a Nabertherm P330 oven in a stepwise temperature program: three plateaus of 1 h at 423K, 523K, and 623K, and one plateau of 2 h at 773K (see Supporting information Figure S1). The heating rate to each plateau was 5 K/min.

2.2. **Catalyst characterization**

The specific surface area of the synthesized catalysts was determined by N$_2$ adsorption on a TriStar II device (Micromeritics) using t-plot method (see Supporting information Section S2). The Pt content of the synthesized catalyst was confirmed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, IRIS intrepid II XSP from Thermo Scientific) (Table 1) (see Supporting information Section S3). The platinum dispersion was determined by hydrogen-oxygen titration.$^{27-30}$ in an Autochem II 2920 device (Micromeritics) with thermal conductivity detector. The samples (0.2 - 0.3 g) were initially pretreated under H$_2$ at 473 K during 30 min and at 723 K during 60 min. Next the samples were cooled to 308 K and consecutive pulses of H$_2$ were injected with an interval of 3 min until no further adsorption was observed. After purging with He for 45 min, consecutive O$_2$ pulses (with intervals of 3 min) were injected until no further adsorption was observed as well. The samples were purged with Ar for 45 min and then H$_2$ pulses were injected. Another cycle of oxygen and hydrogen titration was performed in order to ensure repeatability. A stoichiometric ratio H$_2$:Pt of 1.5 is used to calculate the Pt dispersion.
The platinum reduction was investigated by hydrogen temperature programmed reduction (H\textsubscript{2}-TPR) in an Autochem II 2920 device (Micromeritics) with thermal conductivity detector. The samples (about 0.3 g) were heated up to 873 K during 1 h under a gas (5% H\textsubscript{2} in Ar) flow of 0.17 Nml/s. The degree of platinum reduction was calculated based on the quantity of consumed hydrogen and platinum content. The reduction degree of platinum, obtained by H\textsubscript{2}-TPR, was found to be decreasing with increasing Pt loading, as expected from literature\textsuperscript{28} (Table 1). The platinum dispersion was also inspected by dark field scanning transmission electron microscopy (STEM DF) in a JEM-2200FS Cs corrected microscope device (JEOL) operated at 200kV with Schottky type field emission gun (FEG) and EDX. The samples of all four catalysts were deposited on a lacey carbon film with a copper grid support. Average particle size is similar for all catalysts (about 1 nm) (Table 1). The acidity of catalysts was compared by ammonia temperature programmed desorption (NH\textsubscript{3}-TPD) in an AutoChem 2920 device (Micromeritics). The samples (0.1 – 0.15 g) were pretreated by heating to 873 K and cooling to 373 K under the constant He gas flow of 1 ml/s. Next, the gas flow was switched to 4 vol.% NH\textsubscript{3}-He with a flow rate of 1 ml/s to adsorb ammonia for 1 h. Finally, the sample was heated to 873 K during 50 min and the ammonia desorption rate was recorded by thermal conductivity detector, which was calibrated between every measurement. No significant deviation in NH\textsubscript{3}-TPD spectra and no change of the acidity of the catalysts and pure HUSY zeolite prove that the acidity was not affected by the Pt content (Table 1 and Supporting information Section S7). The concentration of Brønsted acid sites, which was used to determine the ratio of metal over acid site was estimated based on the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of zeolite (which is obtained from ICP-OES) and the fractions of Al(IV) and extraframework Al atoms for HUSY reported in literature\textsuperscript{31-33} assuming that there were no counter-cations in zeolite. As the acidity of HUSY zeolites is not affected by the low Pt contents nor by the applied thermal treatments \textsuperscript{28}, this approach allows a reasonable theoretical estimation of the metal-acid sites ratio. Although pyridine-TPD would be the best generic method to determine the amount of Brønsted acid sites on zeolites, for the material used in our work, the other
methods work equally well. More importantly, the Pt dispersion, obtained by hydrogen-oxygen titration, was used to determine the metal-acid sites ratio. Alternative values for the metal-acid sites ratio were calculated with the acid sites concentrations obtained from ammonia temperature programmed desorption. The procedure for determination of the metal-acid sites ratio is explained in Supporting information Section S8.

The catalyst characteristics are summarized in Table 1. The metal dispersion values obtained by H<sub>2</sub>-O<sub>2</sub> titration are found to be comparable to the reduction degree of platinum, obtained by H<sub>2</sub>-TPR. The reduction profiles are shown in Figure S2 in Supporting Information. According to NH<sub>3</sub>-TPD, all catalysts and pure HUSY had similar total acidity values, proving that loading of this very low Pt quantities does not have an impact on acid properties. The particle size as determined by TEM and H<sub>2</sub>-O<sub>2</sub> does not differ significantly for catalysts with 0.04 wt.%, 0.07 wt.%, and 0.1 wt.%Pt. For 0.5 wt.%Pt a somewhat lower number of larger particles was observed by TEM than by H<sub>2</sub>-O<sub>2</sub> titration (Figure S4 in Supporting information).  

Table 1 Characteristics of the synthesized catalysts

<table>
<thead>
<tr>
<th>Catalyst Pt/HUSY*</th>
<th>0.04 wt.%</th>
<th>0.07 wt.%</th>
<th>0.1 wt.%</th>
<th>0.5 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt loading (wt.%) [ICP]</td>
<td>0.04</td>
<td>0.06</td>
<td>0.09</td>
<td>0.51</td>
</tr>
<tr>
<td>Pt dispersion (%) [H&lt;sub&gt;2&lt;/sub&gt;-O&lt;sub&gt;2&lt;/sub&gt; titration]</td>
<td>80</td>
<td>63</td>
<td>55</td>
<td>28</td>
</tr>
<tr>
<td>Pt reduction degree (%) [H&lt;sub&gt;2&lt;/sub&gt; TPR]</td>
<td>85</td>
<td>65</td>
<td>48</td>
<td>29</td>
</tr>
<tr>
<td>Acidity (mmol/g) [NH&lt;sub&gt;3&lt;/sub&gt; TPD] **</td>
<td>1.00</td>
<td>0.96</td>
<td>1.08</td>
<td>1.30</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[TEM]</td>
<td>0.92</td>
<td>1.02</td>
<td>1.01</td>
<td>0.94</td>
</tr>
<tr>
<td>[H&lt;sub&gt;2&lt;/sub&gt;-O&lt;sub&gt;2&lt;/sub&gt; titration]</td>
<td>1.41</td>
<td>1.59</td>
<td>1.23</td>
<td>3.37</td>
</tr>
<tr>
<td>Specific surface area (m&lt;sup&gt;2&lt;/sup&gt;/g) [N&lt;sub&gt;2&lt;/sub&gt; adsorption t-plot]</td>
<td>498</td>
<td>500</td>
<td>514</td>
<td>520</td>
</tr>
<tr>
<td>n&lt;sub&gt;Pt&lt;/sub&gt;/n&lt;sub&gt;12&lt;/sub&gt; x 10&lt;sup&gt;3&lt;/sup&gt; (mol/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[theoretical acidity]</td>
<td>0.906</td>
<td>1.114</td>
<td>1.562</td>
<td>5.328</td>
</tr>
<tr>
<td>[NH&lt;sub&gt;3&lt;/sub&gt; TPD acidity]</td>
<td>1.641</td>
<td>2.019</td>
<td>2.238</td>
<td>5.633</td>
</tr>
</tbody>
</table>

* HUSY zeolite has SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 12.

** Acidity of pure HUSY zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 12 (determined by NH<sub>3</sub>-TPD) is 1.14 mmol/g.
2.3. **Kinetic measurements**

Experiments were carried out using the high-throughput setup (Zeton) dedicated for a mechanistic investigations (HTK-MI) in two parallel reactors with a length of 89 cm and internal diameter of 11 mm contained in a furnace which enables temperature control at three zones in the reactor. Two gases were supplied for the experiments: hydrogen as reactant, and methane as internal standard for analysis. Gas inlet flow rates are regulated by thermal mass flow controllers (Bronkhorst). Liquid reactants are fed and controlled by an HPLC pump (Knauer Azura P4.1s). The pressure in the reactor is controlled by a membrane back-pressure regulator (Equilibar) piloted with nitrogen. The setup is completely heat-traced (200°C) such that the reactor effluent was kept in the vapor phase. The effluent is analyzed by a gas chromatograph (GC) (6850 Series II, Agilent Technologies) equipped with a FID and a non-polar capillary column (Agilent HP-PONA, 50 m x 200 µm x 0.5 µm polydimethylsiloxane).

Reactants were n-octane (extra pure, 99+%), purchased from Acros Organics, and methylcyclohexane (ReagentPlus®, 99%), purchased from Sigma Aldrich. Methane (N35, 99% purity) and hydrogen (N40, 99.99% purity) were supplied by AirLiquide and used without further purification.

The size of the catalyst particles and the dilution of the catalyst with inert alumina particles (Final advanced materials) were determined to avoid mass or heat transfer limitations. The catalysts were pelletized, crushed and sieved to diameter between 100 and 200 µm and diluted with the alumina particles (150 µm) with a weight ratio 1:3 (catalyst : inert particles). The catalyst was activated in the reactor with hydrogen at a flow rate of 50 NL/h, increasing the temperature to 723 K at 5 K/min and reduction at 723 K during 1 h.

The total flow rate of the liquid reactant(s) was controlled by the pump and also by regularly measuring the weight of the reactant flask. The mixture feeds were gently stirred at specific time intervals to ensure a uniform composition of the fed mixture. The peak areas ($A_i$) of the gas chromatograms were normalized (with Dietz calibration factors $CF_i$) to obtain the mass fraction $y_i$ of each compound, for all compounds in the effluent ($n_{tot, resp}$).

$$y_i = \frac{A_i CF_i}{\sum_{j=1}^{n_{tot, resp}} A_j CF_j}$$
The mass and molar flow rates were calculated based on weight composition and flow rate of the internal standard. The mass balance is considered to be ‘closed’ if the total weight of products and unreacted reactant equals measured reactant mass flow rate within 5%. The carbon balance was closed in all experiments within 5%. The mass flow rates of reactants and particular products are converted into molar flow rates $F_{\text{feed, } i}^0$ and $F_{\text{feed, } i}$, to calculate the total conversion of reactant $i$ $X_i$:

$$X_i = \frac{F_{\text{feed, } i}^0 - F_{\text{feed, } i}}{F_{\text{feed, } i}^0}$$

Selectivity towards all isomers (or different isomer groups) $S_{\text{iso}}$, and cracking products $S_{\text{cr}}$ are obtained by summation of all carbon molar flow rates of isomers/cracking products $S_i$ belonging to a particular group (with $n$ products in the group) and division by the carbon products total flow rate. Corresponding yields of product $i$ $Y_{i,j}$ are obtained by multiplication of selectivity and conversion of reactant $j$.

$$S_i = \frac{\sum_{i=1}^{n} F_i}{\sum_{j=1}^{n_{\text{prod}}} F_j}$$

$$Y_{i,j} = S_i X_j$$

Space times $ST_i$ were calculated for every reactant in mixture based on catalyst weight $W_{\text{cat}}$ and initial molar flow rate of the particular reactant $F_{\text{feed, } i}^0$.

$$ST_i = \frac{W_{\text{cat}}}{F_{\text{feed, } i}^0}$$

2.4. Definition of the experimental space

The reactants chosen as model components for alkanes and cycloalkanes were $n$-octane and methylcyclohexane. The selection of these model components was done based on following criteria: (1) predominance of the families of these components (i.e. alkanes and cycloalkanes) in oil fractions which are processed via hydroconversion; (2) sufficiently extensive reaction network of alkane, in order to be able to observe transition between ideal and non-ideal hydrocracking $^6$, $^{11}$; (3) different carbon number of model reactants, to avoid as much as possible overlap of products from different reactants; (4) similar size of molecule and similar physisorption affinity, in order to avoid any effect of preferential phenomena in this step on conversion and product selectivity $^{21}$, $^{39}$, $^{40}$; and (5) technical requirements of the setup, to ensure the gas phase character of the effluent $^{41}$. 

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The *n*-octane and methylcyclohexane properties with respect to physisorption on different HUSY zeolites are shown in Table 2-3. Almost identical saturation concentration and relatively close physisorption enthalpies indicate that both reactants will have almost the same physisorption properties. Table 4 summarizes the reaction networks of *n*-octane and methylcyclohexane, which are obtained by internally developed program for reaction networks generation (RENGEP). Table 5 compares literature reported activation energies for all, potentially occurring reaction families. The methylcyclohexane reaction network is not so extensive as compared to that of *n*-octane (see Table 4). Additionally, endocyclic β-scissions have very low rate due to a low pre-exponential factor and high entropy loss in the formation of the transition state \(^{11}\), so reactions of ring-opening products, which are also listed in Table 5, are not likely to occur.

Experimental conditions were chosen to ensure adequate comparison of behavior of reactants fed pure and in mixtures. Therefore, the partial pressure of the model components was kept constant in most experiments. This could be achieved by changing the molar hydrogen-to-hydrocarbon ratio (H\(_2\)/HC). However, at low H\(_2\)/HC ratios, change of this parameter can impact the reaction performance \(^{19}\). Furthermore, at higher H\(_2\)/HC ratios reactor effluent will more likely remain completely in a vapor phase. As a result, experiments at high H\(_2\)/HC ratio and partial pressure of 0.05 bar for every reactant were performed. In order to have a proper indication of ideal hydrocracking occurrence, experiments were carried out at two values of total pressure. The temperature range as well as the flow rates of components were set to ensure sufficient conversion (10-90% for *n*-octane and 10-45% for methylcyclohexane) for both reactants, to allow for a meaningful comparison of their kinetic performances, namely in terms of maximum isomer yield. The admixture effect is expected to be maximum when the feed is an equimolar mixture of reactants. Experimental conditions are summarized in Table 6.

**Table 2 Generic molecular properties of *n*-octane and methylcyclohexane**

<table>
<thead>
<tr>
<th>Reactant</th>
<th><em>n</em>-octane</th>
<th>methylcyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon number</td>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>
Table 3 Physisorption properties of n-octane and methylcyclohexane on HUSY zeolite for different SiO$_2$/Al$_2$O$_3$ ratios

<table>
<thead>
<tr>
<th>Pre-exponential factors of Henry coefficient* (mol/kg$_{\text{cat}}$bar) $^{39,40}$</th>
<th>n-octane</th>
<th>methyl-cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 5.4</td>
<td>$7.9 \times 10^4$</td>
<td>$1.6 \times 10^3$</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 60</td>
<td>$9.4 \times 10^5$</td>
<td>$1.9 \times 10^4$</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 12 **</td>
<td>$5.3 \times 10^4$</td>
<td>$1.1 \times 10^3$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physisorption enthalpy* (kJ/mol) $^{39,40}$</th>
<th>n-octane</th>
<th>methyl-cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 5.4</td>
<td>-55.9</td>
<td>-50.1</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 60</td>
<td>-56.5</td>
<td>-50.3</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 12 **</td>
<td>-56.1</td>
<td>-50.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Saturation concentration at 506 K *</th>
<th>n-octane</th>
<th>methyl-cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 5.4</td>
<td>1.07</td>
<td>1.22</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 28</td>
<td>0.68</td>
<td>0.71</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 60</td>
<td>0.61</td>
<td>0.62</td>
</tr>
<tr>
<td>- SiO$_2$/Al$_2$O$_3$ = 12 **</td>
<td>0.87</td>
<td>0.95</td>
</tr>
</tbody>
</table>

* The methylcyclohexane physisorption pre-exponential factor was assumed to be the same as for the alkane with same carbon number$^{11,21}$.

** The data for HUSY with SiO$_2$/Al$_2$O$_3$ ratio of 12 are graphically interpolated based on data for HUSY with SiO$_2$/Al$_2$O$_3$ ratio of 5.4; 28; and 60 zeolites.

Table 4 Reaction networks of n-octane and methylcyclohexane

<table>
<thead>
<tr>
<th>Reactant</th>
<th>n-octane</th>
<th>methylcyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of components in reaction network</td>
<td>22 alkanes</td>
<td>5 cycloalkanes</td>
</tr>
<tr>
<td>Distribution of components (incl. intermediates) within the reaction network</td>
<td>4 monobranched isomers</td>
<td>2 monobranched cycloalkanes</td>
</tr>
<tr>
<td></td>
<td>8 dibranched isomers</td>
<td>3 dibranched cycloalkanes</td>
</tr>
<tr>
<td></td>
<td>4 tribranched isomers</td>
<td>12 cracking products</td>
</tr>
</tbody>
</table>
5 cracking products (in ideal hydrocracking)
75 alkenes
57 carbenium ions
19 cycloalkenes
16 cyclocarbenium ions
10 dienes
25 carbenium ions
7 olefinic carbenium ions

Number of reactions

<table>
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<tr>
<th>Reaction Type</th>
<th>(s,s)</th>
<th>(s,t)</th>
<th>(t,s)</th>
<th>(t,t)</th>
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</thead>
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<td>alkyl-shifts</td>
<td>16.7</td>
<td>13.7</td>
<td>7.7</td>
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<td>PCP branching</td>
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<tr>
<td>β-scissions</td>
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<tr>
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<td>exocyclic β-scissions</td>
<td>76</td>
<td>57</td>
<td>56</td>
<td>22</td>
</tr>
</tbody>
</table>

* (x,x) indicate carbenium ion type of reactant and product – secondary (s) or tertiary (t)

Table 6 Experimental conditions for investigated catalysts: (1) 0.5wt.%Pt/HUSY; (2) 0.1wt.%Pt/HUSY; (3) 0.07wt.%Pt/HUSY; and (4) 0.04wt.%Pt/HUSY
3. Results

3.1. Catalyst screening

The balance between metal and acid sites has been examined by kinetic measurements with pure n-octane over the four catalysts. As mentioned before, the ideal hydrocracking regime is most reliably indicated by a decrease in conversion with increasing total pressure. At the same time, a change of operating conditions does not impact the isomer yield in ideal hydrocracking.

Figure 2 shows the n-octane conversion over the tested catalysts under a wide range of conditions, which allow indication of ideal hydrocracking occurrence in line with previously reported indicators\(^5\). An obvious decrease in conversion at higher total pressure was observed for the 0.5 wt.%Pt (Figure 2a) and for the 0.1 wt.%Pt catalyst (Figure 2b), regardless of the temperature for the various space times. Higher total pressures lead to less pronounced dehydrogenation for thermodynamics reasons, resulting in a reduced supply of alkenes (also see Introduction). This, on its turn, lowers the carbenium ions concentration on the acid sites and, ultimately, the n-octane conversion at the same space time.

Additionally, the total pressure also determines the hydrogen partial pressure. This results in a higher coverage of metal sites with hydrogen at higher pressure. In its turn the latter results in faster hydrogenation reducing the amount of alkenes which re-adsorb on the acid sites to undergo consecutive reactions. In short, the metal sites concentration was sufficient to ensure equilibration of
the (de)hydrogenation reactions\textsuperscript{3,19}. So, ideal hydrocracking occurred at all investigated conditions for \textit{n}-octane over the 0.5 and 0.1 wt.%Pt catalyst. These two catalysts are further referred to as ‘well-balanced’.

Figure 2 \textit{n}-Octane conversion, when fed pure, at various conditions as a function of space time over (a) 0.5wt.%Pt/HUSY, (b) 0.1wt.%Pt/HUSY, (c) 0.07wt.%Pt/HUSY, and (d) 0.04wt.%Pt/HUSY

Overall, lower \textit{n}-octane conversions were observed with 0.07 wt.%Pt (Figure 2c) and 0.04 wt.%Pt catalysts (Figure 2d). Temperatures had to be increased significantly for the 0.04 wt.%Pt to obtain a measurable conversion. The total pressure increase, which was implemented by adjusting the hydrogen pressure and not the \textit{n}-octane partial pressure, did not change the \textit{n}-octane conversion significantly. This indicates that (de)hydrogenation was no longer equilibrated and became kinetically relevant, where conversion does not change if reactant partial pressure is not adjusted\textsuperscript{19}. Therefore, \textit{n}-octane hydrocracking over 0.07 and 0.04 wt.%Pt was non-ideal under the investigated operating conditions. These catalysts will be further referred to as ‘poorly-balanced’.
The evolution of the n-octane isomer yield with conversion is depicted in Figure 3. The 0.1 and 0.5 wt.%Pt catalysts exhibited no effect of the different Pt loading. The experimental points for these catalysts are on a single curve, within the experimental error. A maximum n-octane isomer yield of ca. 55% at a conversion of ca. 75% was observed. The good balance of the metal and acid function for the 0.5 and 0.1 wt.%Pt catalysts, determined via the pressure impact, has been confirmed by the isomer yield evolution with conversion. The maximum yield decreased and shifted to lower conversions over the 0.07 and 0.04 wt.%Pt catalysts. The decrease of n-octane isomer yield maximum, and so the increase of cracking products yield, was obvious for 0.07 wt.%Pt (maximum yield of about 40% at 65% conversion) and, especially, prominent for 0.04 wt.%Pt (maximum yield of about 15% at 45% conversion). Because of the reduced availability of metal sites, alkenes, formed by deprotonation of carbenium ions resulting from acid-catalyzed reactions, were hydrogenated more slowly. Consequently, the likelihood of undergoing consecutive isomerization and β-scissions increases\(^3, 6, 9, 10\). The decrease in maximum isomer yield for 0.07 and 0.04 wt.%Pt catalysts confirms non-ideal hydrocracking behavior over those catalysts.

The balance of metal-acid sites of the studied catalysts was also investigated for methylcyclohexane conversion. The results are shown in Figure 4. Total pressure change did not impact the conversion...
over the catalyst which was found as poorly-balanced for pure \textit{n}-octane. On the contrary, such change was observed over 0.5 wt.%Pt catalyst. Cracking products in low amount were found only in reaction over 0.04 wt.%Pt catalyst (not shown). The potential of methylcyclohexane to yield cracking products is much lower as only entropically not favored endocyclic \(\beta\)-scissions are possible as cracking reactions in the network\textsuperscript{11}. Therefore, in practice, the reaction network is limited to methylcyclohexane isomers. These facts explain maximum observed conversion of about 40%, which corresponds to thermodynamic equilibrium between methylcyclohexane and its isomers\textsuperscript{11}. In conclusion, the experiments with pure methylcyclohexane over examined catalysts showed the decrease in conversion with lower Pt loading like in case of \textit{n}-octane.

![Figure 4] Methylcyclohexane conversion, when fed pure, at various conditions as a function of space time over (a) 0.5wt.%Pt/HUSY, (b) 0.07wt.%Pt/HUSY, and (c) 0.04wt.%Pt/HUSY
3.2. *n-Octane in mixture – impact of methylcyclohexane*

An equimolar mixture of *n*-octane and methylcyclohexane was used to determine the impact of co-reactants on each other’s conversion over the various catalysts. The reaction conditions were set such that the partial pressure of each reactant is the same as when the reactant was fed pure (Table 6). The conversions of pure *n*-octane and in a mixture with methylcyclohexane over the catalysts with 0.1, 0.07, and 0.04 wt.%Pt at a total pressure of 10 bar are shown in Figure 5. (The experimental results at 20 bar and the comparison of results at both pressures are shown in Supporting information Figure S9 and Figure S10.) The total pressure impacted the *n*-octane conversion in the same way over all catalysts like when it is fed pure. Concerning the admixture effect, *n*-octane conversion over 0.1 wt.%Pt (well-balanced) catalyst remained similar upon mixture with methylcyclohexane (Figure 5b). On the other hand, the *n*-octane conversion in a mixture with methylcyclohexane over poorly balanced catalysts (with 0.07 and 0.04 wt.%Pt) was lower than when it was fed pure (Figure 5c and 5d). This decrease is far more evident for the 0.04 wt.%Pt than for the 0.07 wt.%Pt catalyst.
Figure 5 \(n\)-Octane conversion, when fed pure, in 1:1, and in 3:1 \(n/n\) mixture with methylcyclohexane, at 10 bar and different temperatures as a function of space time calculated based on \(n\)-octane flow rate over (a) and (b) 0.1wt.%Pt/HUSY, (c) 0.07wt.%Pt/HUSY, and (d) 0.04wt.%Pt/HUSY

Over the well-balanced catalysts (0.5 and 0.1 wt.%Pt), the \(n\)-octane isomer yield curve in case of admixture with methylcyclohexane was similar compared to that obtained with pure \(n\)-octane (Figure 6). Over a poorly-balanced catalyst (0.07 wt.%Pt), the maximum \(n\)-octane isomer yield was reduced to about 35% at 60% conversion (compared to about 40% at 65% for the pure reactant), see Figure 6. The lower \(n\)-octane isomer yield, particularly in the higher conversion range, was evident and indicative of the methylcyclohexane admixture effect. For the even more poorly-balanced catalyst (0.04 wt.%Pt), the isomer yield was reduced to about 10% at 35% conversion (Figure 6) due to the impact of methylcyclohexane admixture. However, \(n\)-octane isomer yields were already minimal when fed pure and, hence, the impact of methylcyclohexane admixture was less evident. Regarding the pressure
impact, as expected, the total pressure slightly increased octane isomer yield over poorly-balanced catalysts, as for pure \( n \)-octane experiments.

In order to further investigate the methylcyclohexane admixture impact on the reaction pathway, the selectivity of \( n \)-octane to its monobranched and dibranched isomers, and to cracking products as function of conversion has been analyzed in more detail (Figure 7). Note that the ‘dispersion’ in the data for every catalyst originates from the variation in operating conditions (pressure and temperature) \(^ {19} \). Indeed, even if deviations are limited no perfectly unique curves are obtained for product selectivities and yields as a function of the conversion\(^ {3} \). A maximum selectivity to monobranched isomers is achieved when ideal hydrocracking occurs (see Introduction) \(^ {3, 10} \). In the experiments where \( n \)-octane was fed in mixture for both poorly-balanced catalysts lower selectivities to monobranched isomers were observed (Figure 7a). Different selectivities to dibranched \( n \)-octane isomers in experiments with methylcyclohexane admixture indicate that methylcyclohexane does have impact on the poorly-balanced catalysts (with 0.07 and 0.04 wt.%Pt) (Figure 7b). The selectivity of monobranched isomers decreased and the selectivity of dibranched isomers increased upon a reduced availability of the metal function. This can be explained by the higher likelihood to undergo consecutive
acid catalyzed reactions \(^3,10\). Based on these findings, it can be concluded that methylcyclohexane admixture impacts the metal activity in \(n\)-octane hydrocracking.

Figure 7 Selectivity to (a) monobranched and (b) dibranched isomers as a function of \(n\)-octane conversion, when fed pure and in 1:1 \(n/n\) mixture with methylcyclohexane, over different catalysts at conditions of Figure 5 and Figure S9.

3.3. Methylcyclohexane in mixture – impact of \(n\)-octane

Figure 8 shows the methylcyclohexane conversion– in 1:1 and 1:3 \(n/n\) mixture with \(n\)-octane for catalysts with 0.1 wt.%Pt (Figure 8a); and, pure and in an 1:1 \(n/n\) mixture with \(n\)-octane for catalysts with 0.07 and 0.04 wt.%Pt (Figure 8b and 8c) as a function of space time and at a total pressure of 10 bar. (The experimental results at 20 bar and the comparison of results at both pressures are shown in Supporting information Figure S11 and Figure S12.) Space times at which same conversions were reached on Figure 8a, were three times larger for methylcyclohexane in a 1:3 \(n/n\) mixture with \(n\)-octane compared to 1:1 \(n/n\) mixture. Thus, it can be extrapolated with high certainty that conversion of pure methylcyclohexane over catalyst with 0.1 wt.%Pt will be identical as methylcyclohexane conversion in 1:1 \(n/n\) mixture with \(n\)-octane. The methylcyclohexane conversion, hence, remained similar and was not affected by \(n\)-octane admixture for all three catalysts (Figure 8). In the same way, the methylcyclohexane isomer yield was similar irrespective of the \(n\)-octane admixture or not (Figure 9). Such behavior was expected because of the unlikely occurrence of endocyclic beta-scission reactions due to low pre-exponential factor and large entropy loss \(^{11}\). Looking at the selectivity towards all four isomers (Figure 9), the general observation is that it did not significantly change with catalyst,
contrarily to what was observed with octane isomers (Figure 7). As a result, the conversion of methylcyclohexane was not impacted by \( n \)-octane admixture, which was mainly attributed to the limited reaction network.

![Figure 8](image)

Figure 8 Methylcyclohexane conversion, when fed pure, in 1:1, and in 1:3 \( n/n \) mixture with \( n \)-octane, at 10 bar and different temperatures as a function of space time calculated based on methylcyclohexane flow rate over (a) 0.1wt.%Pt/HUSY, (b) 0.07wt.%Pt/HUSY, and (c) 0.04wt.%Pt/HUSY.
4. Discussion

The impact of both metal-acid sites ratio and reactants admixture is summarized by comparing the conversion and isomer selectivity over the various catalysts to those which correspond to ideal hydrocracking in terms of \( n \)-octane (Figure 10a) and methylcyclohexane (Figure 10b). Concerning the impact of admixture on \( n \)-octane (Figure 10a), the key experimental findings are:

(1) over well-balanced catalysts, the \( n \)-octane conversion was not affected by methylcyclohexane admixture (Figure 5a, 5b, S2a, and S2b);

(2) over poorly-balanced catalysts, \( n \)-octane conversion decreased with the addition of methylcyclohexane (Figure 5c, 5d, S2c, and S2d);
(3) the lower the metal site concentration in the catalyst, the more pronounced the decrease in \( n \)-octane conversion (Figure 5c, 5d, S2c, and S2d); and

(4) over poorly-balanced catalysts, methylcyclohexane admixture decreased the \( n \)-octane isomer yield and impacts selectivity towards multibranched isomers (Figure 6a and 6b).

Concerning the impact of admixture on methylcyclohexane (Figure 10b), the main finding is that the methylcyclohexane conversion does not change with \( n \)-octane admixture over both type of catalysts, i.e. neither well-balanced nor poorly-balanced (Figure 8). Additionally, concerning the total pressure effect, it was also found that total pressure change does not impact the \( n \)-octane conversion over a poorly-balanced catalyst (when the reactant partial pressure is kept constant) (Figure 2c and 2d); and increase of total pressure has a positive impact on \( n \)-octane isomer yields for poorly-balanced catalysts (Figure 6a and 6b). In what follows, these findings are used to understand the impact of admixture and role of the metal-acid site ratio, as well as to identify the most impacted reaction step.

Figure 10 Overview of impact of metal-acid ratio and admixture on (a) \( n \)-octane and (b) methylcyclohexane hydrocracking for different catalysts

4.1. Impact of methylcyclohexane admixture on \( n \)-octane hydrocracking over well-balanced catalyst

The impact of the methylcyclohexane admixture on \( n \)-octane hydrocracking over well-balanced catalysts (for pure \( n \)-octane) is analyzed based on experimental findings (1) and findings about the impact admixture of \( n \)-octane to methylcyclohexane hydroconversion. Two catalysts (0.1 and 0.5 wt.\%...
Pt, see Table 1), have been confirmed to ensure \( n \)-octane ideal hydrocracking when fed pure and in mixture with methylcyclohexane at the investigated experimental conditions (Table 6). \( n \)-Octane and methylcyclohexane were selected assuming that both components are physisorbed on the catalyst in a relatively similar amount (Table 2) \(^{21} \). Therefore, the assessment of the most impacted reaction step by admixture is possible. Taking into account the absence of significant physisorption difference and similar experimental behavior, one can conclude that a sufficient availability of metal sites ensures that no inhibitory effects of competitive adsorption on metal sites between \( n \)-octane and methylcyclohexane occurs.

Based on unchanged conversion and product selectivity, it seems that the addition of methylcyclohexane does not have an impact on \( n \)-octane hydrocracking over the well-balanced catalyst, on metal sites, as well as on acid sites (Figure 10a). Anyhow, adsorption on acid sites, c.q. protonation, should be analyzed as the step where competition between two reactants can occur. Kriz and coworkers found that cycloalkanes have higher thermodynamic affinity to protonation than alkanes \(^{26} \), as the cycloalkyl-carbenium ions are known to be more stable than alkyl-carbenium ions \(^{11} \).

Consequently, the competitive protonation would impact overall conversion of one or both reactants (see Introduction). As the size of the reaction network is most extensive for \( n \)-octane (Table 4), an obvious decrease in conversion would be expected if methylcyclohexane was protonated with significant preference. However, no effects of competitive protonation were observed as neither conversion nor product yields change with methylcyclohexane admixture (Figure 10). Apparently, the coverage of the acid sites, at the investigated operating conditions, is sufficiently low. At such low coverages of the acid sites, reactions of all components within both alkane and cycloalkane reaction networks can occur without mutual interference. The potential effect of preferred protonation of methylcyclohexane over \( n \)-octane is not observable on well-balanced catalysts.

For 0.5 wt.% and 0.1 wt.% Pt loadings, the estimated metal-acid distance is rather short (order of tens of nanometers) \(^{16, 44} \). Over large-pore zeolites such as HUSY used in this work, the intimacy between metal and acid sites has been demonstrated to result in ideal hydroconversion behavior \(^{14, 16, 17, 45} \).
Therefore, the metal-acid site ratio is the key parameter for the occurrence of ideal hydrocracking in our work. In the literature, Pt to Brønsted acid sites molar ratios of 0.17\(^{10}\) and 0.01\(^{27}\) were found to be sufficient for ideal hydrocracking of \(n\)-decane\(^{10}\) and \(n\)-hexadecane\(^{27}\), respectively. In this study, the catalysts with a Pt to acid ratio of 0.005328 and 0.001562 were found to ensure \(n\)-octane ideal hydrocracking, confirming that ideal hydrocracking regime is not just dependent on Pt to acid molar ratio, but also on the operating conditions and reactant type\(^{3,19}\).

4.2. **Impact of methylcyclohexane admixture on \(n\)-octane hydrocracking over poorly-balanced catalyst**

According to experimental findings (2), (3), and (4), changes in kinetic behavior of \(n\)-octane in the presence of methylcyclohexane were observed for the weaker metal functions (0.07 and 0.04 wt.%Pt). Both catalysts were experimentally found to be poorly-balanced in pure \(n\)-octane hydrocracking (Figure 10a). For a lower metal site concentration, intermediate (cyclo)alkenes are more prone to undergoing consecutive acid catalyzed reactions (also see Figure 1)\(^{3,13-15}\), with a concomitant impact on the product distribution.

The addition of methylcyclohexane impacts the product distribution of \(n\)-octane hydrocracking. More specifically, it significantly decreases the \(n\)-octane isomer yield over the 0.07 wt.%Pt catalyst in favor of cracked product formation, while the conversion only slightly decreases. The selectivity to monobranched and dibranched \(n\)-octane isomers was to a certain extent affected. Nevertheless, the conversion of \(n\)-octane in mixture seemed not to significantly decrease due to the slightly lower hydrogen partial pressure (which is a result of the experimental plan (Table 6)).

The impact of methylcyclohexane admixture on \(n\)-octane conversion is more evident when the Pt content was lowered (to 0.04 wt.%Pt). Within the \(n\)-octane isomer product distribution, an even lower formation of monobranched isomers and higher formation of dibranched isomers were observed when \(n\)-octane is fed in admixture with methylcyclohexane.

The total pressure increase impacts in a positive way the \(n\)-octane isomer yield, when \(n\)-octane is fed with methylcyclohexane admixture. Hence, the introduction of methylcyclohexane has identical
effects on n-octane hydrocracking as lowering the number of metal sites or increasing the number of Brønsted acid sites would have (Figure 10a)\textsuperscript{10,13}. This indicates that alkane adsorption on metal site and thereby the dehydrogenation reaction was hindered by the presence of the cycloalkane.

4.3. Impact of n-octane admixture on methylcyclohexane hydrocracking

In order to have a global mechanistic picture on the mixture effect, the impact of n-octane on methylcyclohexane conversion is also analyzed. Prior to this analysis, the impact of metal-acid ratio on pure methylcyclohexane hydroconversion is to be elaborated. Methylcyclohexane conversion over the catalysts which were found to be poorly-balanced for n-octane (with 0.07 and 0.04wt.%Pt) was lower compared to the conversion over catalysts where ideal hydrocracking of n-octane occurred (with 0.5 and 0.1wt.%Pt) (Figure 10b). The lower metal-acid site ratio impacts pure methylcyclohexane conversion in the same way like pure n-octane, but does not have any impact on selectivity to methylcyclohexane isomers.

No impact on the methylcyclohexane conversion and selectivity to its isomers was observed (Figure 10b). This finding indicates that there is no impact of n-octane on the activity of both the metal and the acid function during methylcyclohexane hydroconversion. Similarly, Jimenez and coworkers did not observe any change in selectivity to cyclohexane products either when the mixture of different n-alkane and cyclohexane was fed over Pt/HUSY and Pt/Beta catalysts\textsuperscript{22}. The fact that n-octane does not affect the reaction of methylcyclohexane over any of the investigated catalysts can be further understood by assessing the individual reaction steps. It is deduced from the observations that methylcyclohexane preferentially adsorbs on metal sites compared to n-octane. The relatively simple methylcyclohexane reaction network\textsuperscript{11}, which is limited to a few cyclic isomers, potentially explains the absence of n-octane admixture impact on methylcyclohexane. Finally, an additional reason could also be a preferred protonation on acid sites compared to acyclic hydrocarbon structures. This has been already reported\textsuperscript{25,26}, but in our work, no evidence of such an effect was found as methylcyclohexane admixture did not impact the behavior of catalysts under ideal hydrocracking (Section 4.1).
4.4. *Determination of the most impacted reaction step by methylcyclohexane admixture*

In order to determine the most impacted reaction step by methylcyclohexane admixture, all experimental observations are taken into consideration. The mutual admixture impact on every elementary step in hydroconversion of *n*-octane and methylcyclohexane mixture over ideal and non-ideal hydrocracking catalyst is summarized in Figure 11.

Regardless of the catalyst and operating conditions, the experiments have shown that conversion of the reactant with a less extensive reaction network (methylcyclohexane) was not affected by the presence of one with a more extensive one (*n*-octane) (Table 4). This implies that the overall faster acid catalyzed reactions do not play a role in competition between two observed reactants. Therefore, the kinetically relevant step(s) is(are) apparently related to metal catalyzed phenomena – adsorption on (and desorption from) the metal site and (de)hydrogenation surface reactions. A total pressure increase slightly increases *n*-octane isomer selectivity over poorly-balanced catalysts, regardless of methylcyclohexane admixture. Moreover, the methylcyclohexane conversion decreases with metal concentration, but not with the introduction of *n*-octane as co-reactant. Based on those observations, adsorption on (and desorption from) the metal site seems to be the most affected step (Figure 11).

According to these new insights, the admixture leads to a more pronounced non-ideal hydrocracking regime, due to competitive adsorption between alkane and cycloalkane on metal sites. In other words, the preferred adsorption of cycloalkanes on metal sites is proposed to decrease the effective number
of available metal sites for alkanes, creating a poorer balance between metal and acid sites. Thus, the addition of methylcyclohexane to n-octane reinforces the non-ideal hydrocracking behavior. At the limit, it will most likely also induce a shift from ideal to non-ideal hydrocracking, for the right combination of catalyst (metal-acid ratio) and operating conditions, including feedstock composition. In the studied case, the difference in adsorption on metal sites between n-octane and methylcyclohexane is proposed to be the origin of the admixture effect. Therefore, the admixture impact would even be more evident when differences in adsorption on metal sites are more pronounced. To effectively observe a consequent shift from ideal to non-ideal hydrocracking, the size of the reactants could be adjusted and, e.g., additional experiments with larger cycloalkane model molecule could be performed. Furthermore, observed effects could be quantified by a model which includes all reaction steps.

5. Conclusions

The impact of cycloalkane admixture on the hydrocracking of alkane was investigated by kinetic measurements on a Pt/HUSY catalysts with various Pt loadings. No impact of methylcyclohexane addition was observed on the n-octane conversion and product yields over well-balanced hydrocracking catalysts. In contrast to that, higher order product formation was enhanced over non-ideal hydrocracking catalysts. The more non-ideal the hydrocracking was, e.g., by lowering the catalyst’s metal-acid ratio, the more pronounced n-octane conversion decreased with methylcyclohexane admixture. On the other hand, no impact of n-octane on methylcyclohexane conversion was observed. Metal catalyzed reactions (dehydrogenation) have been found to be mostly affected, presumably by competition between of n-octane and methylcyclohexane for the metal sites. The experimental data could be rationalized by assuming a preferential adsorption of cycloalkanes on the metal sites. This decreases the concentration of available metal sites for the alkanes, hindering the establishment of their (de)hydrogenation quasi-equilibrium and, hence, tending to shift the alkane hydrocracking regime from ideal to non-ideal. This consequence of cycloalkane admixture results in lower catalyst performances when hydrocarbon mixtures are fed to the reactor. Therefore,
bifunctional catalyst proven as optimal purely for alkane hydroconversion, could certainly be not optimally for realistic feeds, including cycloalkanes.

**Associated content**

**Supporting Information:** The Supporting Information is available free of charge.

Temperature profile of the calcination program; Catalyst characterization – t-plot data, ICP-OES data, Hydrogen-oxygen titration data, Hydrogen temperature programmed reduction, Transmission electron microscopy (TEM), Ammonia temperature programmed desorption; Determination of metal-acid sites ratio; n-Octane conversion, when fed pure, in 1:1, and in 3:1 n/n mixture with methylcyclohexane, at various conditions as a function of space time calculated based on n-octane flow rate over 0.1wt.%Pt/HUSY, 0.07wt.%Pt/HUSY, and 0.04wt.%Pt/HUSY; Methylcyclohexane conversion, when fed pure, in 1:1, and in 1:3 n/n mixture with n-octane, at various conditions as a function of space time calculated based on methylcyclohexane flow rate over 0.1wt.%Pt/HUSY, 0.07wt.%Pt/HUSY, and 0.04wt.%Pt/HUSY.

**Data availability statement:** The kinetic measurements on hydrocracking which are presented in the article can be found in attachment (Zenodo data base 10.5281/zenodo.4737329). The characterization data (H₂-O₂ titration and N₂ adsorption) of catalysts can be found in attachment (Zenodo data base 10.5281/zenodo.5110006).

**Author information**

**Corresponding Author**

*Joris W. Thybaut:* Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium

E-mail: Joris.Thybaut@ugent.be

**Authors**

*Nebojsa Korica:* Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium
Pedro S.F. Mendes: Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium

Jeriffa De Clercq: Industrial Adsorption and Catalysis Technology, Ghent University, Valentin Vaerwyckweg 1, B-9000 Ghent, Belgium

Notes

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