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Influence of polyvinylpyrrolidone as stabilizing agent on Pt nanoparticles in Pt/H-BEA catalyzed hydroconversion of n-hexadecane

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ABSTRACT

Colloidal Pt particles prepared using polyvinylpyrrolidone (PVP) as a capping agent were loaded on acidic Beta zeolite, with the aim of obtaining bifunctional catalysts with controllable dispersion for the hydroconversion of n-hexadecane (n-C\textsubscript{16}). Among the different approaches to remove PVP, reduction was the most effective whilst maintaining the initial Pt particle size after deposition on the zeolite. The presence of small amounts of nitrogen- and carbon-containing products from PVP decomposition affected the acidity stronger than the Pt metal function. Therefore, it was not possible to establish the effect of Pt particle size on the performance of the Pt/Beta zeolites in n-C\textsubscript{16} hydroconversion and the performance trends were dominated by the acidity differences. Small Pt particles on zeolite obtained by using high PVP/Pt ratios during the colloidal synthesis step presented lower Bronsted acidity than catalysts containing larger Pt particles. The resulting variations in Pt/H\textsuperscript{+} ratios led to a transition of observed ideal cracking behavior for weakly acidic catalysts (small Pt particles, larger amount of PVP residuals) to overcracking behavior for catalysts with stronger acidity. We find that the Pt/H\textsuperscript{+} ratio and the number of acid-catalyzed steps extrapolated to zero conversion are better indicators of ideal cracking behavior than the isomers yield.

1. Introduction

Hydrocracking is an important industrial chemical process for the upgrading of heavy hydrocarbon feedstock to valuable transportation fuels. Bifunctional catalysts containing dehydrogenation/hydrogenation (Pt, Pd, or metal sulfides) and isomerization/cracking (Brønsted acid sites) functions are employed for this purpose [1]. It is generally believed that in a catalyst where these two functions are well balanced and the condition of intimacy is met, isomerization and hydrocracking are consecutive reactions and the rate-determining step is the acid-catalyzed skeletal rearrangement of intermediate alkenes obtained from dehydrogenation of alkanes on metal sites [2,3]. The mechanism involves the dehydrogenation of usually linear paraffinic feedstock to corresponding olefins, their isomerization on acid sites into thermodynamically more stable branched olefins and rehydrogenation to branched paraffins. The formation of branched olefins goes through several steps involving alkylcarbenium ion transition states, which can experience δ-scission (carbon–carbon bond cleavage) reactions yielding smaller hydrocarbons. As the two catalytic functions in hydroconversion are usually physically separated, diffusion of the intermediates between them can play an important role in determining the product distribution [4,5]. Ideal hydrocracking is defined as a regime where the limiting reaction step takes place on the acid sites [6]. Deviations from this ideal behavior are commonly observed as secondary transformation of the primary olefinic products (often called secondary cracking or overcracking). The ratio between the concentrations of accessible metal and acid sites (Pt/H\textsuperscript{+}) is used to quantify the balance between the two types of active sites on the bifunctional hydroconversion reactions [7,8]. Typically, the activity increases with the Pt/H\textsuperscript{+} ratio until a plateau is reached, the transition going together with a shift of the rate-limiting reactions from (de)hydrogenation over metal sites to isomerization/cracking on acid sites.

The acid function is usually a zeolite or an amorphous silica-alumina. For the hydrogenation function, noble metals stand out in performance compared to metal sulfides, but their use is limited to clean hydrocarbon feeds. Pd and Pt are the preferred transition metals for hydrocracking, because Ni is too active in the hydrogenolysis of hydrocarbons, which results in a too high production of light hydrocarbons. A key parameter

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Despite the importance of metal dispersion in hydrocracking catalysts [9], there are relatively few investigations on the impact of metal particle size. This is due to the usual assumption that alkane hydrogenation and dehydrogenation reactions are structure insensitive [10,11]. Nevertheless, it has been reported that Pt can catalyse hydrogenolysis of alkanes during n-alkane hydrocracking [12,13]. While the rate of hydrogenolysis is assumed to be structure insensitive, especially small Pt particles containing undercoordinated metal surface atoms can display high rates of alkane hydrogenolysis [14]. In line with this, hydrogenolysis is reported to be relatively slow on large Pt particles [15]. Conventional methods to deposit noble metals on support materials such as impregnation or ion exchange involve calcination and reduction treatments, which allow for relatively high metal loadings but with poor particle size control [16–18]. Better control of the size and shape of metal particles can be achieved using colloidal synthesis methods. Colloidal nanoparticles are synthesized in a solution employing usually polymers as capping agents, which contain functional groups that can bind to the metal surface [19–22]. Often, this approach is combined with a solution-reduction approach. For example, ethylene glycol (EG) can be used to dissolve metal salt precursors and to reduce the metal cations at elevated temperature [23,24]. Well-defined nanoparticles can for instance be obtained by combining polyvinylpyrrolidone (PVP) as the capping agent with EG as the solvent. Depending on the exact conditions and the use of additives, it is possible to obtain metallic particles in the form of cubes, octahedrons and cuboctahedrons from AgNO₃ [20], nanowires from PdCl₂ [25], nanowires, branched multipods and spheres from Fe₂O₃/Fe₃O₄ [26,27]. An inherent disadvantage is that the capping agent limits the accessibility of the metal surface to reactants. Therefore, the capping agent needs to be removed after the preparation. Washing is a common approach, but not effective in removing all polymer. Thus, it is important to develop additional strategies to remove the residual capping agent from the surface without affecting the shape and size of the prepared particles [28].

In the present work, we intended to study the particle size effect of Pt in Pt-Beta hydrocracking catalysts. We used PVP as the capping agent to prepare uniformly sized Pt nanoparticles, which were deposited on acidic Beta (BEA) zeolite. After deposition and washing, different methods were explored to remove residual capping agent, which include oxidative, reductive and other chemical treatments. The as-prepared catalysts were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermogravimetric analysis/differential scanning calorimetry (TGA/DSC), temperature-programmed hydrogenation (TPH) and IR spectroscopy. The acidic properties of the Pt/BEA zeolites were determined by IR spectroscopy of adsorbed pyridine and deuterated benzene (CD₂CD₂) H/D exchange. The Pt metal phase was characterized by H₂ chemisorption and IR spectroscopy of adsorbed CO. Finally, the catalytic activity in hydrocracking of n-hexadecane (n-C₁₆) of the samples was determined.

2. Experimental methods

2.1. Synthesis Pt nanoparticles

Pt nanoparticle (Pt NP) dispersions in ethanol were obtained using polyvinylpyrrolidone (PVP, Sigma-Aldrich, average MW 40000) as capping agent, H₃PtCl₆·6H₂O (Alfa Aesar, Pt 37.5 %) as the Pt source and ethylene glycol (EG, Sigma-Aldrich 99.8 %) as the reducing agent. In a typical synthesis [20], 2.5 ml of EG was initially refluxed for 5 min at 433 K. Then, 312.5 µl of a 0.375 M solution of PVP in EG (111 g/mol as a monomeric unit) and 46.9 µl of a 0.0625 M solution of H₃PtCl₆·6H₂O in ethanol were added every 30 s during 16 min, making up a total of 10 ml added PVP solution and 1.5 ml added Pt solution, respectively. The molar PVP/Pt ratio was 40. The resulting mixture was refluxed for 5 min. The mixture was then centrifuged at 5000 rpm for 15 min. The nanoparticles were separated and precipitated from the supernatant by adding acetone, followed by centrifugation at 3000 rpm for 5 min. The precipitate was collected and re-dispersed in 3 ml of ethanol with sonication. 9 ml hexane was added and the dispersion was centrifuged at 3000 rpm for 5 min. The precipitate was treated twice with the same solvent mixture. Finally, the precipitate was dispersed in 3 ml ethanol. Other dispersions with different Pt NP sizes were obtained following the same procedure but changing the total amount of PVP solution, i.e. adding 2.5, 0.125 and 0.0125 ml to obtain PVP/Pt ratios of 10, 0.5 and 0.05, respectively. Pt NP dispersions of approximately 3, 4, 7 and 10 nm were obtained according to TEM analysis (Fig. 1 and Figure S1 of Supporting Information). The corresponding Pt particle size distributions are given in Figure S2. Another Pt NP batch with 1.3 nm particles was synthesized following a different approach [29]. An amount of 12.5 ml 0.5 M NaOH solution in EG was added to 12.5 ml of a 0.038 M solution of H₂PtCl₆·6H₂O in EG. The mixture was heated to 433 K and further stirred for 3 h under N₂ atmosphere. The supernatant was precipitated with 0.5 ml 2.0 M HCl and dispersed in a 0.1 mM PVP solution in ethanol.

2.2. Synthesis Pt/Beta

A commercial Beta zeolite from supplier Zeolyst was used as support (Si/Al = 50, BET SA = 403 m²/g). The Pt NP catalysts were prepared by sonication for 3 h of an appropriate amount of colloidal solution in which Beta zeolite powder was dispersed. The targeted Pt loading was 0.5 wt% (Table 1), followed by centrifugation of the solid and drying overnight in air at 373 K. The catalysts are denoted as Pt1.3(PVP)/Beta, Pt3(PVP)/Beta, Pt4(PVP)/Beta, Pt7(PVP)/Beta and Pt10(PVP)/Beta, according to the average Pt particle size of the starting colloidal solution. A reference Pt-Beta sample was obtained by wet impregnation with aqueous solutions of H₂PtCl₆·6H₂O. The targeted metal loading for this sample was 0.5 wt%. The resulting catalysts were dried in air at room temperature for 3 h and calcined at 723 K under flowing air for 4 h.

2.3. Capping agent removal

The initial step for capping agent removal from the nanoparticles consisted of repeatedly washing with solvents and collection by centrifugation, as stated in section 2.1. A solvent-non solvent interaction approach was used, involving repeated steps of non-polar (acetone or hexane) and polar (ethanol) addition with centrifugation. Capping agent removal was therefore improved by subsequent addition of hexane/ethanol mixtures. Even though extensive amounts of PVP can be separated using typical washing and flocculation techniques, resistant polymer residuals always remain.

Additional to the solvent-non-solvent interaction methodology, different treatments were explored for the removal of PVP from the Pt (PVP)/Beta catalysts. Oxidation (OT) or reduction (RT) treatments were performed exposing the sample to oxygen (20% O₂ in He) or hydrogen (20% H₂ in He) flows. The temperature and time were 473 K and 24 for...
the oxidation treatment and 673 K and 2 h (heating rate 0.5 K/min) for the reduction treatment. Similarly, in cyclic oxidation–reduction [30] treatments (ORT) the samples were calcined on in 20% O\textsubscript{2} in He for 30 min (473 K, rate 0.5 K/min) and purged with pure He, which was then followed by reduction in 20% H\textsubscript{2} in He for 30 min (473 K, rate 0.5 K/min). The procedure was repeated twice (3 cycles in total). A chemical (reduction) treatment [31] (CT) was also employed, involving the use of a NaBH\textsubscript{4} solution in tert-butylamine (TBA). An amount of 6 mg of catalyst was treated with 25 ml of NaBH\textsubscript{4}/TBA solution (molar composition 1 NaBH\textsubscript{4}/1 TBA/1 H\textsubscript{2}O) involving stirring the mixture at room temperature for 30 min. Afterwards, the solids were collected by centrifugation at 8000 rpm for 10 min and washed 3 times with ethanol and acetone to remove the excess surface adsorbed amine. Plasma treatment [32] (PL) was carried out under controlled conditions in an air flow of 9 ml/min and atmospheric pressure using a plasma power of 150 W. The final samples were denoted as Ptx(PVP)/Beta-γ, where x refers to the average Pt particle size as previously stated (1.3, 3, 4, 7, 10 nm) and y to the treatment (OT, RT, ORT, CT, or PL). For the plasma treated samples, the PL suffix is followed by the exposure time (5, 15 or 30 min).

### 2.4. Characterisation

The elemental composition of the solids was determined by ICP-OES (Spectro CirosCCD ICP optical emission spectrometer). For analysis, a

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**Table 1**

Physico-chemical properties of the Pt/Beta zeolites.

| Sample          | SA (m\textsuperscript{2}/g)\textsuperscript{a} | V\textsubscript{mes} (cm\textsuperscript{3}/g)\textsuperscript{b} | BAS, pyridine IR (μmol/g) | BAS, H/D exchange (μmol/g) | Pt (wt %) | Pt dispersion\textsuperscript{a} | Pt dispersion\textsuperscript{b} | Pt particle size (nm)\textsuperscript{b} | Pt particle size (nm)\textsuperscript{c} | S\textsubscript{BET} (m\textsuperscript{2}/g) | n\textsubscript{mol} | n\textsubscript{mol} | Pt\textsubscript{H\textsubscript{2O}} (%) |
|-----------------|-----------------|---------------------|--------------------------|---------------------------|------------|-------------------------------|-------------------------------|-----------------------------------|-----------------------------------|-----------------------------|----------------|----------------|------------------|
| Pt-Beta         | 578             | 0.29                | 186 145 92 85            | 0.46                      | 0.21       | 0.67                          | 0.60                          | 1.7                               | 2.9 ± 0.6                       | 372             | 1.39           |                   |
| Pt1.3 (PVP)/Beta-RT | n.d.           | n.d.                | 13 0 0 0                | 0.31                      | 1.98       | 0.54                          | 0.52                          | 2.1                               | 1.6 ± 0.4                       | 313             | n.d.\textsuperscript{1} |                   |
| Pt3(PVP)/Beta-RT | n.d.            | n.d.                | 30 13 0 0              | 0.50                      | 1.39       | 0.54                          | 0.52                          | 2.1                               | 3.3 ± 0.7                       | 309             | 1.31           |                   |
| Pt4(PVP)/Beta-RT | n.d.            | n.d.                | 47 27 3 18             | 0.53                      | 0.51       | 0.44                          | 0.44                          | 2.6                               | 4.2 ± 0.6                       | 258             | 1.40           |                   |
| Pt7(PVP)/Beta-RT | 486             | 0.25                | 171 110 17 57          | 0.48                      | 0.10       | 0.33                          | 0.34                          | 3.5                               | 7.5 ± 0.3                       | 194             | 1.74           |                   |
| Pt10 (PVP)/Beta-RT | 376            | 0.19                | 169 131 75 71          | 0.51                      | 0.05       | 0.18                          | 0.19                          | 6.8                               | 10.4 ± 0.4                      | 102             | 2.57           |                   |

\textsuperscript{a} Brunauer-Emmett-Teller (BET) surface area (P/P\textsubscript{0} = 0.05–0.25), \textsuperscript{b} micropore and d mesopore volumes calculated by the NLDFT method using the adsorption branch of the isotherm (Ar at 87 K assuming slit pores without regularization), \textsuperscript{c} ratio of Pt surface sites and BAS: Pt surface sites from H\textsubscript{2} chemisorption. H\textsuperscript{+} from IR of adsorbed pyridine at 150 °C: H/ Pt ratio based on H\textsubscript{2} chemisorption and Pt metal loading; \textsuperscript{d} D(%) = -29.2305[H/P\textsubscript{F}]\textsuperscript{5} + 134.64[H/P\textsubscript{F}]\textsuperscript{4} - 201.19[H/P\textsubscript{F}]\textsuperscript{3} + 70.105[H/P\textsubscript{F}]\textsuperscript{2} - 98.61[H/P\textsubscript{F}]\textsuperscript{1} [54]; \textsuperscript{e} From TEM measurements, \textsuperscript{f} 1/d(nm\textsuperscript{-1}) = -0.138[H/P\textsubscript{F}]\textsuperscript{5} + 0.794[H/P\textsubscript{F}]\textsuperscript{4} - 1.469[H/P\textsubscript{F}]\textsuperscript{3} + 0.903[H/P\textsubscript{F}]\textsuperscript{2} + 0.703[H/P\textsubscript{F}]\textsuperscript{1} [54]; \textsuperscript{g} S\textsubscript{BET} (m\textsuperscript{2}/g) = -169.517[H/P\textsubscript{F}]\textsuperscript{5} + 788.76[H/P\textsubscript{F}]\textsuperscript{4} - 1237.54[H/P\textsubscript{F}]\textsuperscript{3} + 617.78[H/P\textsubscript{F}]\textsuperscript{2} + 493.46[H/P\textsubscript{F}]\textsuperscript{1} [54]; \textsuperscript{h} n\textsubscript{mol} = M + 2.5 × B + 4 × C, where M stands for the selectivity of monobranched isomers, B for multibranched isomers, and C for cracking product; \textsuperscript{1} not determined due to low conversion levels.
mixture of concentrated HCl, concentrated HNO₃, HF (11 vol% in water) and water was used to completely dissolve the samples. X-Ray Diffraction (XRD) patterns were recorded on a Brucker D2 Endeavor diffractometer using Cu Kα radiation with a scanning speed of 0.02° s⁻¹ in the 2θ range of 0°–10°. IR spectra were recorded in the range of 4000–400 cm⁻¹ on a Brucker Vertex V70v instrument. Pyridine IR spectra were recorded following adsorption of gaseous pyridine on the reduced Pt/ Beta and Pt(PVP)/Beta-RT samples after initial evacuation under vacuum at 773 K. Spectra were then recorded after evacuation for 1 h at 423 K, 573 K and 773 K. H2/CH4 exchange of hydroxyl groups with deuterated benzene (C₆D₆) was followed in situ IR spectroscopy according to a procedure described in detail before [33]. For this purpose, the cell was filled with 10 mbar C₆D₆ (corresponding to 0.33 mmol C₆D₆). The sample was exposed to this atmosphere for 10 s followed by evacuation for 1 h. The final pressure was lower than 10⁻⁶ mbar. Then, the next spectrum of the partially H/D-exchanged sample was recorded. This sequence was automatically repeated with exposure times of 30 s, 5, 10, 20 and 30 min at 303 K, 30 min at 323 K, 30 min at 353 K, 30 min at 373 K, 30 min at 423 K, and 30 min at 523 K. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha XPS apparatus equipped with a monochromatic small-spot Al Kα X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. The background pressure was 2 × 10⁻⁹ mbar. Samples were prepared by pressing the solids onto carbon film. XPS spectra were analyzed using the CasaXPS program. Transmission electron microscopy (TEM) was done on a FEI Tecnai 20 operated at an acceleration voltage of 200 kV. The samples were suspended in ethanol and dispersed over a holey Cu grid coated with carbon film prior to measurements. H₂ uptake measurements were used to titrate the surface metal atoms and to provide an estimate of the active sites on the catalysts. Usually, 50 mg of sample was loaded in a quartz reactor. Prior to dosing, samples were reduced in flowing H₂ (1 h, 673 K, 3 kbar), evacuated at 723 K for 1 h to remove chemisorbed hydrogen and cooled to 353 K under vacuum. Analysis was then performed at 353 K by collecting an adsorption isotherm to determine the H₂ uptake. Temperature-programmed hydrogenation (THH) experiments were conducted by heating the reactor to 1023 K with a rate of 5 K/min in diluted H₂ flow (10% H₂ in Ar, 50 ml/min in total). The products of hydrogenation (CH₄, CO, propane/acetaldehyde) were monitored by online mass spectrometry (MS) with m/z values of 16, 28 and 44, respectively. Thermogravimetric Analysis (TGA) was performed in a Mettler Toledo analyzer. In a typical experiment, an amount of 25 mg of the catalyst sample was placed in a ceramic crucible followed by heating from 323 to 1023 K at a rate of 5 K/min, in an air flow of 50 ml/min. The weight loss and heat flow were recorded. Adsorption and desorption isotherms were measured at 87 K on a Micromeritics ASAP 2020 instrument. The samples were outgassed at 723 K for 6 h prior to the sorption measurements.

2.5. Catalytic activity measurements

In order to perform n-C₁₆ hydroconversion activity measurements, the catalyst was dried in the reactor at 1 bar and 473 K for 1 h in a He flow and subsequently reduced at 60 bar in a H₂ flow. During reduction, the temperature was increased at a rate of 3 K/min to 673 K followed by an isothermal period of 1 h. Then, the temperature of the catalyst bed was lowered to 473 K and the packed bed was wetted by maintaining a liquid flow rate of 1 ml/min for 10 min (chosen to pass a ten-fold of liquid relative to the catalyst bed volume through the catalyst bed before starting the reaction). The reactor was operated at a H₂/n-hexadecane molar ratio of 20 and a weight hourly space velocity (WHSV) of 10 g C₁₆ g⁻¹ cat. h⁻¹ (100 mg catalyst in a 125–250 μm sieve fraction, liquid flow rate n-C₁₆ 1.52 ml/h). The reaction temperature was increased stepwise and the reaction was equilibrated for 3 h before product sampling. The reactor effluent was analyzed by a gas chromatograph equipped with an RTX-1 column and a flame ionization detector.

3. Results and discussion

Representative TEM images of Pt3(PVP)/Beta zeolites. The degree of capping agent removal was followed in a qualitative manner by XPS. TEM images were taken after each treatment in order to determine its influence on the Pt dispersion. Additionally, the N 1s and C 1s XPS signals can be used to probe PVP and residuals in as-prepared and treated catalysts. For Pt3(PVP)/Beta (Fig. 2), we observed a decreased N 1s XPS signal after the reduction treatment. The N 1s peak located at 399.6 eV can be attributed to nitrogen bound to a carbonyl group, as usually observed in amides [34]. Although the C 1s XPS signal also decreased significantly, it is difficult to use this result in a quantitative manner, as adventitious carbon cannot be avoided. The C 1s peaks at 284.5 eV and 288.3 eV can be assigned to C–C bonds coming from linear and cyclic parts of the amide and from the carbonyl group, respectively [35]. The surface amounts were estimated from the N/Si and C/Si atomic ratios (referenced to the Si 2p peak at 102.9 eV) [36]. The resulting ratios listed in Table S1 indicate that the PVP ligand was only partially decomposed using oxidation and cyclic oxidation–reduction treatments. On the other hand, much lower N/Si and C/Si values were obtained following reduction and plasma treatments. It is observed that an increase of the plasma exposure time from 15 to 30 min does not further reduce the amount of N and C retained at the surface. The CT treatment was also effective as shown for sample Pt4 (PVP)/Beta-CT, but in this case a clear Na 1 s signal (binding energy 1072.4 eV) indicates a contamination from the NaBH₄ treatment.

Figure 3 shows representative TEM images of the zeolites loaded with Pt nanoparticles after the treatments. The samples Pt3(PVP)/Beta-OT and Pt3(PVP)/Beta-RT show clustered particles, which appear to be covered by a layer of carbonaceous material, likely originating from the incomplete decomposition of PVP. Such a layer is absent for the other template removal methods. Pt3(PVP)/Beta-CT shows well-defined Pt particles with a cuboctahedron shape, which is typical for Pt obtained using H₂PtCl₆ in combination with PVP and EG [20,37]. Nevertheless, these particles were agglomerated during the CT treatment. In comparison to the oxidative and CT treatments, clustering of the initially dispersed Pt particles in Pt3(PVP)/Beta was much less pronounced when the samples were pretreated in a reducing gas atmosphere or a plasma treatment. The resulting average particle sizes for the Pt3(PVP)/Beta-RT and Pt3(PVP)/Beta-PL30 were 3.3 ± 0.7 nm, 3.1 ± 0.7 nm (Figure S3), which are close to the diameter of the parent Pt3(PVP)/Beta sample. We also found that the Pt1.3(PVP)/Beta-RT sample displayed a particle size of 1.6 ± 0.4 nm, which is close to the Pt1.3(PVP)/Beta parent (Fig. 1).

We then investigated in more detail the reductive treatment by temperature-programmed hydrogenation (THP) and IR spectroscopy. The gaseous products evolving during TPH were followed by mass spectrometry (Fig. 4). CO is the main product at relatively low temperature, while CH₄ is dominant at higher temperatures. Whereas for most samples CO and CH₄ formation ends at 973 K, the decomposition of the capping agent continues up to 1023 K for samples Pt1.3(PVP)/Beta-RT and Pt3(PVP)/Beta-CT. We observed that the extent of capping agent removal by the RT treatment decreases with increasing PVP content. It is likely that methane obtained at such high temperatures is due to hydrogenation of graphitic coke formed by pyrolysis of PVP. As the final reduction temperature of the RT samples was 673 K, not all residual carbonaceous species will be removed and this especially holds for the samples containing small Pt particles (high PVP content).

IR spectra of the Pt(PVP)/Beta-RT samples are shown in Fig. 5. The IR spectrum of Pt10(PVP)/Beta-RT resembles the one of the reduced Pt/
Beta reference sample prepared by impregnation. In the hydroxyl region, both catalysts show peaks associated with bridging OH groups connected to framework Si and Al atoms (3610 cm\(^{-1}\)) \cite{38,39} and terminal OH groups connected to Si (silanol groups, 3735 cm\(^{-1}\)) \cite{40}. The other samples that contain more PVP display a lower intensity of these hydroxyl groups. The catalyst with the highest PVP content, Pt1.3(PVP)/Beta-RT, presents an additional feature around 3420 cm\(^{-1}\), which can be ascribed to adsorbed ammonia \cite{41}. The features in the 2700–3100 cm\(^{-1}\) region relate to hydrocarbon species. We observe bands related to asymmetric (2960–2965 cm\(^{-1}\)) \cite{42,43} and symmetric (2933 cm\(^{-1}\)) \cite{44} stretching vibrations of CH\(_2\) groups present in linear chains and C–H stretching vibrations (2875–2890 cm\(^{-1}\)) \cite{45}, likely belonging to residual acyclic aliphatic species formed during the decomposition of the linear polymer section of PVP. C–O stretching vibrations related to
carbonyl groups can be observed in the 1665–1680 cm$^{-1}$ region [44]. Signals in the range of 1590–1630 cm$^{-1}$ are attributed to NH$_2$ scissoring vibrations from primary amines [46]. Additional features observed at 1450 cm$^{-1}$ and 1360 cm$^{-1}$ for Pt1.3(PVP)/Beta-RT might relate to CH$_2$ bending and C-N stretching vibrations [42,47].

PVP decomposition is thought to start by opening the ring by a C-N cleavage of the bond with the carbonyl group [46]. This is in line with our observation that the N 1 s signal in XPS spectra decreases pronouncedly with respect to the C 1 s signal. IR peaks in the range of 1590–1630 cm$^{-1}$ reveal the formation of a secondary amine, which is likely further removed by reduction leading to NH$_3$. NH$_3$ can re-adsorb on acid sites forming ammonium. As CO evolves at lower temperatures compared to CH$_4$ according to TPH, we infer that decarbonylation [48] occurs before hydrogenolysis of linear hydrocarbons [49,50].

3.1. Characterization of acid and metal sites

Characterization of the acid sites was performed by IR spectroscopy of pyridine adsorbed at 423 K followed by evacuation at 423 K, 573 K and 773 K (Fig. 6). The sample with the lowest PVP content, Pt10(PVP)/Beta-RT, presents two well-defined bands at 1545 cm$^{-1}$ and 1455 cm$^{-1}$, assigned to pyridine adsorbed on Brønsted acid sites (BAS) and Lewis acid sites (LAS), respectively [51,52]. The band at 1490 cm$^{-1}$ corresponds to a vibrational mode of pyridine adsorbed on both sites. We discuss the evolution of the BAS in more detail given their importance to the hydrocracking reaction.

The data clearly show that the amount of BAS gradually decrease with increasing PVP/Pt ratio used in the preparation. The amount of BAS for Pt10(PVP)/Beta-RT is nearly the same as for the Pt-Beta reference catalyst. All the other samples contain substantially less BAS than the reference, indicating that the residual products of PVP decomposition block the acid sites. It is also observed that especially the strong BAS are affected by this treatment. The Brønsted acidity of the samples decreases in the order Pt-Beta > Pt10(PVP)/Beta-RT > Pt7(PVP)/Beta-RT > Pt4(PVP)/Beta-RT > Pt3(PVP)/Beta-RT > Pt1.3(PVP)/Beta-RT.

The BAS density was also determined by IR spectroscopy of the H/D exchange of these sites with deuterated benzene [33,53]. As an example, Fig. 7 shows the deuteroxyl region of samples Pt1.3(PVP)/Beta-RT and Pt4(PVP)/Beta-RT after different H/D exchange degrees. For Pt1.3(PVP)/Beta-RT, the IR spectra only contain a band at 2752 cm$^{-1}$ due to the H/D exchange of silanol groups. This indicates that this sample contains a very low number of BAS. In comparison, the IR spectra of the Pt4(PVP)/Beta-RT sample shows a band at 2662 cm$^{-1}$ due to bridging OD groups (deuterated BAS), followed by the appearance of a band due
to deuterated silanol groups. Compared to the hydroxyl region of the same sample before H/D exchange (Fig. 5), the H/D exchange method allows to distinguish the band due to bridging OD groups much better.

Following literature, we deconvoluted the OD region of the IR spectra after H/D exchange at 303 K for 1800 s and report the BAS densities in Table 1. Compared to the Pt-Beta reference sample, the Pt10(PVP)/Beta-RT sample contains almost the same amount of BAS. With decreasing particle size and increasing amount of PVP used in the preparation, a strong decrease of the amount of BAS is found. This trend is in qualitative agreement with the pyridine IR results.

The effect of PVP addition on the metallic Pt phase was determined by H\textsubscript{2} chemisorption. H/Pt molar ratios were employed to represent the metal dispersion, considering the total Pt content in the samples and the concentration of irreversibly adsorbed hydrogen (H\textsubscript{irr}), assuming H\textsubscript{irr}/P$_{\text{surface}}$ = 1. We also used the correlations from the work of Le Valant et al. [54,55] to determine metal dispersion, particle size and metal surface area [56]. These two methods gave comparable results. The Pt dispersion was highest for the Pt-Beta reference sample. For the Pt(PVP)/Beta samples, the Pt dispersion decreased with lower PVP content in line with the trends seen for the initial colloidal Pt dispersions. Nevertheless, the Pt particle size based on H\textsubscript{2} chemisorption is lower than expected based on the average Pt particle size determined by TEM. A lower H surface coverage at certain experimental conditions [57] or due to strong metal-support interactions [58] have been cited in the literature as the main reasons for metal particle size underestimation by H\textsubscript{2} chemisorption. The Pt/H\textsuperscript{+} values are in the range between 0.05 and 1.98, which are higher than minimum values for ideal n-C\textsubscript{16} hydrocracking reported by Batalha et al. [7,59] From the observed trends, it is
clear that PVP residuals impact more the BAS concentration than the Pt surface area.

3.2. Catalytic activity measurements

Figure 8 shows n-C<sub>16</sub> conversion as a function of temperature for the reduced Pt(PVP)/Beta-RT and Pt-Beta samples. Overall, we observe a strong relation between the n-C<sub>16</sub> conversion and the concentration of BAS, which is expected when acid-catalyzed reaction steps are controlling the overall bifunctional conversion reaction. Nevertheless, the variations in the concentration of BAS also correlate with the changes in Pt particle size. This dependency is caused by the changing amount of PVP used to vary Pt particle size and which cannot be completely removed. We attribute the decrease in BAS concentration to the decomposition products of PVP that remain on the surface of the zeolite and deactivate BAS. This influence is most pronounced for the Pt1.3 (PVP)/Beta-RT sample, which exhibited a very low n-C<sub>16</sub> conversion at a reaction temperature of 673 K. The strong decrease of the surface area and the micropore volume observed for the PVP-containing samples as compared to Pt-Beta may indicate that part of the zeolite pores are blocked by deposits derived from PVP decomposition (Figure S6). Although it has been reported that coke deposits can lower the hydrocracking performance [60], there is no systematic trend between the changes in the textural properties and the catalytic performance. Apparent activation energies (E<sub>app</sub>) for Pt-Beta and Pt7(PVP)/Beta-RT were 155 kJ/mol and 135 kJ/mol, respectively. Samples with a higher PVP content showed a much higher apparent activation energy, i.e. 327 kJ/mol for Pt3(PVP)/Beta-RT and 328 kJ/mol for Pt4(PVP)/Beta-RT. The Pt10(PVP)/Beta-RT displayed two kinetic regimes, i.e., a low E<sub>app</sub> of 120 kJ/mol in the range of 503–518 K and a much higher value of 361 kJ/mol at higher temperatures. The very high E<sub>app</sub> values point to a limitation different from an elementary reaction step. Most likely, with increasing temperature part of the BAS are freed up by further decomposition of residual compounds and/or desorption of products like ammonia. Based on the reaction data, these processes start at 518 K, which suggests that further decomposition of residual products can explain the high E<sub>app</sub> [61].

The product distributions for the various samples are shown in Fig. 9. Fig. 9a shows the isomers yield as a function of the n-C<sub>16</sub> conversion, while Fig. 9b displays the cracked products distribution at a n-C<sub>16</sub> conversion of ~50%. The main products obtained for Pt10(PVP)/Beta-RT are smaller hydrocarbons with only a small contribution of skeletal isomers of the n-C<sub>16</sub> reactant over the whole conversion range. The cracked products distribution, which is skewed towards C<sub>6</sub>-C<sub>7</sub> products, is characteristic for non-ideal hydrocracking due to an imbalance between acid and metal sites, viz. a too weak hydrogenation function [62]. The observed extensive secondary cracking for the sample is consistent with the lowest Pt/H<sup>+</sup> ratio among the investigated catalysts (Table 1). Following a procedure from literature [7,59], the average number of acid-catalyzed steps occurring during n-hexadecane hydroconversion extrapolated to zero conversion was estimated (n<sub>ac</sub>, x→0, Table 1). In the ideal case, this parameter approaches unity, implying that only monobranched isomers are formed at zero conversion. Higher values represent cases in which di-, tri- and higher branched isomers are formed. To determine this parameter, the amount of monobranched and multibranch isomers and the cracked products distribution were considered. The Pt10(PVP)/Beta-RT sample has a high value of n<sub>ac</sub>, x→0 of 2.57, meaning that on average between 2 and 3 acid-catalyzed steps take place at conditions close to zero conversion. This result is consistent with an imbalance between acid-catalyzed cracking and isomerization, on one hand, and olefin hydrogenation, on the other hand. The other catalysts contain more residuals of PVP decomposition and, thus, a lower BAS concentration. Although the available Pt surface area is lower than to be expected on the Pt particle size, the resulting Pt/H<sup>+</sup> ratios are significantly higher than the Pt/H<sup>+</sup> ratio of Pt10(PVP)/Beta-RT. As a result, the isomer yields of these samples are higher and the n<sub>ac</sub>, x→0 lower. Due to the low activity of Pt1.3(PVP)/Beta-RT, no accurate distribution of cracked products could be determined for this catalyst.

Among the samples, Pt3(PVP)/Beta-RT presents a cracked products distribution close to the distribution expected for ideal hydrocracking [8]. The cracked products distribution for the Pt-Beta reference sample is slightly asymmetric with a maximum at C<sub>6</sub> products. Such a distribution can indicate a slight contribution of secondary cracking. This would be consistent with the substantially lower Pt/H<sup>+</sup> ratio of this sample (0.21) in comparison with that of Pt3(PVP)/Beta-RT (1.39), although both values are usually deemed to be sufficiently large for ideal hydrocracking. Inspection of the cracked products distribution shows a strong correlation between the Pt/H<sup>+</sup> ratio and the skewedness towards C<sub>6</sub> hydrocarbons, viz. a lower Pt/H<sup>+</sup> ratio giving rise to more secondary cracking. This trend is also consistent with the variations in the values of n<sub>ac</sub>, x→0. The isomers yield, on the other hand, does not correlate in the same manner with the Pt/H<sup>+</sup> ratio. While for the Pt(PVP)/Beta-RT catalysts a higher Pt/H<sup>+</sup> ratio leads to more isomers at the same conversion level, the Pt-Beta sample presents the highest isomers yields at all conversion levels despite its intermediate Pt/H<sup>+</sup> ratio. We explain this by the much higher activity due to the highest concentration of BAS in this sample. Therefore, Pt-Beta presents a higher conversion at a specific temperature. As the activation barriers for cracking are higher than those for isomerization, this will lead to a higher isomers yield. This influence of the reaction temperature on the ideal hydrocracking behavior has been detailed before by Thybaut et al. [63]. Accordingly,
we infer that the skewedness of the cracked product distribution and $n_{\text{rel}}$ $x=0$ are better, respectively, qualitative and quantitative indicators of the ideal hydrocracking behavior than the isomers yield at a given conversion level.

4. Conclusions

The effect of PVP addition as capping agent for the synthesis of Pt nanoparticles supported over zeolite Beta on the hydroconversion of n-hexadecane was studied. Although Pt particles in the range between 1.3 and 10 nm were obtained varying the amount of PVP in the starting solution and deposited on Beta zeolite, our attempt to obtain bifunctional catalysts using a colloidal synthesis approach was unsuccessful due to the difficulties of completely removing the capping agent from the precursor solutions or the samples. Among the methods to remove the capping agent, reduction in H$_2$ was the most effective. IR spectroscopy and TPH measurements showed that reductive removal of PVP involved ring opening via C-N cleavage belonging to the carbonyl group, followed by NH$_3$ formation by hydrogenation of the resulting secondary amine as well as CO and CH$_4$ production by decarbonylation and hydrogenolysis of the remaining chains. Although the particle size of the as-prepared samples could be maintained by this method, a small amount of nitrogen- and carbon-containing species remained on the catalyst samples. Further characterization of the acid sites and Pt particles showed that the residual species affected the acid sites much more substantially than the metal function. Although the resulting set of Pt (PVP)/Beta catalysts showed a significant variation in Pt particle size, the catalytic behavior was dominated by the stronger variations in the BAS concentration. Therefore, we cannot unequivocally determine the influence of Pt particle size on the catalytic performance. Catalysts with smaller Pt particles obtained by using more PVP during preparation presented much lower Brønsted acidity than catalysts containing larger Pt particles. Catalysts exhibiting a proper balance between acid and metal sites, i.e., having Pt/H$^+$ values in the range of 0.20–2, displayed ideal cracking behavior in n-C$_{16}$ cracking. On the other hand, the catalyst containing larger Pt particles of 7 and 10 nm contained more acid sites and the consequential imbalance between acid and metal sites (Pt/H$^+$ ratio < 0.2) resulted in extensive secondary cracking. The results show that the Pt/H$^+$ ratio and the number of acid-catalyzed steps extrapolated to zero conversions are better indicators of ideal cracking behavior than the isomers yield.

CRediT authorship contribution statement

Douglas Romero: Methodology, Investigation, Data curation, Formal analysis, Validation, Writing – original draft, Visualization. Freddy Oropeza: Investigation, Formal analysis, Validation. Marcello Rigutto: Conceptualization, Writing – review & editing, Supervision. Emiel J.M. Hensen: Conceptualization, Writing – review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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