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# Effect of citric acid addition on the morphology and activity of Ni<sub>2</sub>P supported on mesoporous zeolite ZSM-5 for the hydrogenation of 4,6-DMDBT and phenanthrene



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#### ABSTRACT

Preparing small, highly dispersed Ni<sub>2</sub>P particles is important for improving the hydrogenation ability of Ni<sub>2</sub>P. Here, Ni<sub>2</sub>P nanoparticles (approximately 4.3 nm) on mesoporous zeolite ZSM-5 (Ni<sub>2</sub>P/MZSM-5-CA) were prepared using citric acid (CA) as an assistant agent. The formation mechanism of small Ni<sub>2</sub>P particles when CA was added was investigated by combining UV–vis diffuse reflectance spectroscopy, Fourier transform infrared spectroscopy, and temperature-programmed reduction with a transmission electron microscope and CO chemisorption. The results indicated that the formed CA–Ni complex with high viscosity favors the Ni precursor dispersed on the dried catalyst. After calcination, the released Ni species strongly interacted with surface acidic hydroxyl groups on MZSM-5, leading to the formation of Ni<sub>2</sub>P particles with small sizes and good dispersion under a reducing atmosphere. The reaction rate constants and TOFs over Ni<sub>2</sub>P/MZSM-5-CA ( $16.2 \times 10^{-2} \, \mu$ mol g<sup>-1</sup> s<sup>-1</sup> and  $9.7 \times 10^{-4} \, s^{-1}$ ) are much higher than over Ni<sub>2</sub>P/MZSM-5 ( $8.2 \times 10^{-2} \, \mu$ mol g<sup>-1</sup> s<sup>-1</sup> and  $8.3 \times 10^{-4} \, s^{-1}$ ) in 4,6-dimethyldibenzothiophene hydrogenation.

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#### 1. Introduction

In recent years, with the reduction of petroleum reservoirs and excessive exploitation, the polyaromatic hydrocarbons and bulky organic sulfur compound content in crude oil are increasing [1–3]. To meet increasingly stringent environmental legislation, the production of ultraclean fuel through a hydrotreatment technique over conventional metal sulfide catalysts must be carried out at a high temperature and high pressure [4–6], which greatly increases the production cost of fuel. This is because metal sulfide catalysts with low hydrogenation activity have difficulty removing refractory sulfur-containing compounds, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), and realizing deep satu-

ration of polyaromatics at low temperature and pressure [7–9]. One solution for this problem is to develop a highly active hydrotreatment catalyst that could achieve deep hydrodesulfurization (HDS) of 4,6-DMDBT [10–12] as well as deep saturation of polyaromatics [13].

Noble metal catalysts, such as Pd [14,15], Pt [16], and Pd–Pt [17,18], exhibit high hydrogenation ability, but their sensitivity to sulfur and high cost limit their industrial application. Numerous studies have shown that nickel phosphide (Ni<sub>2</sub>P) catalysts present high intrinsic hydrogenation activity in HDS reactions [19–21]. In addition, the catalytic performance of the Ni<sub>2</sub>P catalyst is closely connected with its active phase morphology [22–24]. It is reported that there are tetrahedral Ni(1) sites and square pyramidal Ni(2) sites in the Ni<sub>2</sub>P active phase [25–27]. The Ni(1) and Ni(2) sites are responsible for desulfurization and hydrogenation, respectively, and the number of Ni(2) sites increases with the decrease of the Ni<sub>2</sub>P particle size. Therefore, a decrease in the Ni<sub>2</sub>P particle size should increase the hydrogenation active sites and improve the hydrogenation activity.

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An alternative approach to obtaining the Ni<sub>2</sub>P active phase with a small size is to increase the dispersion of Ni<sub>2</sub>P particles using a high-surface-area support [22,27–29]. Oyama et al. reported that, relative to a low-surface-area SiO<sub>2</sub>-supported Ni<sub>2</sub>P catalyst, smaller Ni<sub>2</sub>P crystallites were formed on high-surface-area SiO<sub>2</sub> (SiO<sub>2</sub>–H) and had higher activity and better stability in the 4,6-DMDBT HDS reaction [22]. Furthermore, compared with SiO<sub>2</sub>–H, much smaller Ni<sub>2</sub>P particles were obtained by using higher-surfacearea ordered molecular sieves (MCM-41 or SBA-15) as supports [25,29].

Another recent approach to prepare small crystalline Ni<sub>2</sub>P particles is to strengthen the metal–support interaction by choosing supports with unique surface properties [23,30,31]. For instance, Ni<sub>2</sub>P nanoparticles with very small and good dispersion were formed on mordenite nanosheets (NS-HMOR) or mesoporous zeolite ZSM-5. This is because the large number of acidic hydroxyl groups on zeolites can strongly interact with Ni species, resulting in highly dispersed Ni<sub>2</sub>P nanoparticles, which showed high activity in the HDS of 4,6-DMDBT.

Associated studies have shown that the particle size of the bulk Ni<sub>2</sub>P catalyst can be decreased by adding citric acid (CA) to the preparation solution containing nickel nitrate and diammonium hydrogen phosphate [32–34]. The obtained small Ni<sub>2</sub>P particles with a relatively high external surface area shows better activity in the HDS of the 4,6-DMDBT than the Ni<sub>2</sub>P particles prepared in the absence of CA [33]. Possibly, the formed Ni(II)–CA complexes are able to effectively inhibit metal aggregation [33–35], resulting in a bulk Ni<sub>2</sub>P catalyst with small particle size, exposing more active sites. Thus, it should be practicable to improve the Ni<sub>2</sub>P catalyst with small particles by taking advantage of the special surface properties of mesoporous zeolite and the nature of Ni(II)–CA complexes.

We synthesized mesoporous zeolite ZSM-5 (MZSM-5), which is impregnated with a solution containing nickel nitrate, diammonium hydrogen phosphate, and CA to prepare the Ni<sub>2</sub>P catalyst (Ni<sub>2</sub>P/MZSM-5). After a dried sample was calcined and reduced, small Ni<sub>2</sub>P nanoparticles formed on MZSM-5. The formation mechanism of small Ni<sub>2</sub>P particles by adding CA as well as the effect of the amount of CA on the Ni<sub>2</sub>P nanoparticle size in the catalyst preparation was investigated. In addition, the activity of the Ni<sub>2</sub>P/MZSM-5 catalysts was examined with respect to 4,6-DMDBT HDS and phenanthrene hydrogenation.

#### 2. Experimental

#### 2.1. Catalyst

The mesoporous zeolite ZSM-5 (MZSM-5) was synthesized hydrothermally as described in a previous study [13]. The Ni<sub>2</sub>P catalysts were prepared by incipient wetness impregnation of the MZSM-5 support using an aqueous solution containing the required amounts of diammonium hydrogen phosphate ((NH<sub>4</sub>)<sub>2</sub>-HPO<sub>4</sub>), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), and citric acid (CA). The molar ratio of Ni/P/CA was 1:2:*X* (*X* = 0, 1, 2, and 3), and the Ni loading was 6.0 wt.%. After impregnation, the sample was dried at ambient temperature for 12 h in air and then further dried at 100 °C for 12 h. Subsequently, the dried sample was extruded, crushed and sieved to 20–40 mesh, and calcined at 500 °C for 3 h. The catalysts with different amounts of CA were denoted as Ni<sub>2</sub>P/MZSM-5-CA-X (*X* = 0, 1, 2, and 3), where *X* is the CA/Ni mole ratio.

#### 2.2. Characterization

X-ray diffraction (XRD) measurements were carried out on a RIGAKU UltimalV diffractometer using CuK $\alpha$  radiation

 $(\lambda = 0.154059 \text{ nm})$ . The crystallite size of the passivated catalyst was determined by the line broadening of the most intense peaks at  $2\theta = 40.8^{\circ}$ , using the Scherrer equation,  $Dc = K\lambda/\beta \cos(\theta)$ , where *K* is a constant taken as 0.9,  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the width of the peak at half maximum, and  $2\theta$  is the Bragg angle.

The nitrogen adsorption isotherm was measured at the temperature of liquid nitrogen (-196 °C) on a Micromeritics ASAP 2020 M instrument. Approximately 0.15 g of sample was degassed at 200 °C for 10 h before the measurement. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. The mesopore size distribution was obtained by the Bar rett–Joyner–Halenda (BJH) model using the desorption branch.

Transmission electron microscope (TEM) images were taken on a JEM-2100 and FEI Tecnai G<sup>2</sup> F30 instruments, operating at 200 and 300 kV, respectively. Before the measurement, the sample was cut into thin slices and placed onto a Cu grid coated with a carbon membrane. The size distributions of the Ni<sub>2</sub>P phases were obtained by statistical analyses carried out for at least 10 images of 200–300 Ni<sub>2</sub>P particles from different regions of each catalyst. The average Ni<sub>2</sub>P particle size ( $D_{aver}$ ) was calculated according to the equation

$$D_{aver} = \frac{\sum_{i=1}^{n} d_i}{n_i},$$

where  $n_i$  is the number of Ni<sub>2</sub>P particles and  $d_i$  is the size of each Ni<sub>2</sub>P particle.

The ultraviolet–visible (UV–vis) absorption was obtained on a Shimadzu UV-3600 spectrometer. The UV–vis spectrum of the nickel (II) species in the impregnation solution was recorded in the wavelength range 300–1000 nm using 1 cm quartz cells. The UV–vis diffuse reflectance spectrum (DRS) in the range 240–800 nm was also obtained, using BaSO<sub>4</sub> as a reference. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet iS50 instrument. The data were acquired using 16 scans and a resolution of 4 cm<sup>-1</sup>. The speciation diagrams of the Ni(II)–CA species in solutions were predicted and plotted using Medusa software [36].

The amount of residual carbon on the calcined catalysts was measured by a carbon/sulfur analyzer (LECO CS844). Before measurement, the carbon/sulfur analyzer was calibrated by a standard sample. A temperature-programmed reduction (TPR) experiment was carried out on a Micromeritics AutoChem II 2920 automatic analyzer equipped with a thermal conductivity detector (TCD). The calcined sample (60 mg) was reduced under a stream of H<sub>2</sub>-Ar gas mixture (10 vol.% H<sub>2</sub> at a flow rate of 50 mL/min), with a heating rate of 15 °C/min up to 930 °C. To examine the acidity of the support and catalysts, ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) was performed on the same instrument, as described elsewhere [31].

Dynamic CO pulsed chemisorption was also performed on a Micromeritics ASAP 2920 automatic analyzer equipped with a TCD. The passivated catalyst sample (0.06 g, maintained at room temperature for 3 h in 0.5 wt.%  $O_2/N_2$ ) was loaded into a quartz reactor and reduced in H<sub>2</sub> flow (99.999%, 100 mL/min STP) at 500 °C for 2 h with a ramp of 10 °C/min. Then the sample was purged with He (99.999%, 50 mL/min STP) at 500 °C for 2 h and cooled to 35 °C under a He flow. The CO pulse was repeatedly injected until the response from the detector showed no further CO uptake after consecutive injections [31].

The X-ray photoelectron spectroscopic (XPS) experiment was carried out on an ESCALAB MK II instrument. Before XPS characterization, the freshly reduced Ni<sub>2</sub>P catalyst under a H<sub>2</sub> stream was transferred into a bottle filled with cyclohexane at room temperature. The cyclohexane was removed, and the residual catalyst was quickly moved to the sample holder before being loaded into the XPS chamber.

#### 2.3. Activity test

The synthesized Ni<sub>2</sub>P catalyst was tested in a stainless steel fixed-bed continuous-flow reactor. For the HDS of 4,6-DMDBT, the calcined and screened 0.05 g catalyst (20-40 mesh) was fully mixed with silicon carbide (20-40 mesh, 2.0 g) and loaded into the fixed-bed reactor. Then the precursor of the catalyst was converted to the active Ni<sub>2</sub>P phase by the TPR method in H<sub>2</sub> at a flow rate of 160 mL/min. The detailed activation process was as follows: the catalyst bed was heated to 120 °C at 10 °C/min and maintained for 1 h at this temperature, and then further heated to 400 °C at 5 °C/min and from 400 to 550 °C at 2.5 °C/min; then the temperature was maintained at 550 °C for 3 h. Finally, the HDS experiments were performed at a temperature of 300 °C, a pressure of 5.0 MPa, a weight hourly space velocity (WHSV) of 75.0  $h^{-1}$ , a H<sub>2</sub> flow of 60 mL/min, and a liquid feed of 0.5 wt.% 4,6-DMDBT in decalin. The intrinsic HDS activity of the catalyst was also investigated after the effects of mass transfer were eliminated by the Weisz-Prater  $(C_{WP})$  and Mears criteria  $(C_M)$  [37]. The detailed experimental process and reaction conditions, as well as the calculations, are presented in Supplementary Material. The catalytic HDS rate constants  $(k_{HDS})$  and HDS turnover frequencies of 4,6-DMDBT  $(TOF, s^{-1})$  were obtained by the two equations [6,38]

$$k_{\text{HDS}} = \frac{F}{W} \ln\left(\frac{1}{1-x}\right),$$
$$\text{TOF} = \frac{F \times x}{W \times M}$$

where *x* is the conversion of the 4,6-DMDBT (%), *F* is the molar feed rate of the 4,6-DMDBT ( $\mu$ mol s<sup>-1</sup>), *W* is the catalyst mass (g), *k*<sub>HDS</sub> is the HDS rate constant ( $\mu$ mol g<sup>-1</sup> s<sup>-1</sup>), and *M* is the number of mole of loaded sites, which was determined by the CO uptake.

In addition, a phenanthrene (PHE) hydrogenation experiment was performed as follows: The calcined and screened catalyst (0.2 g, 20–40 mesh) was diluted with silicon carbide (1.5 g, 20–40 mesh) before being loaded into the fixed-bed reactor. The activation of the catalyst was the same as described above. The hydrogenation reaction conditions were as follows: a temperature of 260 °C, a total pressure of 5.0 MPa, a H<sub>2</sub> flow of 60 mL/min, a WHSV of 21.0 h<sup>-1</sup>, and 1.0 wt.% PHE in decalin. The reaction product was collected and analyzed using an offline Agilent 7890B GC installed with a flame ionization detector.

#### 3. Results and discussions

#### 3.1. General characterization

Fig. 1a gives the XRD pattern of the synthesized MZSM-5, which displays typical diffraction peaks in the range from  $5^{\circ}$  to  $50^{\circ}$ , consistent with the MFI structure. The N<sub>2</sub> sorption isotherm of MZSM-5 in powder form, as shown in Fig. 1b, shows a hysteresis loop at a relative pressure of 0.45–0.96 due to the introduction of a mesoporous structure. Correspondingly, the mesopore size distribution of the MZSM-5 is mainly centered at 21 nm (inset in Fig. 1b). The mesopore size is in good agreement with the TEM results of the ultrathin section MZSM-5, providing direct evidence for the successful introduction of a sufficient number of hierarchical mesopores into the crystals (Fig. 2). These nanoporous channels can reduce the diffusion limitation on the mass transfer of the bulky molecules. The detailed textural properties of the supports and corresponding catalysts are listed in Table 1. The synthesized



**Fig. 1.** (a) XRD pattern and (b)  $N_2$  adsorption isotherms of the MZSM-5 sample (inset, mesoporous size distribution of the sample).



Fig. 2. TEM image of the sectioned thin MZSM-5 sample.

MZSM-5 specific surface area is 429 m<sup>2</sup>/g, the external surface area is 193 m<sup>2</sup>/g, and the mesoporous volume is 0.43 m<sup>3</sup>/g. After loading of Ni<sub>2</sub>P precursors and carrying out the reduction, the MZSM-5-supported Ni<sub>2</sub>P catalysts show a decrease in textural parameters compared with the MZSM-5 support. It is worth noting that there are no significant differences in the textural properties for the

Table	1

The textural and acidic properties of the samples.

Sample	$S_{\text{BET}} (m^2/g)^{\text{a}}$	$V_{\rm micro} (\rm cm^3/g)^b$	$V_{\rm meso}~({\rm cm}^3/{\rm g})^{\rm c}$	$S_{\rm mic} \left( m^2/g \right)^{\rm d}$	$S_{\rm ext} \left( m^2/g \right)^{\rm e}$	Acidic amounts (µmol/g)
MZSM-5 <sup>f</sup>	429	0.10	0.43	236	193	176
MZSM-5	365	0.08	0.27	193	172	-
Ni <sub>2</sub> P/MZSM-5-CA-0	261	0.05	0.36	113	148	160
Ni <sub>2</sub> P/MZSM-5-CA-1	258	0.05	0.39	109	148	143
Ni <sub>2</sub> P/MZSM-5-CA-2	262	0.05	0.37	115	146	120
Ni <sub>2</sub> P/MZSM-5-CA-3	259	0.05	0.39	112	147	114

<sup>a</sup> BET surface area.

<sup>b</sup> Microporous pore volume, obtained from the *t*-plot method.

<sup>c</sup> Mesoporous pore volume obtained from the *t*-plot method.

<sup>d</sup> Microporous surface area.

<sup>°</sup> External surface area obtained from the *t*-plot method.

<sup>f</sup> The sample was in powder form, and other samples were formed into tablets at a pressure of 10 MPa.

MZSM-5-supported  $Ni_2P$  catalyst with different CA/Ni ratios, suggesting that the CA addition and its amount have little influence on the textural properties of the catalyst.

The XRD results of the passivated Ni<sub>2</sub>P/MZSM-5-CA-*X* (X = 0, 1, 2, and 3) samples are shown in Fig. 3. A typical peak at 40.7 associated with the Ni<sub>2</sub>P phase (PDF: 03-0953) was detected, demonstrating that the Ni<sub>2</sub>P active phases were formed on Ni<sub>2</sub>P/MZSM-5-CA-*X* (X = 0, 1, 2, and 3) catalysts. This peak at 40.7 is broadened with increasing CA/Ni mole ratios, suggesting that relatively smaller Ni<sub>2</sub>P particles could be formed with an increase in the CA/Ni mole ratio. Analysis of the Ni<sub>2</sub>P phase size calculated by the Scherrer equation suggests that the particle size of the Ni<sub>2</sub>P active phase is decreased with an increasing CA/Ni ratio, from 9.0 to 8.2, to 6.9, and then to 6.8 nm (Table 2). There is no significant decrease in the size of Ni<sub>2</sub>P particles as the CA/Ni mole ratio is up to 3 (6.8 nm). Therefore, it can be concluded that the CA addition in the impregnation solution plays an essential role in the formation of smaller Ni<sub>2</sub>P nanoparticles.

Fig. 4 shows the TEM images of the reduced Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, 2, and 3) samples, giving information about the particle size and dispersion of the Ni<sub>2</sub>P active phase. Compared with the Ni<sub>2</sub>P/MZSM-5-CA-0 sample (Fig. 4a), much smaller Ni<sub>2</sub>P particles were formed on Ni<sub>2</sub>P/MZSM-5-CA-X (X = 2, 3) samples (Fig. 4c and d), suggesting that adding the CA to the impregnation solution resulted in the formation of Ni<sub>2</sub>P particles with small sizes. To insight into the fact that whether the nickel species are inside of the micropores of MZSM-5, the mesopore-free zeolite ZSM-5-supported Ni<sub>2</sub>P (Ni<sub>2</sub>P/ZSM-5) catalyst in the presence of CA was prepared and characterized by TEM imaging and energy-dispersive X-ray spectroscopy (EDX). It is clear that micropore



Fig. 3. XRD patterns of the (a)  $Ni_2P$  (PDF: 03-0953), (b)  $Ni_2P/MZSM-5$ -CA-0, (c)  $Ni_2P/MZSM$ -5-CA-1, (d)  $Ni_2P/MZSM$ -5-CA-2, and (e)  $Ni_2P/MZSM$ -5-CA-3 samples.

structures are observed (Fig. S1 in the Supplementary Material). The EDX elemental mapping analysis suggests that some Ni and P species are present besides the Si, Al, and O in the selected zone (Fig. S2), and the Ni and P content is 0.33 and 0.08 wt.% (Table S1), respectively. These results demonstrate that Ni and P species existed in the micropore channels of ZSM-5, indicating that Ni species could be inside MZSM-5 micropores, and not all Ni species are Ni<sub>2</sub>P on the external surface of zeolite crystals. Meanwhile, the micropore volume of the  $Ni_2P/MZSM$ -5-CA-X (X = 0, 1, 2, and 3) catalysts is also decreased relative to that of the MZSM-5 support, suggesting that some Ni and P species can migrate into the MZSM-5 micropore channels during the catalyst preparation. The highresolution TEM image of Ni<sub>2</sub>P/MZSM-5-CA-2 shows that the Ni<sub>2</sub>P particles with a visible lattice spacing of approximately 0.22 nm are consistent with the {111} crystallographic planes of Ni<sub>2</sub>P, which have a *d*-spacing value of 0.221 nm (Fig. S3). The size distribution of the Ni<sub>2</sub>P particles was also analyzed by statistics method, and the results are shown in Fig. 5. The Ni<sub>2</sub>P particle size on the Ni<sub>2</sub>P/MZSM-5-CA-0 catalyst ranges from 3 to 18 nm (Fig. 5a), while that on Ni<sub>2</sub>P/MZSM-5-CA-X (X = 2, 3) samples are mainly 2–7 nm (Fig. 5c and d). The calculated average sizes of the Ni<sub>2</sub>P particle on these samples decrease as follows: Ni<sub>2</sub>P/MZSM-5-CA-0  $(8.3 \text{ nm}) > \text{Ni}_2\text{P}/\text{MZSM-5-CA-1}$  $(7.1 \text{ nm}) > Ni_2P/MZSM-5-CA-2$  $(4.5 \text{ nm}) \approx \text{Ni}_2\text{P}/\text{MZSM-5-CA-3}$  (4.3 nm), which is in good agreement with the XRD analysis results.

Generally, small Ni<sub>2</sub>P particles with good dispersion could provide a large number of active sites in the hydrotreatment reaction, which can be determined by the CO chemisorption method [39,40]. Table 2 presents the CO chemisorption results of the reduced Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, 2, 3) samples. Clearly, Ni<sub>2</sub>P/MZSM-5-CA-2 (146 µmol/g) and Ni<sub>2</sub>P/MZSM-5-CA-3 (147 µmol/g), with similar Ni<sub>2</sub>P particle sizes, have much higher CO uptake values than those of Ni<sub>2</sub>P/MZSM-5-CA-0 (93 µmol/g) and Ni<sub>2</sub>P/MZSM-5-CA-1 (118 µmol/g). This result further confirms that adding CA to the impregnation solution for the catalyst preparation can favor the formation of small Ni<sub>2</sub>P particles, leading to the exposure of more active sites.

The acidity of the MZSM-5 support and reduced Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, 2 and 3) samples was measured by NH<sub>3</sub>-TPD experiments, and these results are exhibited in Fig. 6 and Table 1. The NH<sub>3</sub> desorption profiles in the range of 300–450 °C were observed for MZSM-5 and its supported catalysts, which correspond to the desorbed NH<sub>3</sub> in interaction with the strong acidic sites [41]. After the introduction of Ni and P species and reduction, the number of acidic sites of 176 µmol/g for MZSM-5 was decreased to 160 µmol/g for the Ni<sub>2</sub>P/MZSM-5-CA-0, which was due to the Ni species interacting with the acidic hydroxyl groups on MZSM-5; this is discussed in detail in our previous work [31]. When Ni and P species are introduced onto MZSM-5 by adding CA, the number of acidic sites on the reduced catalysts was further decreased. The numbers

Table 2
The Ni <sub>2</sub> P particle size, CO uptake, and carbon content of the samples

Sample	$D_c (nm)^a$	$D_{\rm aver.}  (\rm nm)^{\rm b}$	CO uptake (µmol/g)	Residual carbon (%) <sup>c</sup>
Ni <sub>2</sub> P/MZSM-5-CA-0	9.0	8.3	93	-
Ni <sub>2</sub> P/MZSM-5-CA-1	8.2	7.1	118	0.171
Ni <sub>2</sub> P/MZSM-5-CA-2	6.9	4.5	146	0.196
Ni <sub>2</sub> P/MZSM-5-CA-3	6.8	4.3	147	0.253

<sup>a</sup> Determined by the Scherrer equation.

<sup>b</sup> Obtained by statistical analyses of the TEM images.

<sup>6</sup> Calcined supported Ni<sub>2</sub>P catalysts.



Fig. 4. TEM images of the reduced (a) Ni<sub>2</sub>P/MZSM-5-CA-0, (b) Ni<sub>2</sub>P/MZSM-5-CA-1, (c) Ni<sub>2</sub>P/MZSM-5-CA-2, and (d) Ni<sub>2</sub>P/MZSM-5-CA-3 samples.

of acidic sites on MZSM-5, Ni<sub>2</sub>P/MZSM-5-CA-0, Ni<sub>2</sub>P/MZSM-5-CA-1, Ni<sub>2</sub>P/MZSM-5-CA-2, and Ni<sub>2</sub>P/MZSM-5-CA-3 are 176, 160, 143, 120, and 114  $\mu$ mol/g, respectively. These results indicate that adding CA to the catalyst impregnation solution can favor the Ni species interaction with MZSM-5 through the surface acidic hydroxyl groups.

The state of the Ni and P species on the freshly reduced Ni<sub>2</sub>P catalysts was analyzed by the XPS technique, and the spectrum and the surface atom ratio on the catalyst are shown in Fig. 7 and Table 3, respectively. As reported in the literature [28,38,42], Ni and P species in the Ni<sub>2</sub>P phase can exist as Ni<sup>δ+</sup> (0 <  $\delta$  < 1) and P<sup>δ-</sup> (0 <  $\delta$  < 1), which correspond to binding energies of 852.5 to 853.4 eV and 129.2 to 129.5 eV, respectively. In our case, the Ni2p peak with a binding energy of 852.4 eV and a P2p peak with binding energy of 129.2 eV suggested that the Ni<sub>2</sub>P active phase was formed on both the reduced Ni<sub>2</sub>P/MZSM-5-CA-0 and Ni<sub>2</sub>P/ MZSM-5-CA-2 catalysts. In addition, a small peak with binding energy of 855.5 eV on both the samples was corresponding to the Ni<sup>2+</sup> species, along with satellite peaks at approximately 6.0 eV above the Ni<sup>2+</sup> species, which may be due to the oxidation in the process of sample transfer [27]. Meanwhile, broad peaks were detected for the P2*p* XPS spectra on the two samples (Fig. 7), which could involve the contributions of both  $PO_4^{3-}$  and  $H_2PO_3^{-}$  species [27,38], respectively. The surface atom ratio on both of the catalysts shows a high P/Ni ratio on reduced Ni<sub>2</sub>P/MZSM-5-CA-0 (4.03) and Ni<sub>2</sub>P/MZSM-5-CA-2 (3.70) catalysts, which means that most P species were enriched on the catalyst surface. Ni<sub>2</sub>P/MZSM-5-CA-2 shows a higher Ni (or P)/(Si + Al) ratio (0.041 or 0.16) compared with the Ni<sub>2</sub>P/MZSM-5-CA-0 (0.032 or 0.13), which may be because more of the Ni<sub>2</sub>P active phase was dispersed on the external surface as CA was added.

#### 3.2. Ni(II)-CA structure identification in the impregnation solution

Generally, the complex structure of Ni(II)–CA depends on the parameters of Ni species concentration, CA concentration, and



Fig. 5. The size distributions of Ni<sub>2</sub>P particles on reduced (a) Ni<sub>2</sub>P/MZSM-5-CA-0, (b) Ni<sub>2</sub>P/MZSM-5-CA-1, (c) Ni<sub>2</sub>P/MZSM-5-CA-2, and (d) Ni<sub>2</sub>P/MZSM-5-CA-3 samples.



Fig. 6.  $\rm NH_3-TPD$  profiles of the (a) MZSM-5 support and the reduced (b)  $\rm Ni_2P/MZSM-5-CA-0,$  (c)  $\rm Ni_2P/MZSM-5-CA-1,$  (d)  $\rm Ni_2P/MZSM-5-CA-2,$  and (e)  $\rm Ni_2P/MZSM-5-CA-3$  samples.

the pH value of the solution [36,4]. In the present work, the Ni species concentration is 0.716 M, and the pH value is approximately 3.6–4.1 for the employed impregnation solution. In this case, the

speciation diagram of the Ni(II)–CA species in solutions was predicted using Medusa software, and the results are shown in Fig. 8. When the CA/Ni ratio in the impregnation solution was 1, the Ni(II)–CA structure was Ni(cit)<sup>–</sup>; when the CA/Ni ratio in the impregnation solution was 2 or 3, the Ni(II)–CA structures were the same as each other, Ni(Hcit)(cit)<sup>3–</sup>.

To confirm the prediction of Ni(II)-CA complex structure, impregnation solutions with different CA/Ni ratios were analyzed by UV-vis and FT-IR spectroscopy. Fig. 9 shows the UV-vis spectra of the impregnation solution with CA/Ni ratios of 0, 1, 2, and 3. Generally, the absorption bands at 390-400 and 650-750 nm, corresponding to the two spin-allowed  $3A_{2g} \rightarrow 3T_{1g}$  (P) and  $3A_{2g} \rightarrow$ 3T<sub>1g</sub> (F) transitions, are assigned to the octahedral nickel species in aqueous solution [43]. In this work, the impregnation solution without CA shows two absorption bands at 397 and 650-750 nm (Fig. 9a), typical of Ni (II) ions in an octahedral coordination of  $[Ni(H_2O)_6]^{2+}$ . When the impregnation solution contains CA, a blue-shift phenomenon is observed, indicating that the Ni(II)-CA complex is formed in the aqueous solution (Fig. 9b-d) [5,43]. For example, when the CA/Ni ratio in solution is 1, 2, and 3, the absorption band at 397 nm shifts to 392, 390, and 390 nm, respectively, which could be due to the replacement of the H<sub>2</sub>O in [Ni  $(H_2O)_6]^{2+}$  by CA. These results suggest that the structure of the Ni(II)-CA complex is associated with the CA/Ni ratio in the



Fig. 7. The XPS spectra of (a) Ni 2p and (b) P 2p in the reduced Ni\_2P/MZSM-5-CA-0 and Ni\_2P/MZSM-5-CA-2 samples.

impregnation solution. In addition, the same structured Ni(II)-CA complex should be formed at CA/Ni ratios of 2 and 3 in the solution. The suggestion is further confirmed by the FT-IR spectra of the impregnation solution with different CA/Ni ratios, and the results are shown in Fig. 10. There are three absorption bands at 1636, 1400, and 1385 cm<sup>-1</sup> observed on all samples, which corresponding to the vibration of H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>, respectively [44– 46]. When CA was added into the impregnation solution, two other absorption bands at 1730 and 1571 cm<sup>-1</sup> appear, which are assigned to the vibration of the nondissociated carboxyl group in CA and the symmetric vibration of COO<sup>-</sup> in the Ni(II)–CA complex, respectively [45]. It is found that the absorption intensity at 1730 cm<sup>-1</sup> is much stronger for the impregnation solution with a CA/Ni ratio of 2 or 3 than for that with a CA/Ni ratio of 1. These results suggest that the formed Ni(II)-CA complexes at CA/Ni ratios of 2 and 3 have more residual nondissociated carboxyl groups than those with a CA/Ni ratio of 1, indicating that the CA/Ni ratio in impregnation affects the Ni(II)-CA complex structure.

Based on the UV–vis and FT-IR results, as well as the prediction from Fig. 8, the proposed structure of Ni(II)–CA complexes in the impregnation solution are shown in Fig. 11. At a CA/Ni ratio of 1, the structure of the Ni(cit)<sup>–</sup> complex shows that Ni<sup>2+</sup> ions are complexed with CA via three carboxyl groups and one hydroxyl group, as well as two H<sub>2</sub>O molecules (Fig. 11b). At CA/Ni ratios of 2 or 3, four carboxyl groups and two hydroxyl groups of the two CA molecules involve with the coordination of Ni<sup>2+</sup> species to form Ni(Hcit) (cit)<sup>3–</sup> complex, remaining uncoordinated carboxyl groups (Fig. 11c).

#### 3.3. Ni(II)-CA structure identification on the dried catalyst

After impregnating the MZSM-5 support with a solution containing Ni, P, and CA, the dried samples were also analyzed by FT-IR and UV-vis spectroscopy and the results are shown in Fig. 12. In contrast to the FT-IR spectra of impregnation solutions with different CA/Ni ratios, similar results are obtained on these dried  $Ni_2P/MZSM$ -5-CA-X (X = 0, 1, 2, and 3) catalyst samples (Fig. 12a). The absorption bands at 1634, 1402, and 1383  $cm^{-1}$ for all the samples are assigned to the vibration of H<sub>2</sub>O, NO<sub>3</sub>, and  $PO_4^{3-}$ , respectively [44–46]. After CA is introduced, two absorption bands at 1726 and 1575 cm<sup>-1</sup> appear, which correspond to the vibration of the nondissociated carboxyl group in CA and the symmetric vibration of COO<sup>-</sup> in the Ni(II)-CA complex, respectively [45]. It is notable that a very low absorption intensity at 1726 cm<sup>-1</sup> in the dried Ni<sub>2</sub>P/MZSM-5-CA-1 sample indicates that most carboxyl groups in CA were involved with the formation of the Ni(II)-CA complex. In contrast, a relatively high absorption intensity at 1726 cm<sup>-1</sup> in the Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/ MZSM-5-CA-3 samples suggests that besides the coordinated carboxyl groups, many residual carboxyl groups are nondissociated from the Ni(II)–CA complex or CA. These results indicate that Ni (II)-CA complexes with different structures may be formed on the MZSM-5 surface due to the change in CA/Ni ratio in impregnation solutions. This suggestion is further supported by the analysis of UV-vis spectra for the dried  $Ni_2P/MZSM$ -5-CA-X (X = 0, 1, 2, and 3) samples (Fig. 12b). The band at 409 nm for the dried  $Ni_2P/$ MZSM-5-CA-0 sample shifts to low wavelengths at 403, 397, and 397 nm for the dried  $Ni_2P/MZSM$ -5-CA-X (X = 1, 2, and 3) samples, respectively. Combined the FT-IR and UV-vis results, it could be suggested that the Ni(II)-CA complex on the dried Ni<sub>2</sub>P/MZSM-5-CA-1 sample is mainly in the form of Ni(cit)<sup>-</sup>, while on the dried Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/MZSM-5-CA-3, samples are dominantly in the form of Ni(Hcit)(cit)<sup>3-</sup>.

#### 3.4. Discussion of small Ni<sub>2</sub>P particle formation

## 3.4.1. Facilitation of the formation of small $\text{Ni}_2\text{P}$ particles by CA addition

CA addition plays an important role in the preparation of small Ni<sub>2</sub>P particles on the MZSM-5 support. It has been reported that when aqueous chelated metal complexes are utilized to prepare supported metal catalysts, a metal complex film with a high viscosity can be formed on the support surface, which can greatly restrict the aggregation of metal species [33,34]. In this work, the formed

Table	3
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The XPS analysis results of the reduced  $Ni_2P/MZSM\mathchar`s\mbox{-}5\mbox{-}CA\mbox{-}0$  and  $Ni_2P/MZSM\mbox{-}5\mbox{-}CA\mbox{-}2$  samples.

Catalysts	Ni2p <sub>3/2</sub> (binding	g energy) <sup>a</sup>	$P2p_{3/2}$ (binding energy) <sup>a</sup>			Superficial atomic ratio		
	Ni <sup>2+</sup>	Ni <sub>2</sub> P	$PO_4^{3-}$	$H_2PO_3^-$	Ni <sub>2</sub> P	P/Ni	Ni/(Si + Al)	P/(Si + Al)
Ni <sub>2</sub> P/MZSM-5-CA-0	855.3 (33.8)	852.4 (66.2)	134.5 (47.8)	133.4 (45.0)	129.2 (7.2)	4.03	0.032	0.13
Ni <sub>2</sub> P/MZSM-5-CA-2	855.7 (39.4)	852.3 (60.6)	134.7 (48.5)	133.7 (42.8)	129.2 (8.7)	3.67	0.041	0.16

<sup>a</sup> The data in parentheses are atom percentages.



**Fig. 8.** Predominance area diagrams for aqueous Ni(II)–CA solution. [Ni(II)] aq = 0.716 M. Dotted lines correspond to CA concentrations for (a) CA/Ni(II) = 1, (b) CA/Ni(II) = 2, and (c) CA/Ni(II) = 3 used in the present work.



Fig. 9. UV-vis spectra of the impregnation solution with different CA/Ni molar ratios.

Ni(II)–CA complex could favor the Ni species being highly dispersed on the mesopore surface and on the outer surface of MZSM-5, preventing the aggregation of Ni species compared with that without CA addition during the catalyst preparation process.

During the calcination of the dried catalyst, the Ni(II)–CA complexes on the MZSM-5 surface are gradually decomposed (Fig. S4 in the Supplementary Material), and the released Ni species may be able to interact with acidic hydroxyl groups on the zeolite surface [31]. As discussed in the NH<sub>3</sub>-TPD characterization, the acidic sites on the reduced Ni<sub>2</sub>P/MZSM-5-CA-*X* (X = 0, 1, 2, and 3) catalysts are decreased compared with those on the MZSM-5 support. These results indicate that CA addition favors the Ni species interacting with acidic hydroxyl groups on the MZSM-5, and the formed Ni<sub>2</sub>P active phase can cover the acidic sites.

The TPR results confirm the strong interactions between Ni species and the MZSM-5. Fig. 13 gives the TPR curves of the calcined Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, 2, and 3) samples. For the reduction profile of the calcined Ni<sub>2</sub>P/MZSM-5-CA-0 sample, the temperature



Fig. 10. FT-IR spectra of the impregnation solution with different CA/Ni molar ratios.

peaks at 669 °C and 785 °C are assigned to the reduction of Ni and P species, respectively [31]. The temperature peak of the Ni species shifted from 669 °C to 705, 719, and 719 °C, respectively, for calcined Ni<sub>2</sub>P/MZSM-5-CA-X (X = 1, 2, 3) samples. These results prove that the Ni-support interaction became stronger with the increase in the amount of CA addition to benefit the dispersion of the Ni<sub>2</sub>P active phase on MZSM-5, which is supported by the XRD, TEM, and CO uptake results as discussed above. In addition, the temperature interval of the reduction peaks of the Ni and P species decreased from 116 °C for Ni<sub>2</sub>P/MZSM-5-0 to 62 °C for Ni<sub>2</sub>P/MZSM-5-CA-1 and disappeared for  $Ni_2P/MZSM-5-CA-X$  (X = 2, 3). The transformation of the oxide precursors into phosphides begins with the reduction of nickel oxide reduction; then the formed Ni assists the production of volatile phosphorus species and the formation of the nickel phosphide phases [47]. Therefore, the CA-added Ni<sub>2</sub>P catalyst with a small reduction-peak interval could enable the reaction between the Ni species and the reduced P species in a timely manner to form relatively small Ni<sub>2</sub>P nanoparticles. The strengthened interaction of Ni with MZSM-5 inducing the highly dispersed small Ni<sub>2</sub>P particles is in agreement with the XRD analysis results and the TEM observations, as discussed above. The Ni<sub>2</sub>P particle sizes are 9.0, 8.2, 6.9, and 6.8 nm on Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, 2, and 3) by XRD analysis, and the values for those samples are 8.3, 7.1, 4.5, and 4.3 nm, when statistically calculated based on the TEM images.

## 3.4.2. Effect of the different Ni(II)–CA structures on the Ni<sub>2</sub>P particle size

As discussed above, the different Ni(II)–CA structures, Ni(cit)<sup>–</sup> and Ni(Hcit)(cit)<sup>3–</sup>, can be formed by changing the CA/Ni ratios and the pH values in the impregnation solution, which may change the interaction between Ni species and MZSM-5 support. In contrast to Ni(cit)<sup>–</sup>, the Ni(Hcit)(cit)<sup>3–</sup> complex has remaining carboxyl groups, which benefit the formation of a relatively strong interaction between surface hydroxyl groups of zeolite and carboxyl groups in Ni(Hcit)(cit)<sup>3–</sup> via hydrogen bond (Fig. S5 in the Supplementary Material) [48]. In this manner, relatively small Ni<sub>2</sub>P particles could be formed after the catalyst calcination and reduction. For instance, when the CA/Ni ratio is 1, the interaction of the Ni(cit)<sup>–</sup> complex with the zeolite is relatively weak, resulting in a Ni<sub>2</sub>P active phase with average particle size 7.1 nm on the Ni<sub>2</sub>P/MZSM-5-CA-1 catalyst. In contrast, when the CA/Ni ratio is 2 or 3, the interaction of the Ni(Hcit)(cit)<sup>3–</sup> complex with the zeo-



Fig. 11. Molecule structure of the (a) citric acid and the Ni(II)-CA complexes of (b) Ni(cit)<sup>-</sup> and (c) Ni(Hcit)(cit)<sup>3-</sup>. The hydrogen atom was hidden.



**Fig. 12.** The FT-IR (a) and UV-vis (b) spectra of the dried samples of  $Ni_2P/MZSM-5-CA-X$  (X = 0, 1, 2, and 3).

lite is relatively strong, resulting in a Ni<sub>2</sub>P active phase with average particle size 4.3–4.5 nm on the Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/MZSM-5-CA-3 catalysts. It is mentioned above that the reduction temperature of Ni species on the Ni<sub>2</sub>P/MZSM-5-CA-1 sample is 705 °C, lower than those of 719 and 719 °C on Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/MZSM-5-CA-3 (Fig. 13), suggesting that a relatively strong Ni–support interaction exists in Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/MZSM-5-CA-3.

# 3.4.3. Effect of the residual carbon in the catalyst on the formation of $Ni_2P$ particles

It is reported that the when CA was used as a chelating agent to prepare the bulk metal phosphide (Ni<sub>2</sub>P, MoP) catalyst, the unde-



Fig. 13.  $H_2$  TPR profiles of the calcined (a)  $Ni_2P/MZSM$ -5-CA-0, (b)  $Ni_2P/MZSM$ -5-CA-1, (c)  $Ni_2P/MZSM$ -5-CA-2, and (d)  $Ni_2P/MZSM$ -5-CA-3 samples.

composed carbonaceous residuals could exist in the catalyst precursor, and could act as a structure promoter to inhibit the aggregation of active phases [33,34,49]. In our case, the residual carbon in the calcined Ni<sub>2</sub>P catalyst increased with the increase in the amount of CA in the catalyst preparation (Table 2), which is able to inhibit the growth of nickel oxide particles during the calcination process, leading to the formation of small Ni<sub>2</sub>P particles.

To verify this judgment, an additional carbon-containing Ni<sub>2</sub>P/ MZSM-5 catalyst (Ni<sub>2</sub>P/MZSM-5-C) was prepared as follows: First, the MZSM-5 support was impregnated with the CA solution. After drying, the sample was calcined at 350 °C for 4 h under N<sub>2</sub>. Then the obtained C-containing MZSM-5 was impregnated with the solution containing Ni and P precursors. The dried sample was calcined at 500 °C for 3 h in O<sub>2</sub>-Ar mixed gas (5 mol.% O<sub>2</sub> in Ar). The Ni loading was 6.0 wt.%, the Ni/P molar ratio was 1:2, and the residual carbon in this catalyst is 0.153 wt.%. The Ni<sub>2</sub>P particle size on the Ni<sub>2</sub>P/MZSM-5-C catalyst is 8.5 nm by XRD data, a little smaller than that on Ni<sub>2</sub>P/MZSM-5-CA-0 catalyst (9.0 nm). In addition, the CO chemisorption results show that the CO uptake over Ni<sub>2</sub>P/MZSM-5-C (99 µmol/g) is higher than that over Ni<sub>2</sub>P/MZSM-5-CA-0 (93 µmol/g, Table 2). These results indicate that the residual carbon in the catalyst promotes the formation of small Ni<sub>2</sub>P particles. It is found that the reduction temperature of Ni<sub>2</sub>P/MZSM-5-C (708 °C) is higher than that of Ni<sub>2</sub>P/MZSM-5-CA-0 (669 °C, Fig. S6 in the Supplementary Material), which implies that the residual carbon strengthened the interaction between the Ni species and MZSM-5 for the Ni<sub>2</sub>P/MZSM-5-C catalyst. The strengthened interaction should facilitate the formation of a small Ni<sub>2</sub>P active phase on the Ni<sub>2</sub>P/MZSM-5-C catalyst. Therefore, it could be concluded

that the residual carbon in the calcined  $Ni_2P/MZSM$ -5-CA-X (X = 1, 2, and 3) catalysts also plays a role in inhibiting the growth of the nickel oxide particles and benefiting the formation of the small  $Ni_2P$  particles on the MZSM-5.

#### 3.5. Activity of the Ni<sub>2</sub>P/MZSM-5-CA

The catalytic performance of the CA-promoted Ni<sub>2</sub>P catalysts supported on MZSM-5 was first examined in the HDS of the 4,6-DMDBT. Fig. 14 shows the dependence of 4,6-DMDBT conversion over  $Ni_2P/MZSM$ -5-CA-X (X = 0, 1, 2, and 3) catalysts on reaction time. Clearly, the Ni<sub>2</sub>P/MZSM-5-CA-0 catalyst exhibits the lowest catalytic activity (conversion of 35.1% at 15 h). In contrast, the catalytic activity over the CA-added Ni<sub>2</sub>P catalysts is gradually increased with increasing CA amount. For example, the Ni<sub>2</sub>P/ MZSM-5-CA-2 catalyst has a much higher catalytic activity (conversion of 41.3% at 15 h) than the Ni<sub>2</sub>P/MZSM-5-CA-1 catalyst (conversion of 38.3% at 15 h). These results suggest that the catalytic activity of the MZSM-5-supported Ni<sub>2</sub>P catalysts was obviously increased when the Ni<sub>2</sub>P particle size was decreased from 8.3 nm on Ni<sub>2</sub>P/MZSM-5-CA-0 to 7.1 nm on Ni<sub>2</sub>P/MZSM-5-CA-1 and 4.5 nm on Ni<sub>2</sub>P/MZSM-5-CA-2. However, by further increasing the amount of CA in the catalyst preparation, the obtained Ni<sub>2</sub>P/ MZSM-5-CA-3 catalyst exhibits comparable 4,6-DMDBT conversion compared with Ni<sub>2</sub>P/MZSM-5-CA-2 catalyst (41.3% vs 41.2% at 15 h). This may be due to the fact that the formed Ni<sub>2</sub>P phases on these two catalysts have similar particle size and dispersion, which was confirmed by the XRD, TEM, and CO uptake.

To compare the intrinsic HDS catalytic activity, the reaction rate constants ( $k_{HDS}$ ) and TOFs for the HDS of the 4,6-DMDBT over these supported Ni<sub>2</sub>P catalysts were also obtained in the absence of mass transfer limitations, and these results are listed in Table 4 (the fitting curves are given in Fig. S7 in the Supplementary Material). Clearly, it is found that  $k_{HDS}$  increased with an increase in the amount of the CA addition: Ni<sub>2</sub>P/MZSM-5-CA-0 < Ni<sub>2</sub>P/MZSM-5-CA-1 < Ni<sub>2</sub>P/MZSM-5-CA-2. This can be explained by the fact that the addition of different amounts of CA could change the CA-Ni (II) complex structure and the strength of the interaction between the Ni species and MZSM-5 support, altering the particle size of the formed Ni<sub>2</sub>P phase. The Ni<sub>2</sub>P particle size on the Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/MZSM-5-CA-3 (3–6 nm) is smaller than on Ni<sub>2</sub>P/MZSM-5-CA-0 (4–12 nm) and Ni<sub>2</sub>P/MZSM-5-CA-1 (4–10 nm, Fig. 4), and



**Fig. 14.** 4,6-DMDBT conversion as a function of reaction time for the ( $\blacksquare$ ) Ni<sub>2</sub>P/MZSM-5-CA-0, ( $\bullet$ ) Ni<sub>2</sub>P/MZSM-5-CA-1, ( $\blacktriangle$ ) Ni<sub>2</sub>P/MZSM-5-CA-2, and ( $\checkmark$ ) Ni<sub>2</sub>P/MZSM-5-CA-3 catalysts (reaction conditions: 0.05 g catalyst, total pressure 5.0 MPa, temperature of 300 °C, H<sub>2</sub> flow of 60 mL min<sup>-1</sup>, WHSV of 75.0 h<sup>-1</sup>, 0.5 wt.% 4,6-DMDBT in decalin).

#### Table 4

Intrinsic activity of the Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, 2, and 3) catalysts in the 4,6-DMDBT HDS.<sup>a</sup>

Catalyst	$k_{ m HDS} (10^{-2}\mu{ m mol}{ m g}^{-1}{ m s}^{-1})^{ m b}$	TOF $(10^{-4} \text{ s}^{-1})$
Ni <sub>2</sub> P/MZSM-5-CA-0	8.2 ± 0.15	8.3 ± 0.17
Ni <sub>2</sub> P/MZSM-5-CA-1	11.5 ± 0.39	8.9 ± 0.23
Ni <sub>2</sub> P/MZSM-5-CA-2	$16.2 \pm 0.43$	9.7 ± 0.19
Ni <sub>2</sub> P/MZSM-5-CA-3	16.1 ± 0.69	$9.6 \pm 0.34$

<sup>a</sup> Reaction conditions: 0.05 g catalyst, total pressure 5.0 MPa, temperature 300°C, H<sub>2</sub> flow rate 60 mL min<sup>-1</sup>, 0.5 wt.% 4,6-DMDBT in decalin. The 4,6-DMDBT conversion is controlled by changing the WHSV. <sup>b</sup> Adj.  $R^2 > 95\%$ .

the average Ni<sub>2</sub>P particle sizes on Ni<sub>2</sub>P/MZSM-5-CA-0, Ni<sub>2</sub>P/MZSM-5-CA-1, Ni<sub>2</sub>P/MZSM-5-CA-2, and Ni<sub>2</sub>P/MZSM-5-CA-3 are 8.3, 7.1, 4.5, and 4.3 nm (Table 2), respectively. The smaller Ni<sub>2</sub>P particles could expose more active sites, supported by the increasing CO uptakes (Table 2), which improves the catalytic activity. Because the Ni<sub>2</sub>P/MZSM-5-CA-2 and Ni<sub>2</sub>P/MZSM-5-CA-3 catalysts have analogous Ni<sub>2</sub>P particle size distributions and CO uptakes, the reaction rate constants on the two catalysts are at similar levels.

The catalytic activity of these catalysts was also compared using the TOF based on the active site, which was measured by CO chemisorption (Table 4). It is found that the TOF value is gradually increased with decreasing particle size of the Ni<sub>2</sub>P phase, although there was measurement error in the TOF values (Fig. S8 in the Supplementary Material). Oyama and co-workers reported that the 4,6-DMDBT HDS reaction is structure-sensitive [22], and the Ni<sub>2</sub>P particle size can be decreased by using a high-surface-area support, leading to the a higher TOF in the HDS of the 4,6-DMDBT [25]. Similar results were also reported by Cecilia et al. [38], and the TOF is increased with decreasing Ni<sub>2</sub>P particle size that was obtained by changing metal loadings. However, for the bulk metal phosphide catalysts, Smith et al. [50] reported the TOF is increased with increasing particle size of Co<sub>x</sub>Ni<sub>2</sub>P catalysts in the HDS of the 4,6-DMDBT. They explain that the reason for this phenomenon is related to the surface acidity induced by the incomplete reduction of phosphate species [50]. In a subsequent study for the bulk  $Ni_{x}$ -MoP catalyst, the TOF is increased with an increase in the particle size of Ni<sub>x</sub>MoP [33]. The authors explain that the electron density of the Mo in Ni<sub>x</sub>MoP is increased with increasing Ni content and facilitates the dissociation of the 4,6-DMDBT molecule, leading to the high HDS activity [47]. These results imply that the TOF in the HDS of the 4,6-DMDBT for the metal phosphide catalysts should be affected by many factors, such as the particle size, the metal electron density, and the surface properties.

The product selectivity in the HDS of the 4,6-DMDBT reaction on these Ni<sub>2</sub>P/MZSM-5-CA-X (X = 0, 1, and 2) catalysts was compared at the low and similar conversion level (about 20%, Table 5). In general, the 4,6-DMDBT molecule undergoes HDS via direct desulfurization (DDS) and hydrogenation (HYD) by two parallel reaction pathways [51–53]. From Fig. S9 in the Supplementary Material, DM-BP is 3,3'-dimethylbiphenyl from the HDS of 4,6-DMDBT by the direct desulfurization (DDS) pathway; DM-CHB and DM-BCH are 3,3'-dimethylcycohexylbenzene and 3,3'dimethyl bicyclohexyl, respectively, by the hydrogenation (HYD) pathway. Some hydrogenated sulfur-containing intermediates, such as 4,6-dimethyltetrahydrodibenzothiophene (DM-TH-DBT), 4,6-dimethylhexahydrodibenzothiophene (DM-HH-DBT), and 4,6dimethylperhydrodibenzothiophene (DM-PH-DBT), can be formed in the HYD pathway [51]. As can be seen in Table 5, DM-CHB and DM-BCH are produced in greater proportions than DM-BP, indicating that the HYD pathway is preferred for all employed catalysts. This is in line with the results presented by Prins [14] and Oyama

Catalyst	Conv. (%) <sup>a</sup>	Product s	Product selectivity (%)					DMBCH+DMCHI DMBP	DMBCH+DMCHIb SHYD
		DMBP	DM THDBT	DM HHDBT	DM PHDBT	DM BCH	DM CHB		
Ni <sub>2</sub> P/MZSM-5-CA-0	20.1	4.2	41.1	9.5	9.5	10.5	25.3	8.5	0.59
Ni <sub>2</sub> P/MZSM-5-CA-1	20.7	3.6	44.0	7.1	8.3	8.3	28.6	10.3	0.62
Ni <sub>2</sub> P/MZSM-5-CA-2	19.4	3.4	43.7	5.7	8.2	9.0	29.9	11.4	0.68

**Table 5** Product selectivity of 4, 6-DMDBT over  $Ni_2P/MZSM$ -5-CA-X (X = 0, 1, and 2) catalysts.

<sup>a</sup> 4,6-DMDBT conversion.

<sup>b</sup> The SHYD is the total selectivity of DM-THDBT, DM-HHDBT, and DM-PHDBT.

[25], who reported that 4,6-DMDBT desulfurization mainly takes place through the HYD route due to the steric hindrance induced by the methyl groups at the 4 and 6 positions.

Moreover, the ratio of HYD to DDS ((DMBCH + DMCHB)/DMBP) is increased following the order: Ni<sub>2</sub>P/MZSM-5-CA-0 (8.5) < Ni<sub>2</sub>P/ MZSM-5-CA-1 (10.3) < Ni<sub>2</sub>P/MZSM-5-CA-2 (11.4), which should be associated with the difference in Ni<sub>2</sub>P particle size. The Ni<sub>2</sub>P particles with small size benefit the HYD pathway in the HDS of the 4,6-DMDBT. Oyama et al. have proposed that two types of Ni sites, tetrahedral Ni(1) and square pyramidal Ni (2) sites, exist in the Ni<sub>2</sub>P particles, and the Ni(1) sites are responsible for the direct desulfurization, while the Ni(2) sites are highly active for the hydrogenation [25]. As the Ni<sub>2</sub>P crystallite size goes down, the number of Ni(2) sites is increased, resulting in high HYD selectivity of the Ni<sub>2</sub>P catalyst with small size [25]. In this work, the particle size of the prepared Ni<sub>2</sub>P active phase on Ni<sub>2</sub>P/MZSM-5-CA-0 (8.3 nm), Ni<sub>2</sub>P/MZSM-5-CA-1 (7.1 nm), and Ni<sub>2</sub>P/MZSM-5-CA-2 (4.5 nm) gradually decreased. Thus, the Ni<sub>2</sub>P particles with small size facilitate HYD.

Furthermore, the (DMBCH + DMCHB)/SHYD ratio was increased with the decreased Ni<sub>2</sub>P particle size (Table 5), suggesting that C-S bond breaking occurred more easily on the small Ni<sub>2</sub>P particles. In addition, small Ni<sub>2</sub>P particles may lead to the adsorption of 4,6-DMDBT with less steric hindrance [22]. In this manner, the adsorbed molecules could swing around to cause interaction of the phenyl rings with the surface, resulting in hydrogenation and subsequent desulfurization [22]. On the other hand, Smith and co-workers reported that when the bulk Ni<sub>2</sub>P catalyst was prepared in the presence of CA, the DDS pathway was accelerated with the decrease in the Ni<sub>2</sub>P particle size [33,34]. They explained that the Brønsted acidity from the incomplete reduction of phosphate salts can promote the migration of methyl groups to give isomerized products such as 2,8-DMDBT. The isomerized products with less steric hindrance could easily adsorb onto the small Ni<sub>2</sub>P particle via  $\sigma$  adsorption, leading to the facilitation of the DDS pathway. As a result, both the Ni<sub>2</sub>P particle size and the surface properties affect the contribution of the HYD and DDS pathways to 4,6-DMDBT conversion.

To further investigate the hydrogenation ability of the Ni<sub>2</sub>P/ MZSM-5-CA-X (X = 1, 2 and 3) catalysts, phenanthrene hydrogenation was performed. Fig. 15 shows the dependence of phenanthrene conversion over  $Ni_2P/MZSM$ -5-CA-X (X = 0, 1, 2, and 3) catalysts on the reaction time. It is clear that the phenanthrene conversion is increased with the increase in the amount of CA for these catalysts. For example, the phenanthrene conversion over Ni<sub>2</sub>P/MZSM-5-CA-0 is 63.2% at 54 h, much lower than that over Ni<sub>2</sub>P/MZSM-5-CA-1, Ni<sub>2</sub>P/MZSM-5-CA-2, and Ni<sub>2</sub>P/MZSM-5-CA-3 (83.6, 90.1, and 90.4%). These results indicate that increasing the CA content in the catalyst impregnation solution could improve the prepared Ni<sub>2</sub>P active phase with high dispersion and small particles size, leading to the Ni<sub>2</sub>P particle exposing more hydrogenation active sites, as discussed above. The product selectivity of phenanthrene hydrogenation was analyzed at a similar conversion level, and the results are shown in Table S2 in the Supplementary Material. According to the literature [54–56], the aromatic ring of



**Fig. 15.** Phenanthrene conversions as a function of reaction time for ( $\blacksquare$ ) Ni<sub>2</sub>P/MZSM-5-CA-0, ( $\bullet$ ) Ni<sub>2</sub>P/MZSM-5-CA-1, ( $\blacktriangle$ ) Ni<sub>2</sub>P/MZSM-5-CA-2, and ( $\blacktriangledown$ ) Ni<sub>2</sub>P/MZSM-5-CA-3 catalysts.

the phenanthrene can first be hydrogenated to dihydrophenanthrene (DHP) and 1,2,3,4-tetrahydrophenanthrene (THP), and further deeply hydrogenated to octahydrophenanthrene (OHP) with symmetric and asymmetric and perhydrophenanthrene (PHP, Fig. S10). OHP and PHP are usually considered to be deep hydrogenation products (DHPS). The DHPS selectivity follows the order Ni<sub>2</sub>P/MZSM-5-CA-1 (29.9%) > Ni<sub>2</sub>P/MZSM-5-CA-0 (28.8%) > Ni<sub>2</sub>P/ MZSM-5-CA-2 (26.1%). The DHPS selectivity may depend not only on the Ni<sub>2</sub>P particle size but also on the acidity of the catalyst. The Ni<sub>2</sub>P/MZSM-5-CA-0, Ni<sub>2</sub>P/MZSM-5-CA-1, and Ni<sub>2</sub>P/MZSM-5-CA-2 catalysts have Ni<sub>2</sub>P particles sizes 8.3, 7.1, and 4.5 nm, respectively, while their acidic site concentrations are 160, 143, and 120 µmol/g.

#### 4. Conclusions

Small and highly dispersed Ni<sub>2</sub>P nanoparticles supported on mesoporous zeolite ZSM-5 (MZSM-5) are successfully synthesized by a CA-assisted incipient wetness impregnation method. Ni can be coordinated with CA in the impregnation solution to form Ni(II)-CA complexes with different structure, Ni(cit)<sup>-</sup> and Ni(Hcit)(cit)<sup>3-</sup>, by changing the CA/Ni ratios. After impregnation and drying, the highly viscous Ni(II)-CA complex may favor the good dispersion of the Ni precursor on the MZSM-5 surface. In addition, the different Ni(II)–CA structures, Ni(cit)<sup>–</sup> and Ni(Hcit)(cit)<sup>3–</sup>, led to different interaction between Ni species and the MZSM-5 support. In the calcination process, the released Ni species can interact strongly with MZSM-5 through surface acidic hydroxyl groups, leading to the formation of small Ni<sub>2</sub>P particles with good dispersion under the reduction atmosphere. Compared with the Ni<sub>2</sub>P catalyst prepared without CA, CA-assisted Ni<sub>2</sub>P catalysts show high activity in the 4,6-DMDBT HDS and phenanthrene hydrogenation reactions.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.11.019.

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