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ZSM-5-supported multiply-twinned nickel particles: Formation, surface properties, and high catalytic performance in hydrolytic hydrogenation of cellulose



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1. Introduction

ABSTRACT

Nickel multiply-twinned particles (Ni MTPs) imbedded onto ZSM-5 were prepared, and their formation and chemical and electronic properties were characterized by HRTEM, XPS, CO-FTIR, and H₂-TPD. HRTEM showed the formation of Ni MTPs with triangular, square, hexagonal, and spherical shapes. The multiply-twinned particles were composed of *f.c.c.* nanocrystals dominated by (111) crystal face. Ni MTPs indicate an enhanced CO adsorption capability as compared with ordinary Ni particles. Ni MTPs were electron deficient and inherently strained, which is responsible for high catalytic activity in the hydrolytic hydrogenation of cellulose.

Al₂O₃, Ni/SiO₂, and Ni/bentonite [21].

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probably due to their limitation in separation, thermal stability, and catalytic properties.

In 1966, Ino observed that small polycrystalline nuclei were Hydrolytic hydrogenation of cellulose into hexitols is one of the formed by deposition of Au on an NaCl surface in ultrahigh vacuum efficient methods for converting biomass to fuels and chemicals and these anomalous Au particles were assumed to be multiply-[11–13]. High yield of hexitols was obtained on noble metal catatwinned particles (MTPs) [1,2]. Since that, extensive efforts have been devoted to synthesizing MTPs for the *f.c.c.* metals (especially, Au, Ag, Cu, Pt, Pd, and Ru) and investigating the crystal growth mechanisms and their potential application in catalysis, gas sensors, and electronics [3–7]. The most notable example for the application of MTPs in catalysis is the case of supported Au nanoparticles. Au MTPs were reported to be one of the most stable forms of Au nanoparticles with a diameter <5 nm [8–10]. Although the strategies for synthesizing of MTPs with controlled size, composition, and shape have achieved great progresses in these years, Ni MTPs have been rarely studied so far in heterogeneous catalysis,

lysts, especially on Ru catalysts [14-17]. However, utilization of noble metals is practically hindered because of high cost and limited resource. Recently, Ni-based catalysts were designed to replace noble metal catalysts for achieving high yield of hexitols [18–20]. However, conventional Ni catalysts supported on various supports, such as Al₂O₃, SiO₂, bentonite, TiO₂, kieselguhr, ZnO, activated carbon, and carbon nanotubes, were less selective to the production of hexitols [21], mainly due to the degradation of glucose prior to hydrogenation and further hydrogenolysis of hexitols. The degradation of glucose is costly because it will lead to a decrease in hexitols yield and to serious coking and blocking of metal surface. The hydrogenolysis of hexitols on metal sites would increase hydrogen consumption, resulting in a complex distribution of products in liquid phase and a large amount of by-products in gas phase. For example, hydrogenolysis and aqueous phase reforming reactions occur seriously, which results in a significant loss of hexitols over Ni-based catalysts, such as Ni/

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The authors previously showed that hydrogenation/dehydrogenation activity of Ni catalysts had a significant effect on hexitols yield. A Ni/ZSM-5 catalyst gave excellent hydrogenation activity but lower dehydrogenation activity; thus it produced hexitols in high yield [21]. However, there is still little knowledge about the relation between the excellent hydrogenation activity and the structural/chemical/electronic properties of Ni/ZSM-5. The present work has been undertaken to investigate the formation of Ni MTPs on ZSM-5 and the possible reasons for the high activity of Ni MTPs observed in the hydrolytic hydrogenation of cellulose.

2. Experimental

2.1. Catalyst preparation

A Ni MTPs/ZSM-5 catalyst was prepared by a modified impregnation method. In detail, 1.66 g ZSM-5 powder was mixed with an aqueous Ni(NO₃)₂ solution (15 mL) at room temperature. The mixture was ultrasonically treated for 0.5 h to have a well-dispersed suspension. Then, the excess water was evaporated slowly at 70 °C with stirring. Viridescent powder was collected and vacuum-dried at 60 °C for 12 h. The powder was further calcined under Ar atmosphere at increasing temperatures with a heating rate of 5 °C min⁻¹ to 450 °C and for 2 h at this temperature. The catalyst sample was reduced under H₂ atmosphere at increasing temperatures with a heating rate of 5 °C min⁻¹ to a certain temperature at which it was further reduced for 2 h before use for hydrogenation reaction and characterization. For comparison, another Ni catalyst on ZSM-5 was also prepared by traditional incipient wetness impregnation method and designated as Ni/ ZSM-5-IM. Typically, 1 mL Ni(NO₃)₂ solution was added to ZSM-5 support, and the sample was dried at room temperature. This process was repeated twice in order to deposit adequate Ni. The process for calcination and reduction is identical to that for Ni MTPs/ZSM-5.

Ni/ZSM-5-DP was prepared by deposition–precipitation method. In detail, the ZSM-5 powder was put into a Ni(NO₃)₂ solution and dispersed by ultrasonic treatment for 0.5 h. A Na₂CO₃ solution was added dropwise into the mixture at 40 °C with stirring. After that, the mixture was aged at 40 °C for 2 h, filtrated, dried at 60 °C for overnight, and finally calcined under Ar at 450 °C for 2 h. The catalyst so prepared is designated as Ni/ZSM-5-DP.

2.2. Catalyst characterization

X-ray powder diffraction data were recorded with a Bruker D8 Advance X-ray diffractometer using Cu K α source ($\lambda = 0.154$ nm) in a 2 θ range from 10° to 80° with a scan speed of 10° min⁻¹.

H₂-temperature-programmed desorption (H₂-TPD) and NH₃temperature-programmed desorption (NH₃-TPD) were conducted on a Tianjin XQ TP-5080 chemisorption instrument. The effluent gas was analyzed by a thermal conductivity detector (TCD). As for a typical TPD test, 100 mg of a fresh catalyst sample was loaded into a quartz tube, heated at 150 °C for 30 min in nitrogen, and then cooled to room temperature. The sample was reduced in a 10% H₂/N₂ flow at desired temperature (360 °C for Ni MTPs/ZSM-5 and 300 °C for Ni/ZSM-5-DP) with a heating rate of 10 °C min⁻¹. After reduction, the sample was cooled to room temperature and then exposed to a probe gas stream (H₂ or NH₃ at a flow rate of 30 mL min⁻¹) for 30 min. The sample was flushed with He for 2 h to reach a stable background. Then, temperature-programmed desorption was carried out in a He stream at a flow rate of 30 mL min⁻¹ and at a temperature ramp rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed using X-ray photoelectron spectroscopy (XPS, VG Microtech 3000 Multilab). Binding energy (BE) values were referenced to the binding energy of the C 1s core level (284.8 eV).

Transmission electron microscope (TEM) images were taken with a JEOL JEM-2010 instrument with an accelerating voltage of 200 kV. Prior to TEM characterization, the samples were dispersed into ethanol solution with ultrasonic treatment for 15 min and then dropped onto a carbon film on copper grid.

In situ FTIR spectroscopy measurements were taken on a Bruker V 70 spectrometer to examine the surface of Ni MTPs using CO as a probe adsorbent. The catalyst sample was reduced in an IR cell with H_2 at 360 °C for 1 h, then purged with N_2 at 360 °C for 30 min, and cooled to room temperature, followed by the sample was exposed to pure CO for 15 min and the spectra were recorded. Typically, 100 scans were recorded at a resolution of 4 cm⁻¹ using an MCT detector.

2.3. Activity measurement

Microcrystalline cellulose (relative crystallinity of about 74.6%) was purchased from Alfa Aesar, which was dried at 70 °C for 24 h before use. The catalyst sample (100 mg) was firstly reduced in a quartz tube at appropriate temperature (360 °C for Ni MTPs/ZSM-5 and 300 °C for Ni/ZSM-5-DP, respectively) for 2 h. The catalyst sample was transferred to reactor (30-mL Teflon inlet) containing 10 mL water, and then, 0.3 g microcrystalline cellulose was loaded into the reactor. The reactor was introduced with 4 MPa H₂ (RT) to start the reaction. After reaction, the reactor was cooled to room temperature by ice water. The product mixture was centrifuged and dried at 70 °C for overnight. The cellulose conversion was calculated by the weight difference in the solid before and after reaction. The products in aqueous phase were firstly acetylated and then identified by GC/MS (Agilent 5975/6890 N) with a HP-5 column (30 m \times 0.25 μ m \times 0.25 mm i.d). The liquid products were analyzed by a HPLC system (Shimadzu LC-20AB) equipped with RI detector (Shimadzu RID-10A) and an Aminex HPX-87H column (Bio-Rad, 300×7.8 mm), using 5 mM H₂SO₄ as eluent with a flow rate of 0.7 ml min⁻¹ at 60 °C. The targeted polyols (hexitols, glycerol, propylene glycol, and ethylene glycol) were determined quantitatively by using HPLC based on calibration curves of stand compounds.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows TEM micrographs of supported Ni MTP catalysts prepared. The calcined sample before reduction (Fig. 1a and b) contains irregularly shaped NiO particles, which are foamlike with a coating layer (Fig. 1b). The size of these foam-like NiO particles is 50–100 nm, which is largely different from an average size of 23 nm estimated by XRD (Fig. 2). It is hence assumed that the foam-like porous NiO particles are polymorphs, consisting of two or three single nanocrystals.

During reduction, NiO particles collapsed with releasing lattice oxygen and then formed smaller Ni particles with triangular, square, hexagonal, and spherical shapes (Fig. 1c), which were quite different in morphology from the ordinary Ni nanoparticles on Ni/ZSM-5-DP (Fig. 1g). Such a unique structure has been confirmed to be multiply-twinned nickel particles in the previous study [22]. Fig. 1d shows the HRTEM micrograph of a typical multiply-twinned decahedral nickel particle, which is composed of five *f.c.c.* tetrahedral Ni nanocrystals dominated by (111) crystal face. The nanocrystals were joined by twin boundaries with a gap of



Fig. 1. TEM images of ZSM-5-supported Ni catalysts: (a and b) Ni MTPs/ZSM-5 before reduction; (c and d) reduced Ni MTPs/ZSM-5; (e and f) Ni/ZSM-5-DP before reduction; and (g and h) reduced Ni/ZSM-5-DP.

7.35°, sharing axes of fivefold symmetry [23]. According to the *d*-band center theory, multiply-twinned structure has crystal defects or intrinsic elastic tensile strain, which could modify the *d*-band structure and upshift the *d*-state closer to the Fermi level [24,25], thus giving unusual surface sites. A few bulk particles with the size of 50–100 nm were also found in Fig. 1c, which might be due to incomplete reduction in some NiO particles.

The textural properties of ZSM-5, reduced Ni MTPs/ZSM-5, and reduced Ni/ZSM-5-DP catalysts are summarized in Table 1. Ni MTPs/ZSM-5 had a larger specific area and pore volume compared to those of Ni/ZSM-5-DP and ZSM-5 samples. The pore size distributions of these three samples are also given in Fig. 3. The Ni-unloaded ZSM-5 showed a dominant peak at 0.61 nm and another peak at 0.83 nm, indicating a microporous structure. For Ni/ZSM-5-DP, the presence of Ni particles has no effect on the pore size distribution, suggesting that Ni particles were exclusively



Fig. 2. XRD patterns of (a) calcined Ni/ZSM-5-DP and (b) calcined Ni MTPs/ZSM-5 before reduction.

adsorbed on the outer surface of ZSM-5. The loading of Ni MTPs increased the surface area from 230.2 to 269.1 $m^2 g^{-1}$ (Table 1). This may be due to the formation of a new type of micropores at 0.92 nm (shown in Fig. 3).

3.2. Chemical and electronic properties

The number of exposed Ni atoms was determined by H₂-TPD (Fig. 4). Ni/ZSM-5-DP has a higher nickel metal surface area (192.6 m² g⁻¹) than Ni MTPs/ZSM-5 (177.1 m² g⁻¹), suggesting that more Ni atoms were exposed on the surface of Ni/ZSM-5-DP. The strength of the diffraction peaks for Ni species in Ni/ZSM-5-DP was weaker, indicating that it has a smaller particle size with higher dispersion compared with the Ni MTPs/ZSM-5.

Fig. 5 shows the NH₃-TPD profiles of Ni-loaded and Ni-unloaded ZSM-5 catalysts. The NH₃ desorption at temperatures below 400 °C was assigned to weak acid sites, while that above 400 °C were strong acid sites. The amount of NH₃ desorbed above 400 °C from either Ni MTPs/ZSM-5 or Ni/ZSM-5-DP was much smaller than that from the ZSM-5 support, suggesting that the strong acid sites decreased on the loading of Ni. A desorption peak appeared in the range of 400–550 °C for Ni MTPs/ZSM-5, which should be ascribed to new acidic sites of medium strength.

XPS analysis was performed in order to observe the evolution of Ni species during the preparation process. Fig. 6 shows the XPS spectra of Ni 2p3/2 for the Ni MTPs/ZSM-5 samples at different stages of preparation. The values of the binding energy (BE) of Si 2p, Al 2p, and Ni 2p core electrons are listed in Table 2. The dried sample (before calcination) presented two Ni 2p peaks at 856.4 and 857.3 eV (after deconvolution), which were assigned to Ni(H₂O)_x(NO₃)₂ and Ni(OH)₂, respectively, indicating that $Ni(H_2O)_x(NO_3)_2$ was partly hydrolyzed to $Ni(OH)_2$ at the drying stage. For the calcined one, Ni 2p3/2 showed two peaks at 854.4 and 856.5 eV. The former peak was associated with their regularly shaped NiO particles, and the latter was a characteristic of NiO. As for the reduced sample, a new peak appeared at 853.3 eV, indicating the formation of metallic nickel particles (Ni MTPs confirmed by HRTEM). In addition, the BE of the Ni $2p_{3/2}$ for Ni⁰ at 853.3 eV was higher than the standard value of Ni⁰, indicating that Ni MTPs were electron deficient. This may be because that the reduction was made ex situ and so some oxidized nickel species like NiO might be formed through oxidation of Ni⁰ between the reduction and the XPS measurement. When the sample was cleaned by argon ion sputtering for 2 min, the peak for the Ni^0 $2p_{3/2}$ became dominant with no shift and the satellite line for Ni^{2+} still remained, 82

Catalyst	$S_{Micro}(m^2g^{-1})$	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Particle size (nm)		SA_{Ni}^{b} (m ² g _{Ni} ⁻¹) (based on H ₂ -TPD data)
				XRD	TEM	
Ni MTPs/ZSM-5	269.1	0.149	0.61	18	19	177.1
Ni/ZSM-5-DP	229.2	0.118	0.62	16	13	192.6
ZSM-5	230.3	0.117	0.61			

^a Specific area in the range of the micropore region (S_{Micro}) is calculated by using BET method, pore size distribution and pore volume are calculated from the Ar adsorption isotherm using H-K method.

^b bNi metal-specific surface area (SANi) is calculated from the monolayer adsorption of hydrogen based on H2-TPD curves.



Fig. 3. Micropore size distribution of ZSM-5-supported Ni catalysts. The pore size distribution is calculated from the Ar adsorption isotherm using H-K method.

indicating the existence of non-reduced nickel ions. Pawelec et al. previously reported that the non-reduced nickel ions interacted with the lattice oxygen existed on zeolite according to XPS analysis, as a result of an incomplete reduction of NiO during hydrogen treatment [26].

The surface of supported Ni particles was examined by FTIR using CO as a probe molecule. Fig. 7 shows time-dependent FTIR spectra for CO adsorbed on Ni MTPs/ZSM-5 and Ni/ZSM-5-DP catalysts reduced at room temperature and 200 °C. Two weak absorption bands were observed at 2171 and 2107 cm⁻¹ for Ni/ZSM-5-DP measured at room temperature (Fig. 7a), and these bands disappeared on N₂ purging. These two bands were assigned to residual gaseous CO. CO adsorption band was not observed after N₂ purging for 8 min, suggesting that no CO adsorption occurred on Ni/ZSM-5-DP. By contrast, CO adsorption behavior on Ni MTPs/ZSM-5 was different and CO adsorption band was located at 1950 cm⁻¹ (Fig. 7b). This band was attributed to bridge-type carbonyls connected with two or more Ni⁰ atoms [27-29]. Even after N₂ purging for 26 min at room temperature, the adsorption band little weakened, suggesting a strong adsorption of carbonyl complexes on the Ni MTPs/ZSM-5 catalyst.

Ni MTPs/ZSM-5 presented strong absorption spectra at the frequency region of 2035–2203 cm⁻¹, which was attributed to linear



Fig. 4. H₂-TPD patterns of Ni/ZSM-5-DP and Ni MTPs/ZSM-5.



Fig. 5. NH₃-TPD profiles of ZSM-5, Ni MTPs/ZSM-5, and Ni/ZSM-5-DP.

CO species adsorbed on the metallic Ni atom with low valence (Ni^{δ^*}) . Purging by N_2 causes a minor decrease in the intensity of the bands at 2035–2213 cm⁻¹, corresponding to strong adsorption forms. It is difficult to figure out the difference in Ni species in electronic states since no well-resolved band was observed.

Fig. 7c shows the FTIR results measured at 200 °C for the reduced Ni MTPs/ZSM-5 sample. After N₂ purging at 200 °C with prolonged time, i.e., at low CO coverage, some well-resolved bands appeared at 2283–2059 cm⁻¹. The intensity of these bonds decreased with decreasing CO coverage, which were assigned to terminal carbonyls on various Ni²⁺ species. The band at 2181 cm⁻¹ was assigned to CO interacting to Ni²⁺ with σ band [30,31]. Such a stable CO adsorption band could be explained by the high electrophilicity of Ni²⁺ cations in ZSM-5 matrix according



Fig. 6. XPS spectra of Ni species of Ni MTPs/ZSM-5 samples at different stages of preparation: (a) dried; (b) calcined; (c) reduced, and (d) reduced and then treated by Ar+ sputtering for 2 min.

to the literature [28]. The band at 2111 cm⁻¹ with a shoulder at 2121 cm⁻¹ could be due to terminal carbonyls on Ni^{δ+} species with π -type back bonding. Considering that the surface atoms of Ni MTPs on ZSM-5 were coordinatively unsaturated, we demonstrated that the bands at 2121 and 2111 cm⁻¹ should be attributed to terminal carbonyls on Ni MTPs. Moreover, these peaks associated with Ni MTPs were still evident after N₂ purging for 20 min at 200 °C, indicating a strong adsorption of CO on Ni MTPs. After N₂ purging at 200 °C, some new peaks with similar relative intensities appeared at 2017, 2008, and 1993 cm⁻¹, which could be assigned to Ni species such as physisorbed Ni(CO)₄ and Ni(CO)₃ [32]. Interestingly, several quite sharp bands at the lower frequency (i.e., 1900–1970 cm⁻¹) appeared in the typical region of bridge-type species after heating at 200 °C.

The FTIR results after N_2 purging at 200 °C allow us to consider the features of the surface of Ni MTPs on ZSM-5. According to the spectra, all these bands of bridge-type species at the lower frequency (i.e., 1900–1970 cm⁻¹) increased with N₂ purging at 200 °C, while the bands of terminal carbonyls at the higher frequency (2181, 2121, and 2111 cm⁻¹) decreased in intensity, indicating the terminal carbonyls were converted to the bridge-type ones at low CO coverage. Here, some well-resolved bands of bridge-type species were observed, suggesting the presence of several kinds of adsorbed CO species with different adsorption energies. The presence of different kinds of adsorbed CO species indicated the existence of various types of surface atoms with different electronic states on Ni MTPs, naming the strain on Ni MTPs was heterogeneous, and the electronic state of the surface atom was changed with strain accordingly.

3.3. Formation mechanism of Ni MTPs

Even though all *f.c.c.* metals could form MTPs in the early synthesis strategies theoretically and experimentally, Ni MTPs are seldom found in the nickel catalysts. The forming mechanism of Ni MTPs has not been reported and still unclear up to now. Herein, we made a discussion for the formation of Ni MTPs based on the characterization and experimental data.

Compared to the conventional impregnation, both ultrasonically treatment and controlled evaporation processes were applied in the preparation of Ni MTPs/ZSM-5, and these two additional procedures may be attributed to the formation of Ni MTPs. As shown in Fig. 8, the pH value of the impregnation solution changed largely during the volatilization process (evaporating at 70 °C with a rate of 6 mL h^{-1}). At first, the pH value decreased from 2.4 to 1.9 linearly in the first 80 min and then increased up to 2.5 within the next 40 min. The changes of the pH value in the evaporation process may be caused by the following transformations: As shown in Scheme 1, firstly, the nickel ions reacted with the surface hydroxyl groups of ZSM-5 to release protonic hydrogen into the solution or exchanged with Al in the framework, thus causing a gradual decrease in pH value; secondly, with further evaporating of excess water at the last 40 min, the nickel nitrate solution was saturated and it deposited with the leached Al³⁺ subsequently onto the surface of ZSM5, which was demonstrated with the results of XPS analysis. Table 1 summarizes the atomic ratio of Ni/Al, Si/Al, and Ni/(Ni + Si + Al) on the surface of Ni MTP/ZSM-5 at different forming stages. The surface Si/Al atomic ratio in the Ni-containing sample after impregnation was 3.4, which is much lower than that (SiO₂/Al₂O₃ 25.5) in the bulk. A similar trend was also found in Pawelec's work [26], and they cautiously deduced that it might be caused by Al leaching from the framework. Moreover, the metal composites decomposed to form an alumina overlayer on the foam-like NiO particles at high temperature during calcination, as observed in the TEM images (Fig. 1b). The decomposition behavior of Ni and Al complexes was different that the Al precursor was preferentially decomposed during raising temperature to form an alumina overlayer and then the Ni precursor decomposed at

Table 2

The distribution of Al, Si, and Ni on the surface of Ni MTP/ZSM-5 at different stages of preparation based on XPS analysis.

Samples	Binding energy (eV)			Atomic ratio		
	Si 2p	Al 2p	Ni 2p _{3/2}	Ni/Si	Si/Al	Ni/(Al + Si + Ni)
Dried	103.3	74.7	856.4 (Ni(H ₂ O) _x (NO ₃) ₂) 857.3 (Ni(OH) ₂)	0.14	3.4	0.10
Calcined	103.2	74.9	854.4 (Ni δ [*]) 856.5 (Ni ²⁺)	0.24	2.2	0.14
Reduced	103.4	75.1	853.3 (Ni ⁰) 856.2 (Ni ²⁺)	0.05	8.6	0.04
Reduced (Ar ⁺ sputtering)	103.4	75.1	853.1 (Ni ⁰) 856.1 (Ni ²⁺)	0.10	6.7	0.09



Fig. 7. Time-dependent FTIR spectra of CO adsorbed on supported Ni particles: (a) reduced Ni/ZSM-5-DP at RT, (b) reduced Ni MTPs/ZSM-5 at RT, and (c) reduced Ni MTPs/ZSM-5 at 200 $^{\circ}$ C.

relative higher temperature, releasing out gaseous NO_x or H₂O, thus resulted in the formation of a porous NiO particles. It is noticed that the surface Ni/(Ni + Si + Al) atomic ratio on the reduced Ni MTPs/ZSM-5 increased to 0.09 from 0.04 after Ar+ sputtering, supporting that Ni MTPs were coated with alumina overlayer, and more Ni atoms were exposed as alumina overlayer was etched by Ar+ sputtering.

We proposed that alumina overlayer had a determinant influence on the formation and the ultimate microstructure of the resulting Ni MTPs. It was reported that the surface-stabilizing agent and the subtle control of nucleation and kinetics were the key factors for synthesis of metal MTPs by seeded solutions [33]. In present work, the alumina overlayer worked as surface-stabilizing agent for the formation of Ni MTPs, because in the initial reduction stage of the foam-like NiO polymorphs, the alumina layer could inhibit rapid growth of Ni nanocrystals, and the steric hindrance favored the formation of Ni MTPs. In addition, the strong interactions between Ni particles and alumina layer made Ni MTPs anchored on the ZSM-5 matrix more strongly. By contrast, the Ni MTPs were not formed in the Ni/ZSM-5-IM (conventional impregnation method) and the Ni/ZSM-5-DP (deposition–precipitation method). The surface alumina overlayer could not be formed when the evaporation process was not included, thus because of the absence of the transformations in Scheme 1.

3.4. Catalytic performance

The Ni MTPs/ZSM-5, Ni/ZSM-5-IM, and Ni/ZSM-5-DP catalysts were compared for the hydrolytic hydrogenation of microcrystalline cellulose, and the Ni MTPs/ZSM-5 and Ni/ZSM-5-DP for the hydrogenolysis and dehydrogenation of sorbitol. The results obtained are summarized in Table 3. When Ni-unloaded ZSM-5 was used, sorbitan and isosorbide were obtained in a total yield of 65.3% at 80.5% conversion (Table 3, entry 8), indicating that the intra-molecular dehydration reaction mainly occurred at present conditions. It is interesting, in contrast, the yield of dehydration products such as sorbitan and isosorbide was quite low over the Ni MTPs/ZSM-5 and Ni/ZSM-5-DP catalysts. According to the NH₃-TPD results, the ZSM-5 had more strong acid sites compared to Ni MTPs/ZSM-5 or Ni/ZSM-5-DP. We propose that the strong acid sites are beneficial for the intra-molecular dehydration reaction of sorbitol. Considering that the molecule size of sorbitol $(0.547 \times 0.64 \text{ nm})$ is larger than the pore size of the channels in ZSM-5 [34], we propose that sorbitol may be dehydrated exclusively on the strong acid sites over the outer surface of ZSM-5.

As shown in Table 3, both Ni MTPs/ZSM-5 and Ni/ZSM-5-DP catalysts showed poor activities for the hydrogenolysis and dehydrogenation of sorbitol (Table 3, entry 2, 3, 5, 6), which are required for suppressing the cost of hexitols in the hydrolytic hydrogenation of cellulose. High hydrogenation activity and low dehydrogenation activity are essential for high production of hexitols on Ni catalysts. The Ni MTPs/ZSM-5 is a promising catalyst, but the Ni/ZSM-5-DP is not. According to the H₂-TPD results in Table 1, Ni MTPs/ZSM-5 has less Ni⁰ active sites than Ni/ZSM-5-DP, but it presented a much higher hydrogenation activity, indicating that the amount of active sites was not a dominant factor for the hydrogenation activity. The fundamental reason for the difference in hydrogenation activity between these two catalysts might be the intrinsic hydrogenation activity of two types of Ni nanoparticles. A comparison of TOF value for hexitol formation between Ni MTPs/ZSM-5 and Ni/ZSM-5-DP shows that the intrinsic hydrogenation activity of Ni MTPs/ZSM-5 is much higher than that of Ni/ZSM-5-DP (6.0 versus 1.6 h^{-1} , Table 3, entry 2 and 5, respectively).

The hydrogenation of glucose over Ni MTPs/ZSM-5 in the presence/absence of 0.2 MPa CO was conducted, in order to investigate the effect of coadsorption of CO on Ni MTPs. As shown in Fig. 9, in the presence of CO, the conversion of glucose and the selectivity of hexitols were 18.5% and 2.2%, while in the absence of CO, they were 22.8% and 60.9%, respectively. The results thus indicated that the presence of CO could inhibit the hydrogenation of glucose as the active sites on Ni MTP/ZSM-5 were partly occupied by CO.

Ni MTPs were considered to provide some unusual active sites for hydrogenation due to the unique structure, which was demonstrated by using CO-FTIR. Those active sites for adsorption of CO were similar to that of the glucose, since the glucose hydrogenation on Ni MTPs was largely suppressed in the presence of CO (Fig. 9). Several remarkably distinct adsorbed CO species were



Fig. 8. The change of pH value of impregnation solution as a function of time during the preparation of Ni MTPs on ZSM-5.



 $\mbox{Scheme 1.}$ The proposed surface reactions in aqueous $\mbox{Ni}(\mbox{NO}_3)_2$ solution during impregnation.

observed over Ni MTPs (Fig. 7), indicating the existence of various types of surface Ni atoms with different electronic states, naming the strain on Ni MTPs was heterogeneous as the electronic state of the surface atom changed with strain accordingly. It is in consistent with the result of DFT calculation on the adsorption of CO on strained Au(111) slabs [25]. Based on the *d*-band model for the MTPs of 3 *d* transition metals, an increase in tensile strain of surface atoms shifted the *d*-band center closer to the Fermi level, resulting in enhanced interaction between surface atoms and adsorbed molecules because fewer of the antibonding states of



Fig. 9. The effect of CO on the hydrogenation of glucose over Ni MTPs/ZSM-5. Reaction conditions: 4.0 MPa H_2 , 1 g glucose, 10 mL H_2 O, 120 °C, 1 h.

Ni-adsorbate bond were occupied [35,36]. This is in agreement with our conclusion that the remarkably enhanced CO adsorption capability originates from the low-coordinated surface nickel atoms with inherent strain. In the case of cellulose hydrogenation,

Table 3				
Catalytic conversion	of microcrystalline	cellulose o	ver Ni cataly	sts.

Entry	Catalyst	Substrate	Reaction conditions	Conversion ^b (%)	Product yield ^c (%)					$TOF^{e}(h^{-1})$
					Hexitols	Glycerol	EG	PDO	Ad	
1	Ni/ZSM-5-IM	Cellulose	4.0 MPa H ₂ , 2.5 h	92.0	23.7	7.6	7.7	29.0	9.7	-
2	Ni MTPs/ZSM-5	Cellulose	4.0 MPa H ₂ , 2.5 h	94.1	63.6	1.2	0.6	1.4	2.1	6.0
3		Sorbitol	4.0 MPa H ₂ , 4 h	17.5	-	2.3	1.5	0.3	3.6	0.7
4		Sorbitol	0.1MPaN ₂ , 4 h	16.4	-	0.7	1.9	3.9	3.7	-
5	Ni/ZSM-5-DP	Cellulose	4.0 MPa H ₂ , 2.5 h	93.4	18.9	5.2	2.2	1.8	1.9	1.6
6		Sorbitol	4.0 MPa H ₂ , 4 h	22.6	-	4.5	3.5	4.7	2.1	0.6
7		Sorbitol	0.1 MPa N ₂ , 4 h	15.7	-	0.6	1.9	2.8	2.6	-
8	ZSM-5	Sorbitol	0.1 MPa N ₂ , 4 h	80.5	-	-	-	-	65.3	-

^a Reaction conditions: 240 °C, 10 mL H₂O, substrate 0.3 g, catalyst 0.1 g, reactor (50 mL) with a diameter of 30 mm.

^b Cellulose conversion was calculated with the initial weight of solid (cellulose and catalyst) divided by that of the residual solid after reaction, and sorbitol conversion was calculated by HPLC.

^c The yield of the product = (moles of carbon in the product)/(moles of carbon in the substrate).

^d The dehydration products include sorbitan and isosorbide.

^e TOF value in cellulose hydrogenation is calculated based on hexitol formation and TOF value in the hydrogenolysis and dehydrogenation of sorbitol is calculated based on sorbitol consumption.

carbonyl group of glucose would preferentially be adsorbed on the coordinatively unsaturated and inherently strained surface atoms of Ni MTPs and then readily hydrogenated into primary hydroxyl group.

4. Conclusion

The nickel nanoparticles on Ni MTPs/ZSM-5 were confirmed to be multiply-twinned particles composed by 5 f.c.c. tetrahedral nanocrystals. Ni MTPs present a higher hydrogenation activity as well as lower hydrogenolysis and dehydrogenation activity and so produce hexitols with a high yield (63.6%). The Ni MTPs are inherently strained and show an enhanced capability of CO adsorption. The higher adsorption energy for the adsorbate was rationalized by the *d*-band center model: the inherently strained and coordinatively unsaturated Ni MTPs are of higher *d*-band center (closer to Femi level), thus resulting in less occupancy of the antibonding states of Ni-adsorbate bond. Therefore, it is reasonable to suppose that the adsorption and activation of the primary carbonyl group of hexose are greatly improved on Ni MTPs and easily be attacked by active hydrogen. The inherently strained Ni MTPs with electronic deficiency is the main reason for the high inherent hydrogenation activity of Ni MTPs/ZSM-5.

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