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Effect of surface composition on the catalytic performance of molybdenum phosphide catalysts in the hydrogenation of acetonitrile

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Abstract

A series of molybdenum phosphide catalysts with initial Mo/P ratios varying in a narrow range of 0.90–1.10 was prepared by temperature-programmed reaction; characterized by X-ray diffraction, BET, elemental analysis, X-ray photoelectron spectroscopy, and CO chemisorption measurements; and tested for the hydrogenation of acetonitrile at different pressures (0.1–1.0 MPa) and temperatures (473–513 K). The catalysts exhibited attractive catalytic activity, especially at a H_2 pressure above 0.2 MPa. The surface composition of the MoP catalysts could be fine-tuned by the initial Mo/P ratio, which consequently led to different surface properties (e.g., CO uptakes) and catalytic behaviors. Catalysts with high initial Mo amount gave high selectivity to the primary amine, ethylamine, whereas those with high initial P amount created more condensed amines, diethylamine and triethylamine.

Keywords: Molybdenum phosphide; Hydrogenation; Acetonitrile; Selectivity; Amine; Ethylamine; Diethylamine; Triethylamine

1. Introduction

The catalytic hydrogenation of nitriles is an important route for the production of various lower-aliphatic amines that are widely used in the pharmaceutical, agriculture, textile, rubber, and plastic industries. In the process of nitrile hydrogenation, the partially hydrogenated reaction intermediates (imines or Schiff bases) are highly reactive and usually form a mixture of primary, secondary, and tertiary amines that leads to costly product separation processes. An ideal way to solve this problem is to improve the activity and selectivity in the production of amines.

As reviewed by Volf and Pašek [1] and de Bellefon and Fouilloux [2], the activity and selectivity for nitrile hydrogenation are affected by reaction conditions, nitriles, and catalysts. Of these factors, the catalyst plays a decisive role in determining the reaction selectivity. There is consensus that the selectivity to primary amines is high over Ru and Ni, whereas Cu and Rh tend to form secondary amines and Pd and Pt have a high propensity to form tertiary amines [2–5]. Furthermore, the acid–base properties of the catalyst support also have a strong effect on the selectivity [6–9], because the acidic sites are partially responsible for condensation reactions giving condensed amines [10,11].

Up to now, most catalysts applied in nitrile hydrogenation have been transition metals, especially those from the eighth group. However, other nonmetal catalysts (e.g., transition metal phosphides [TMPs]) have been reported only rarely. The TMPs, including MoP [12,13], WP [14], and iron group phosphides [15], are regarded as new active catalytic materials in the hydrotreatment of fuels [16]. As far as we know, only a few researchers [17–19] have studied TMPs as catalysts for hydrogenation reactions other than hydrodesulfurization (HDS) or hydrodenitrogenation (HDN), and no study of the catalysis of nitrile hydrogenation on metal phosphides has been reported. Ni_2P is known to be a better catalyst than MoP in hydrotreatment [16]. For the hydrogenation of acetonitrile, however, we found MoP to be the better catalyst. Therefore, in this study we chose MoP as catalyst and investigated its catalytic activity for the hydrogenation of acetonitrile, which also can be used as a

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probing molecule to study the acid–base properties of catalysts [20–22].

TMPs are usually prepared from the corresponding metal phosphate or phosphate-like precursors by means of temperature-programmed reaction (TPR) [12]. Some studies [23–26] indicated that the composition in the precursors could have a significant effect on the catalytic activity due to the formation of a less active phosphide phase at low P content, or blocking of active sites by excessive P at high P content. In the present work, to avoid the phase change of metal phosphides and decrease the blocking by excessive P, we prepared a series of MoP catalysts by controlling the initial Mo/P ratios in a narrow range of 0.90 to 1.10, close to that expected from the stoichiometry of MoP.

Our results show that the prepared MoP catalysts have different surface compositions when the initial Mo/P ratio changes. The catalysts show quite attractive catalytic performance in the hydrogenation of acetonitrile, especially at a H_2 pressure above 0.2 MPa. Furthermore, the selectivity to amines can be fine-tuned by the initial Mo/P ratio.

2. Experimental

2.1. Catalyst preparation

We have described the preparation of bulk MoP catalysts with different initial Mo/P ratios (Mo/P = 0.90, 0.95, 1.00, 1.05, and 1.10) in a previous publication [27]. First, stoichiometric amounts of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] were mixed with diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] in distilled water. The white solid obtained after evaporation of the water was calcined in air at 773 K for 4 h. The calcined solid was subsequently ground to a powder, and further pressed into pellets, crushed, and sieved to obtain 20- to 40-mesh particles. The particles thus obtained were placed into a quartz reactor and reduced by the TPR method [12] from room temperature (RT) to 573 K in 30 min and from 573 to 923 K in 175 min at a rate of 2 K/min in flowing H_2 (150–200 ml/min). The final temperature of 923 K was maintained for 120 min, followed by cooling to RT in H_2. The sample was then passivated at RT for 6 h in a stream of 1 vol% O_2/N_2 to prevent violent oxidation of the freshly prepared catalysts.

For the sake of brevity, the catalysts with different initial Mo/P ratios were denoted as MoP(0.90), MoP(0.95), MoP(1.00), MoP(1.05), and MoP(1.10).

2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns were obtained on a Rigaku MiniFlex diffractometer with a Cu$K\alpha$ ($\lambda = 1.5418$ Å) radiation source operated at 30 kV and 15 mA. Diffraction patterns were collected from 20° to 80° at a speed of 5°/min. The particle size of the phosphides was determined using Scherrer's equation, $d = 0.9\lambda/\beta\cos\theta$, where d is the mean crystal size (in nm), λ is the wavelength of the X-ray radiation (in nm), β is the full width at half maximum (in radians), and θ is the diffraction angle (in degrees).

The BET surface areas were measured on an ASAP 2000 system with nitrogen adsorption at 77 K. Elemental analysis was carried out with an inductively coupled plasma (ICP) instrument (Plasma-Spectra-II, Leeman Inc., USA) on the prepared MoP catalysts that had been dissolved in aqua regia in a microwave digester.

X-ray photoelectron spectra (XPS) of the catalyst samples were recorded on a KROTOS AMICAS spectrometer (Shimadzu, Japan) with a magnesium K_α ($h\upsilon = 1253.6$ eV) as a radiation source, operating at 10 mA and 12 kV. The residual pressure inside the analysis chamber was about 2×10^{-6} Pa. Charging effects were corrected by adjusting the binding energy of C 1s to 284.8 eV. The precision of the binding energy values was 0.2 eV. MoP(1.00) was chosen for in situ XPS measurement. The sample was first pressed into a pellet, placed on a silica holder, and then pretreated in a H_2 flow at 873 K for 1 h. The in situ XPS analysis was performed after the chamber was cooled to RT and degassed to a vacuum of about 2×10^{-6} Pa.

CO chemisorption measurements were carried out using a CHEMBET-3000 chemisorption analyzer (Quantachrome Instruments). The passivated catalyst (0.5–1.0 g) was purged in a flow of He at RT and then reduced at 873 K in an 80-ml/min flow of H_2 for 1.5 h. After evacuation, the CO chemisorption was measured at 313 K.

2.3. Hydrogenation of acetonitrile

The hydrogenation of acetonitrile was performed in a continuous-flow system. A quartz tube (40 cm long, 7 mm o.d., and 6 mm i.d.) and a stainless tube (35 cm long, 10 mm o.d., and 8 mm i.d.) were used for the reaction at ambient and high pressures, respectively. Before any measurement, 0.25 g of catalyst was pretreated at 873 K in a 90-ml/min flow of hydrogen for 60 min, followed by cooling in hydrogen flow to the desired reaction temperature. Hydrogen was bubbled at a flow rate of 20 ml/min through a stainless saturator containing acetonitrile at 283 K, and then introduced into the reactor. The reactants and products were analyzed by an online gas chromatograph (HP 6890N) equipped with a flame ionization detector and a chromosorb 103 column (3 mm × 2 m).

The conversion is defined as

$$\text{conversion (mol\%)} = 100 \times \frac{CH_3CN_{\text{in}} - CH_3CN_{\text{out}}}{CH_3CN_{\text{in}}}.$$

The selectivity was calculated based on the peak areas of the gas chromatogram by considering the different sensitivity factors of the flame ionization detector. The selectivity to product i is defined as

$$\text{selectivity}_i \text{ (mol\%)} = 100 \times \frac{(\text{corrected area})_i}{\text{sum of all corrected areas}}.$$

3. Results

3.1. Characterization of the catalysts

Fig. 1 shows the XRD patterns of the MoP catalysts. All the patterns demonstrate the same peaks at 28.2, 32.4, 43.3, 57.5, 65.2, 67.8, and 74.4°, similar to the standard pattern of MoP from the JCPDS powder diffraction file (PDF card 24-0771) [28] and those reported in the literature [12,13,27, 29–32]. The estimated average crystallite size was 50 nm for MoP(0.90), 47 nm for MoP(0.95), 47 nm for MoP(1.00), 47 nm for MoP(1.05), and 53 nm for MoP(1.10) (Table 1), based on Scherrer's equation applied to the (101) diffraction peak at 43.3°.

The MoP catalysts had low BET surface areas of about 10 m^2/g (Table 1) similar to those of other bulk TMPs, including iron group phosphides [15], MoP [13,33], and WP [14]. The low surface area of the bulk TMPs was likely due to the high preparation temperature, which can lead to the sintering of the formed crystallites [14].

Elemental analysis (Table 1) showed that the Mo/P ratios in the bulk were close to those in the precursors. The XPS results (Table 1) indicated that the Mo/P surface ratios were lower than that expected from the MoP stoichiometry, indicating that the MoP surface was P-enriched. The P enrichment was higher at higher P content in the precursors. In addition, O species were detected by XPS, which originated from the passivation by air in the preparation process. The surface layer containing O species was usually called a passivating layer, because it prevented the phosphide crystallite from violent oxidation by air [23]. There was a high content of O species at high P content in the precursors. The oxidation states of the Mo and P species were also obtained from the XPS analysis (spectra not shown). Both the Mo and P species exhibited two oxidation states, a low-valence species (MoP) and a high-valence species $[Mo(PO_4)_2]$.

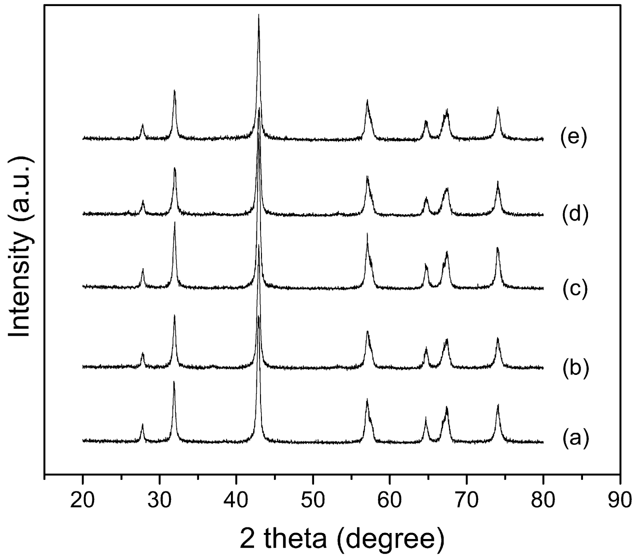


Fig. 1. XRD patterns of (a) MoP(0.90), (b) MoP(0.95), (c) MoP(1.00), (d) MoP(1.05), and (e) MoP(1.10).

MoP(1.00) was chosen for in situ XPS analysis where the sample was pretreated at 873 K in H_2 flow. The results showed that the MoP surface could not be recovered by a H_2 pretreatment, because the O species (PO_4^{3-}) remained in the surface, even with the O/P ratio decreased from 5.0 to 2.9. At the same time, a slight P loss from the surface was observed, with the Mo/P ratio increasing from 0.77 to 0.82.

The CO uptake was determined to evaluate the surface concentration of the metallic sites of the MoP catalysts. As listed in Table 1, the CO uptake increased from 1.2 for MoP(0.90) to 1.8 for MoP(1.00). However, the CO uptake of MoP(1.10) was as high as 7.4, much higher than those of the other two catalysts, indicating that a high concentration of metallic Mo sites was present in the surface of MoP(1.10).

3.2. Hydrogenation of acetonitrile

Fig. 2 shows the catalytic performance of the MoP catalysts with different initial Mo/P ratios in the hydrogenation of acetonitrile at ambient pressure and 473 K after 120 min on stream. According to the gas chromatography analysis, the hydrogenation products were ethylamine (EA), diethylamine (DEA), triethylamine (TEA), and traces of hydrocarbons. For this series of MoP catalysts, the conversion of CH_3CN roughly increased with the initial Mo/P ratio and reached an optimal value at initial Mo/P = 1.00. The order for the CH_3CN conversion was MoP(1.00) > MoP(1.10) ≈ MoP(1.05) > MoP(0.95) > MoP(0.90).

The turnover frequencies (TOFs) were calculated from the conversions and CO uptakes (Table 1). MoP(1.00) had the highest TOF of 72 h^{-1} among the tested catalysts, comparable to

Table 1
Some physicochemical data of the MoP catalysts

Catalysts	Crystallite size[a] (nm)	BET result (m^2/g)	Bulk composition	Surface composition	CO uptake[b] ($\mu mol/m^2$)	TOF[c] (h^{-1})
MoP(0.90)	50	9.3	$Mo_{0.85}P$	$Mo_{0.71}PO_{5.36}$	1.2	22
MoP(0.95)	47	10.1	$Mo_{0.94}P$	$Mo_{0.73}PO_{5.47}$	–	–
MoP(1.00)	47	11.1	$Mo_{0.97}P$	$Mo_{0.77}PO_{5.04}$	1.8	72
MoP(1.05)	47	8.6	$Mo_{1.07}P$	$Mo_{0.88}PO_{4.00}$	–	–
MoP(1.10)	53	9.1	$Mo_{1.09}P$	$Mo_{0.90}PO_{3.20}$	7.4	10

[a] Calculated by Scherrer's equation for the (101) diffraction peak at 43.3°.
[b] Stoichiometry of CO/active site is assumed to be 1 for the tested samples.
[c] After 120 min on stream. Reaction conditions: 0.25 g catalyst, H_2/acetonitrile = 16.3, 473 K, and ambient pressure.

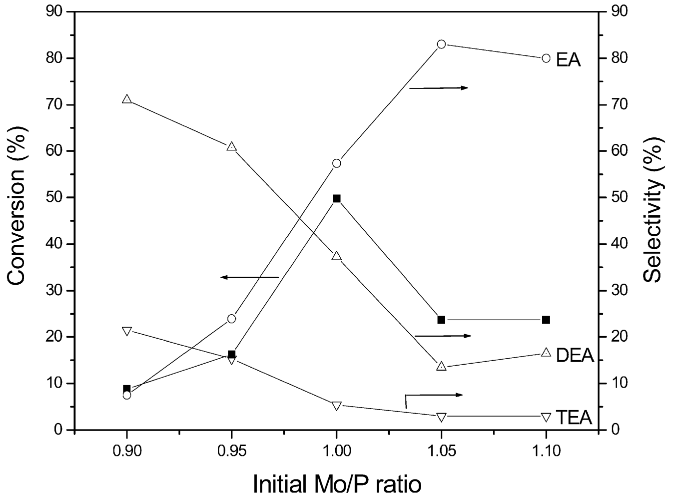


Fig. 2. Catalytic performance of the MoP catalysts with different initial Mo/P ratios for acetonitrile hydrogenation after 120 min on stream. Reaction conditions: 473 K, ambient pressure, WHSV = 4800 ml g^{-1} h^{-1}, H_2/acetonitrile = 16.3.

that of some Ni catalysts measured under similar reaction conditions [34]. MoP(1.10) had a lower TOF than MoP(0.90), even though its conversion was higher than that of MoP(0.90).

Fig. 2 also indicates that the selectivities to amine products were dependent on the initial Mo/P ratios. The selectivity to primary amine (EA) was higher for catalysts with high initial Mo/P ratios, with MoP(1.10) giving the highest selectivity of about 80%. In contrast, the condensed amines (DEA and TEA) were the main products for catalysts with low initial Mo/P ratios. The selectivity to DEA for MoP(<1.00) was >60%, and the total selectivity to the condensed amines was about 90%. For this series of MoP catalysts applied in the hydrogenation of acetonitrile at ambient pressure, the selectivity to EA was in the order MoP(1.10) ≈ MoP(1.05) > MoP(1.00) > MoP(0.95) > MoP(0.90), whereas the selectivities to DEA and TEA were in the reverse order.

Fig. 3 shows the conversion of acetonitrile at different H_2 pressures (0.1–1.0 MPa) for the MoP catalysts as a function of time on stream. MoP(0.90) had very low activity at ambient pressure, whereas MoP(1.00) and MoP(1.10) showed high initial activity but suffered severe deactivation. The activity and stability of all of the catalysts were greatly improved with increasing H_2 pressure. In the steady state of the reaction, MoP(1.00) gave complete conversion of CH_3CN when the H_2 pressure reached 0.2 MPa, whereas for MoP(1.00) and MoP(1.10), the pressure point of complete conversion was at 0.4 MPa and 1.0 MPa, respectively.

Fig. 4 shows the effect of H_2 pressure on the activity and the selectivities to amine products for the MoP catalysts. For MoP(1.10), the selectivities to amines are hardly affected by the H_2 pressure. For MoP(1.00), the selectivity to TEA increased gradually with the H_2 pressure, whereas the selectivities to EA and DEA decreased slightly. More clearly than MoP(1.00), MoP(0.90) showed an increasing tendency of TEA selectivity and decreasing tendency of DEA selectivity against H_2 pressure.

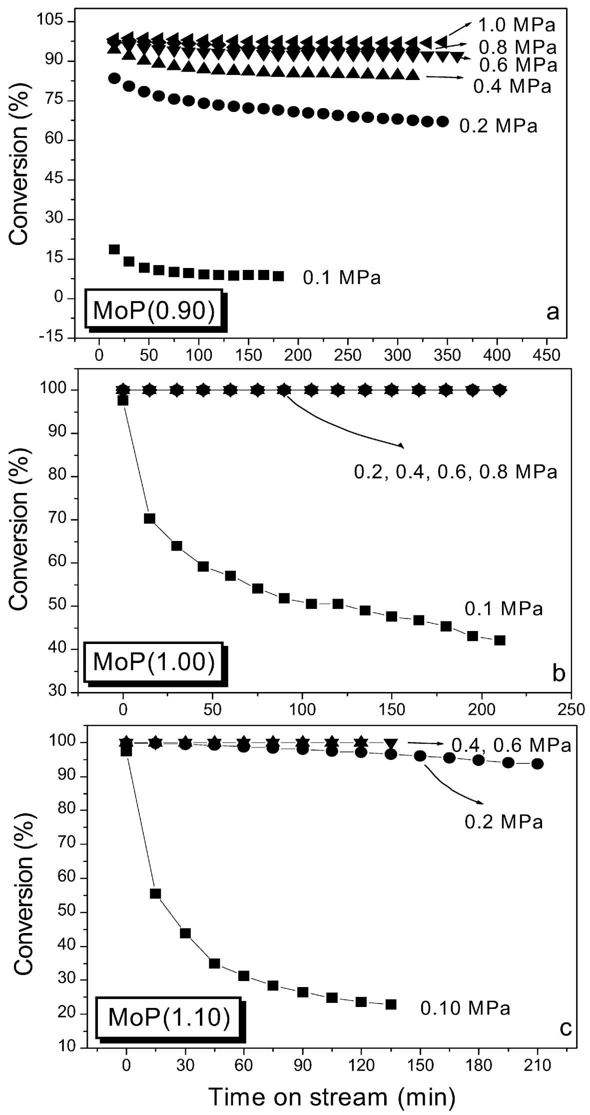


Fig. 3. Conversion of acetonitrile at different pressures of H_2 (0.1–1.0 MPa) for (a) MoP(0.90), (b) MoP(1.00), and (c) MoP(1.10) as a function of time on stream. Reaction conditions: $T = 473$ K, WHSV = 4800 ml g^{-1} h^{-1}.

Fig. 5 shows the effect of temperature on the activity and the selectivities to amine products for the MoP catalysts at ambient pressure. The activity increased with reaction temperature (Fig. 5a), whereas the selectivities were differently affected by temperature (Figs. 5b–5d). For MoP(1.00), the effect of temperature on the selectivities was not clear. For MoP(0.90), however, the selectivities to DEA and TEA decreased at elevated temperatures with increasing EA selectivity, whereas for MoP(1.10), the selectivities to amine products were reversely affected by temperature.

4. Discussion

4.1. Surface properties of MoP catalysts with different initial Mo/P ratios

It is well known that for the preparation of TMPs, the P amount in the precursor is required to be slightly higher than

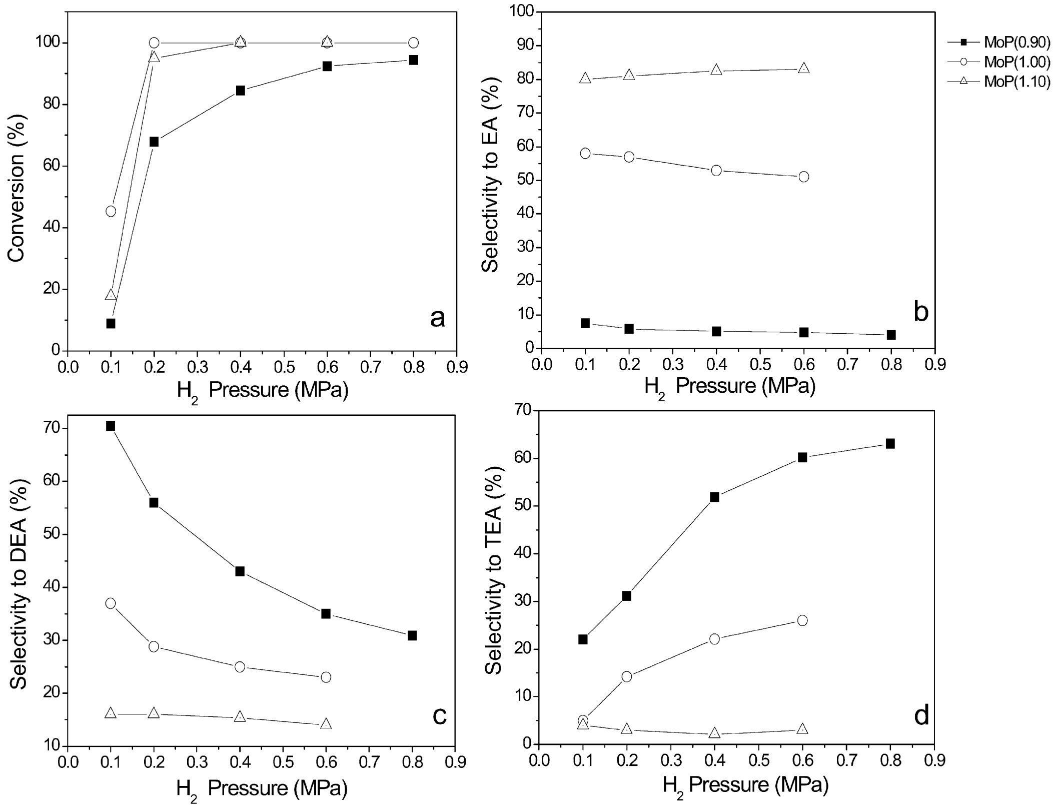


Fig. 4. Effect of H_2 pressure on the (a) conversion and the selectivities to (b) EA, (c) DEA, and (d) TEA for MoP(0.90), MoP(1.00), and MoP(1.10). Reaction conditions: $T = 473$ K, WHSV $= 4800\ \text{ml}\,\text{g}^{-1}\,\text{h}^{-1}$, reaction time = 180 min.

that expected from the stoichiometry of the TMPs to avoid the formation of a phase deficient in phosphorus, due to P loss during the preparation process [24,35]. In the present work, however, we found that the MoP catalysts could be synthesized without any additional phase (Fig. 1) by tuning the Mo/P ratios in the oxidic precursors close to the stoichiometry of MoP (0.90–1.10), even though the initial P amount was slightly insufficient.

When MoP catalysts are prepared with different initial Mo/P ratios and have the same bulk constitution, their surface composition must differ. This is indeed demonstrated by the XPS analysis (Table 1). For this series of catalysts, the surface was P-enriched; that is, the surface P/Mo ratios were higher than that expected from the stoichiometry of MoP. Abu and Smith [33] also observed a slight P enrichment for bulk MoP. Korányi [36] reported this effect for other unsupported TMPs, such as Ni phophides, and ascribed it to surface oxidation. In this study, the prepared MoP catalysts became more P enriched at higher initial P amount concomitantly with the increasing O content in the surface, which also implies that surface oxidation might lead to P-enrichment.

The P-enrichment can have an obvious effect on the surface properties of the MoP catalysts. On the one hand, the excessive P may block surface metallic sites [24]. As a result, for catalysts with lower initial Mo/P ratios, the stronger P-enrichment leads to more blocking of metallic sites, and thus lower CO uptakes, whereas CO uptakes are higher for catalysts with higher initial Mo/P ratios (Table 1). But the CO uptake of MoP(1.10) was much higher than those of MoP(1.00) and MoP(0.90). We assume that more P is lost from the surface of MoP(1.10) than from the surface of the others when the catalysts were pretreated at high temperatures in H_2 flow. This surface loss of P is supported by the in situ XPS results. On the other hand, the surface P species, including phosphide and phosphate, may result in the acidic properties of the metal phosphides, as observed by Abu and Smith [33] and ascribed to the incomplete reduction of the metal phosphates. Although we detected residual phosphate species in the reduced MoP surface as shown by the in situ XPS analysis, the causal relationship between this species and the acidic properties awaits more direct experimental proof.

4.2. Catalytic performance of MoP catalysts with different initial Mo/P ratios

Up to now, most catalysts applied in nitrile hydrogenation have been transition metals, especially those from the eighth group. In this study, we describe for the first time a new type of nonmetal catalyst, MoP, in the hydrogenation of acetonitrile. At ambient pressure and 473 K, MoP catalysts with initial Mo/P $\geqslant 1$ gave initial conversions of 100% (Fig. 3). Although showing low activity in the steady state of the reaction due to deactivation, MoP(1.00) gave the highest TOF value (Table 1), 72 h^{-1}, close to the activity of some Ni catalyst under similar reaction conditions [34]. The activity of the MoP catalysts seems to be very sensitive to H_2 pressure. All of the catalysts exhibiting significantly improved activity and stability at ele-

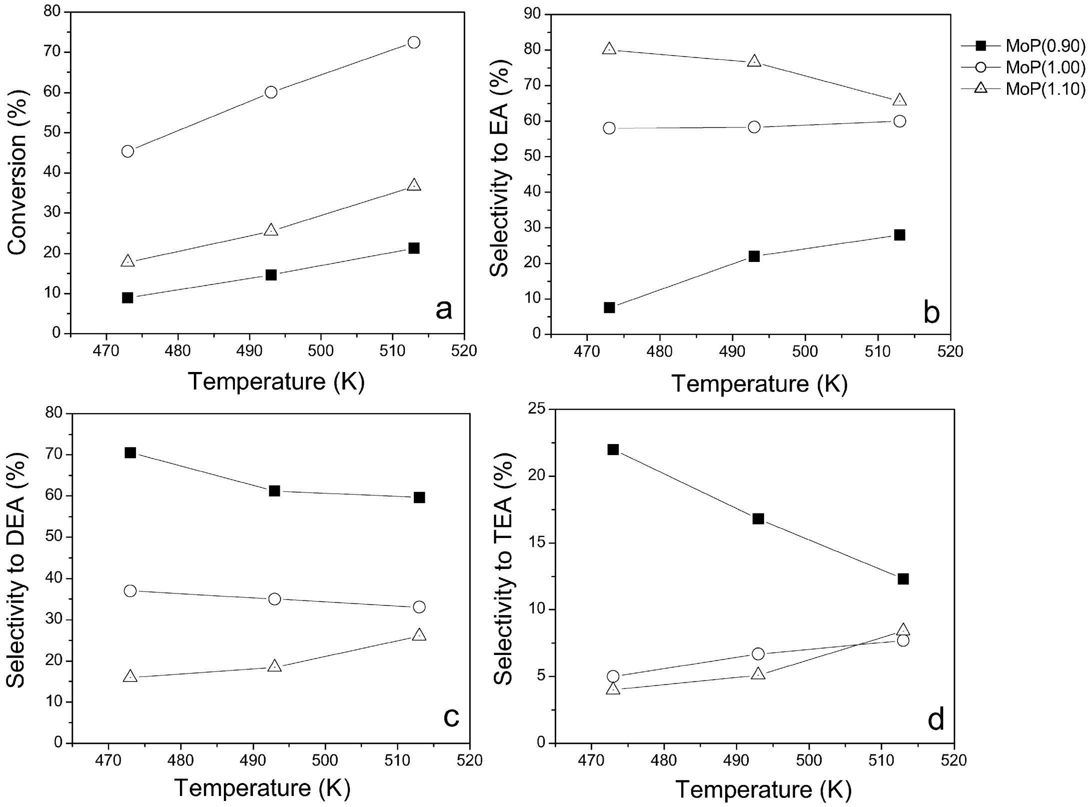


Fig. 5. Effect of temperature on the (a) conversion and the selectivities to (b) EA, (c) DEA, and (d) TEA for MoP(0.90), MoP(1.00), and MoP(1.10). Reaction conditions: ambient pressure, WHSV = 4800 ml g^{-1} h^{-1}, reaction time = 180 min.

vated H_2 pressure (Fig. 3). Especially when the H_2 pressure was increased beyond 0.2 MPa, MoP(1.00) attained a conversion of 100% with no deactivation.

Another interesting property is that the selectivities of the MoP catalysts can be fine-tuned by the initial Mo/P ratio (Fig. 2). MoP(1.10) gave the highest selectivity to EA (∼80%) at ambient pressure and 473 K, with a small decrease observed at elevated H_2 pressure (Fig. 4). Some nickel catalysts supported on basic supports gave high selectivity (80–90%) to EA, whereas some supported on neutral or acidic supports gave a value $<20\%$ [37]. Our MoP(1.10) catalyst showed an EA selectivity comparable to those of the supported Ni catalysts on basic supports despite slightly higher temperature (473 K). When the initial Mo/P ratio was decreased, condensed amines (DEA and TEA) were the main products. In addition, the selectivities to DEA and TEA could be further fine-tuned by the H_2 pressure. DEA had a higher selectivity at low pressures, whereas TEA had a higher selectivity at high pressures (Fig. 4).

In summary, MoP is a promising catalyst in the hydrogenation of acetonitrile because the catalytic activity is very sensitive to the H_2 pressure, and the reaction selectivity can be tuned by changing the initial Mo/P ratio in a narrow range.

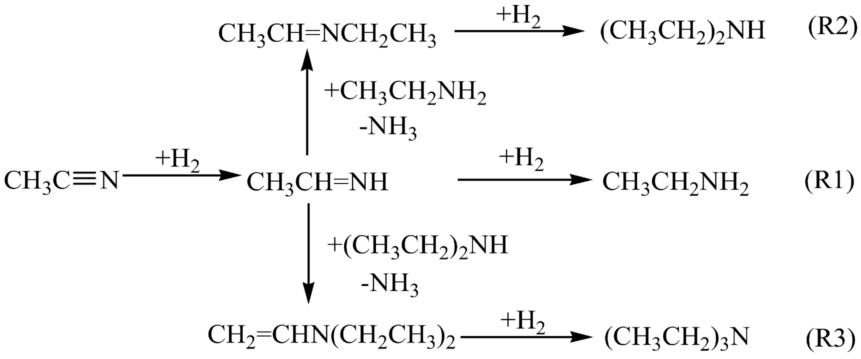
4.3. Reaction mechanism of the hydrogenation of acetonitrile on the MoP catalysts

Although the hydrogenation of acetonitrile is widely used in the industry, its mechanism remains incompletely understood. Von Braun's mechanism [38] lacks sufficient experimental proof. The bifunctional mechanism of Verhaak et al. [10] fails to confirm some views [3,5,39]. Recently, Huang and Sachtler [40–42] proposed a novel mechanism through H/D exchange experiments, in which dissociation of C–H bonds of some CH_3CN molecules results in H transfer to other CH_3CN molecules.

In accordance with the literature [2,5,10,38,41–45], we present a general scheme for acetonitrile hydrogenation in Scheme 1. In this scheme, the addition of a H_2 molecule to the carbon–nitrogen triple bond of acetonitrile forms a reactive imine intermediate, which results in either the primary amine (EA) through further hydrogenation (reaction R1), or the secondary/tertiary amine (DEA/TEA) through a condensation reaction with the primary/secondary amine (reaction R2/R3).

Verhaak et al. [10] proposed that the hydrogenation step proceeded on the metallic sites of the catalysts, while the condensation reaction proceeded on the acidic sites. In the present work, the surface Mo species of the MoP catalysts were expected to play the role of metallic sites for reaction R1, whereas the surface P species were associated with the acidic sites for reactions R2 and R3 to produce DEA and TEA in the hydrogenation of acetonitrile.

On the one hand, CH_3CN or the formed amines can be strongly adsorbed on the metallic sites and prevent reaction R1 [46–48]. That is why the MoP catalysts [especially MoP(1.00) and MoP(1.10)] showed high initial activity but suffered rapid deactivation (Fig. 3). However, with increasing H_2 pressure,



$$\begin{tikzcd}
& CH_3CH{=}NCH_2CH_3 \arrow[r, "+H_2"] & (CH_3CH_2)_2NH \quad (R2) \\
CH_3C{\equiv}N \arrow[r, "+H_2"] & CH_3CH{=}NH \arrow[u, "+CH_3CH_2NH_2" right, "-NH_3" left] \arrow[r, "+H_2"] \arrow[d, "+(CH_3CH_2)_2NH" right, "-NH_3" left] & CH_3CH_2NH_2 \quad (R1) \\
& CH_2{=}CHN(CH_2CH_3)_2 \arrow[r, "+H_2"] & (CH_3CH_2)_3N \quad (R3)
\end{tikzcd}$$

Scheme 1. Reaction scheme for acetonitrile hydrogenation.

the strongly adsorbed species can be readily substituted by hydrogen species on the active sites, consequently improving the activity and stability of the MoP catalysts (Figs. 3 and 4a). On the other hand, the strongly adsorbed species can migrate from the metallic sites to the surface acidic sites and free the former for more hydrogenation reactions (R1), a phenomenon known as synergetic effect [49]. MoP(1.10) has more surface Mo sites but few acidic sites, leading to a slight synergetic effect between these two active sites. This effect is enhanced when the number of acidic sites increases for MoP(1.00) and MoP(0.90). Therefore, MoP(1.10) showed lower activity than MoP(1.00) (Fig. 3) and even lower TOF than MoP(0.90) (Table 1) in the steady state of the reaction. However, a comparable amount of metallic and acidic sites may be necessary for an optimal synergetic effect on the activity. That is why MoP(1.00) showed the highest activity and TOF.

Because EA is formed through reaction R1, proceeding on the metallic sites, while DEA and TEA are formed by reactions R2 and R3, respectively, proceeding on the acidic sites, the selectivities to these amine products increase monotonically with the amount of the corresponding active sites in the MoP surfaces (Fig. 2). Furthermore, with the increase of the H_2 pressures, the strongly adsorbed amines can be removed from the metallic sites by hydrogen species to the adjacent acidic sites. As a result, more condensation reactions can proceed on the acidic sites. This effect becomes stronger for the catalysts with a higher amount of surface P species. This is why MoP(0.90) and MoP(1.00) showed an increasing selectivity to TEA at elevated H_2 pressures (Fig. 4).

Finally, two factors should be noted to explain the effect of temperature on selectivity (Fig. 5). First, the acid–base interaction between acidic sites and amines is in the order EA < TEA < DEA [50] according to their basic character [51]. Second, the temperature effect is stronger for reaction R1 than for R2 and R3, because the condensation reaction has a higher activation energy than the hydrogenation reaction [47]. On the surface of MoP(0.90), the major species is the P species, and the formed amines adsorb mostly on the acidic sites. Based on the first factor, EA would be expected to desorb more easily at elevated temperatures compared with the other amines, resulting in increased selectivity to EA and decreased selectivities to DEA and TEA. On the surface of MoP(1.10), a certain amount of metallic sites exist for reaction R1, but few acidic sites exist for reactions R2 and R3. Due to the second factor, the selectivity to EA decreases, and those to DEA and TEA increase, with increasing reaction temperature. Comparable amounts of surface metallic and acidic sites in MoP(1.00) might result in a balance between these two factors and consequently in little change in the selectivities.

5. Conclusion

In the present work, MoP catalysts showed the same bulk phase of MoP but a different surface composition with changes in the initial Mo/P ratio of 0.90–1.10. In situ XPS analysis indicated that the MoP surface could not be recovered by pretreatment with H_2; some O species remained. The MoP catalysts were used to catalyze the hydrogenation of acetonitrile for the first time. At ambient pressure and 473 K, the catalysts exhibited high initial activity but suffered severe deactivation. When the H_2 pressure was increased, the activity and stability were greatly improved. Furthermore, the selectivities to amine products could be fine-tuned by the initial Mo/P ratio of the catalysts. The primary amine was produced mainly at high Mo content, whereas the condensed amines were produced mainly at high P content. It is assumed that the surface Mo species act as metallic sites to form EA, while the surface P species are responsible for the production of DEA and TEA. Therefore, MoP can be considered a promising catalyst for the hydrogenation of acetonitrile.

Acknowledgments

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