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1. Introduction

Selective hydrogenation of α,β -unsaturated aldehydes has attracted much attention in recent years because the products are widely used in pharmaceuticals, perfumes and flavors.¹ One of the main challenges is to improve the reduction of C=O to produce unsaturated alcohols because the hydrogenation of the C=C bond is thermodynamically favoured.²⁻⁴ Selective hydrogenation of cinnamaldehyde (CAL) is a representative example of these reactions. The hydrogenation of CAL proceeds via first hydrogenation of C=C and C=O double bonds to hydrocinnamaldehyde (HALD) and cinnamyl alcohol (COL), respectively, followed by total hydrogenation of these products to hydrocinnamyl alcohol (HALC) (Scheme 1). It's well known that noble metals (Pt, Pd, Au, Rh and Ru) are much more active in the hydrogenation of CAL.⁵⁻⁸ Among them, Pt-based catalysts have been the focus for a long time due to their excellent catalytic performance in the hydrogenation of carbonyl compounds.9-13 However, for large-scale



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The introduction of a suitable co-catalyst is a promising way to improve the catalytic efficiency of Pt catalysts. Herein, SBA-15 modified with well-dispersed Mo₂N nanoparticles (NPs) is synthesized by anchoring phosphomolybdic acid (HPM) on aminated SBA-15 (SBA-15-NH₂) primarily, followed by nitridation treatment under NH₃. After loading of Pt, the Pt-Mo₂N/SBA-15 catalyst with close-contact Pt and Mo₂N NPs can be formed. The intensive interaction of Pt and Mo₂N benefited from the close contact is verified by XRD and XPS tests. As a result, the ternary Pt-Mo₂N/SBA-15 catalysts have shown superior performance to Pt/SBA-15 catalysts for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. The TOF over the 1 wt% Pt-Mo₂N/SBA-15 catalyst is close to that over the 3 wt% Pt/SBA-15 catalyst, but its selectivity to cinnamyl alcohol (COL) is 2.5 times that of 3 wt% Pt/SBA-15. The promoted activity of Pt-Mo₂N/SBA-15 is mainly attributed to the synergistic effect of Pt and Mo₂N NPs, which can cause the full development of the catalytic ability of Pt, thus reducing the Pt usage, through increasing the dispersion of Pt NPs and the fraction of Pt⁰ species in the catalyst.

practical application, it is very essential to decrease the usage of Pt due to its high cost and scarcity. Many methods have been developed to enhance the performance of Pt-based catalysts by tuning the species, shape or size of the platinum NPs. Special supports may lead to high catalytic performances as compared with conventional supports because of the specific interactions between the support and Pt nanoparticles, such as carbon nanotubes^{14,15} and graphene.¹⁶ Meanwhile, addition of a metal co-catalyst (oxide) to supported Pt catalysts is a promising route. Typically, the use of a second metal (Fe, Co)¹⁵ or metal oxides (TiO₂,¹⁷ ZnO (ref. 18)) to promote the catalytic activity of Pt has been demonstrated, which is ascribed to the electron transfer between the promoters and the metallic Pt.

Recently, transition metal nitrides and carbides have received special attention in the catalysis field including





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traditional catalysis and electrocatalysis.¹⁹⁻³⁰ For example, the nitrides and carbides of molybdenum (Mo₂N, Mo₂C) possess similar catalytic properties to Pt-group metals,³¹ which should be due to the fact that the incorporation of nitrogen or carbon atoms into the lattice of Mo atoms extends the Mo-Mo bond distance and shifts of the d-band centre to a value below the original Fermi level. In traditional catalysis, most of the attention has been focused on reactions involving hydrogen activation/transfer, and efficacies of some metal nitrides parallel to those of precious metals have also gained attention, 25, 26, 32-34 although direct substitution of these noble metals is often lacking. What's more, based on our earlier works,^{35–39} the experimental and theoretical studies indicated that carbides (WC, Mo₂C) and nitrides (WN) are effective co-catalysts of precious metals (Pt, Pd) facilitating the electro-oxidation of fuel molecules via a "synergistic action" mechanism. However, there is little report on the application of transition metal nitrides in selective hydrogenation so far. Therefore, we wonder whether the synergistic effect between Pt and Mo₂N could also be effective for enhancing the selectivity to COL at high conversion of CAL with less consumption of Pt.

Generally, the obtained metal nitrides have wide size distributions in the range of micrometers,⁴⁰⁻⁴³ which is a disadvantage to the possibility of Pt being in contact with Mo₂N. So, the key is to explore an effective method to obtain supported Mo₂N with a small size. Fortunately, in our previous work, small-sized and well-dispersed WN NPs of 2-3 nm on GO-derived graphene were synthesized successfully by using heteropolyacid H₄SiW₁₂O₄₀ clusters as a W source.³⁹ Thus, another heteropolyacid cluster, the Keggin-type phosphomolybdic acid (H₃PMo₁₂O₄₀, HPM), would be a suitable precursor for the synthesis of small-sized Mo₂N NPs in view of its small size, close to the nanometer level, and stable structure.44 Besides, SBA-15, as a kind of ordered mesoporous material, has a high specific surface area and suitable pore structure, which could facilitate the dispersion of Mo₂N. SBA-15 is always inert in selective catalysis on account of the weak acidity resulting from the silanol groups located on the pore walls. Thus, the inactive siliceous properties of ordered mesoporous SBA-15 make it an ideal support for investigating the interaction between Pt and Mo2N with less interruption by metal-support interaction.45

Encouraged by the above considerations, in this study, SBA-15 modified with Mo_2N ($Mo_2N/SBA-15$) was synthesized by anchoring HPM clusters on aminated SBA-15, followed by nitridation under an NH_3 atmosphere. Then, the ternary Pt- $Mo_2N/SBA-15$ sample was obtained by the reduction of the Pt precursor on the $Mo_2N/SBA-15$ composite. Meanwhile, the catalytic performance was investigated over the ternary Pt- $Mo_2N/SBA-15$ sample for the selective hydrogenation of CAL. The results showed that the ternary Pt- $Mo_2N/SBA-15$ sample was superior to Pt/SBA-15 in selective hydrogenation of CAL to COL. The excellent performance of the Pt- $Mo_2N/SBA-15$ catalyst could be attributed to the enhancement of Pt dispersion and the increase in the amount of Pt⁰ species, resulting

from the synergistic effect between Pt and Mo_2N . The method developed here provides a new strategy for increasing the selectivity to unsaturated alcohols with low usage of Pt.

2. Experimental sections

2.1. Chemicals

Keggin-type phosphomolybdic acid ($H_3PMo_{12}O_{40}$, HPM), H_2PtCl_6 and 3-ammonia propyl triethoxy silane ($NH_2(CH_2)_3$ -Si(OC_2H_5)₃, APTES) were purchased from Sinopharm Chemical Reagent Co., Ltd. Triblock poly(ethylene oxide)-*b*poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer Pluronic P123 ($M_w = 5800$, $EO_{20}PO_{70}EO_{20}$), 5 wt% Pt/C hydrogenation catalyst and CAL were purchased from Aldrich. Isopropanol, tetraethyl orthosilicate (TEOS) and ethanol were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Silica gel was purchased from Aladdin. All regents were used as received without further purification.

2.2. Catalyst preparation

SBA-15 was synthesized according to the method of Stucky and coworkers.⁴⁶ Typically, 4.0 g of Pluronic P123 was dissolved in 120 mL of 2 mol L^{-1} hydrochloric acid solution and 30 mL of water at around 30 °C followed by the addition of 8.5 g of TEOS. After being stirred at 40 °C for 24 h, the mixture was transferred into an autoclave and aged at 100 °C for 24 h. Then, the white precipitate was collected by filtration and dried at 80 °C. The product was obtained by removing the template at 550 °C for 5 h.

SBA-15 modified with amine groups (SBA-15-NH₂) was prepared as follows: 0.5 g of SBA-15 was added to 2.0 mL of APTES diluted with 2.0 mL of ethanol. After stirring for 24 h, the excess APTES was removed by washing with ethanol and centrifugation. Finally, the obtained solid was dried at 60 °C for 12 h.

HPM/SBA-15-NH2 was synthesized through a solventevaporation-induced impregnation and vacuum-assisted process. In a typical procedure, the as-prepared 0.5 g SBA-15-NH₂ was placed in a suction bottle, and then the bottle was sealed with a dropping funnel containing 0.15 g of HPM in a 10 mL mixed solution of ethanol and water. After the suction bottle had been maintained under vacuum for 30 min, the HPM solution was added dropwise, so that the HPM solution would aid full infusion into the pore of SBA-15-NH₂. Then, the suspension was transferred into a 50 mL beaker and stirred at room temperature (20-30 °C) until removal of the solvent. After washing with ethanol and drying at 60 °C for 4 h, the precursor HPM/SBA-15-NH2 was heated to 600 °C inside a tubular furnace with a heating rate of 3 °C min⁻¹ under a N2 atmosphere. Then, when the temperature reached 600 °C, N₂ was cut off and the sample was exposed to pure NH₃ (80 ml min⁻¹) for 3 h at 600 °C. After slowly cooling to room temperature, the black powder Mo₂N/SBA-15 was obtained.

The 3 wt% Pt- $Mo_2N/SBA-15$ sample was formed by a sodium borohydride (NaBH₄) method according to a

procedure described earlier.⁴⁷ Typically, 0.3 g of $Mo_2N/SBA-15$ composite was impregnated with 2.4 g of ethanol solution of H_2PtCl_6 (19.3 mmol L^{-1}). After 6 h of stirring, the slurry was evaporated to remove the excess solvent, followed by drying at 120 °C overnight. Then, the catalyst precursors were reduced in an aqueous solution of NaBH₄. The 1 wt% Pt- $Mo_2N/SBA-15$ and 2 wt% Pt- $Mo_2N/SBA-15$ samples were also prepared by the same method. As references, Pt supported on SBA-15 with different Pt contents (1 wt%, 2 wt% and 3 wt%) and silica gel with a 3 wt% Pt content were also prepared under similar conditions, which were denoted as 1 wt% Pt/SBA-15, 2 wt% Pt/SBA-15, 3 wt% Pt/SBA-15 and 3 wt% Pt/SiO₂, respectively.

2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 Advance X-ray diffractometer with Cu K α (λ = 1.5418 Å) radiation (40 kV, 40 mA). The scan range of the wide-angle XRD was 10–80°. As for the small-angle XRD, the scan range was 0.5–5°, and the scanning rate was 1° min⁻¹.

The properties of the porous structures were derived from N_2 adsorption-desorption isotherm measurement at -196 °C with a Micromeritics Tristar II surface area and porosity analyzer for mesoporous materials. In each case, the catalyst (more than 100 mg) was degassed under vacuum at 150 °C for 5 h before measurement. The pore size distribution and surface area were determined from desorption isotherms by the BJH and BET methods, respectively.

The morphology and structure of the samples were analyzed by a JEM-2100 transmission electron microscope (TEM) with an acceleration voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) was performed by using a Kratos-AXIS ULTRA DLD with an Al K α radiation source. Binding energies (BE) are referenced to the C (1s) binding energy of carbon taken to be 284.7 eV.

The content of platinum and molybdenum in the Pt- $Mo_2N/SBA-15$ catalysts was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), which was performed by using a PerkinElmer Optima 7000DV analyzer. Before measurement, each sample was dissolved in a diluted HF and chloroazotic acid solution.

The content of molybdenum in $Mo_2N/SBA-15$ was also analyzed by X-ray fluorescence spectrometry (XRF) using a Bruker S4 Explorer instrument.

2.4. Selective hydrogenation of cinnamaldehyde

The catalyst (50 mg) was degassed at 150 °C for 2 h in pure N₂. Then, the catalyst was mixed with 1.00 g of CAL and 30 mL of isopropanol. The mixture was subsequently transferred to a 100 mL autoclave. After flushing again three times with N₂ at 5 bar and three times with H₂ at 5 bar, the reaction was allowed to proceed at 80 °C under 10 bar of H₂ for 2 h.

The products were analyzed by GC (Agilent 7820 A) with a flame ionization detector (FID) and a HP-5 capillary column (30 m \times 0.32 mm \times 0.25 mm). Quantitative analysis of the

products was performed *via* calibration curves using benzyl alcohol as an internal standard. The products were further identified by GC-MS (Agilent 6890/5973N).

3. Results and discussion

3.1. Synthesis and characterization of Pt-Mo₂N/SBA-15

The Pt-Mo₂N/SBA-15 sample was prepared by the four steps shown in Scheme 2: firstly, the positively charged APTES reacts with the surface Si-OH of SBA-15 to form SBA-15-NH₂ with a positive surface charge (step 1). The Fourier transform infrared (FT-IR) spectra of SBA-15-NH₂ (Fig. S1[†]) show that the functional groups (-NH₂) are grafted on the surface of mesoporous silica SBA-15, and the content of APTES on SBA-15-NH₂ is about 16.2 wt% as clarified by the thermogravimetric test (Fig. S2[†]). Secondly, the welldispersed Mo₂N modified SBA-15 (Mo₂N/SBA-15) was synthesized by anchoring HPM on SBA-15-NH2 (step 2, Fig. S3[†]), followed by nitridation under an NH₃ atmosphere (step 3). The Mo₂N loading was about 22 wt% for the Mo₂N/SBA-15 sample based on ICP-OES. It was further confirmed by X-ray fluorescence spectrometry (XRF) analysis (Table S1[†]). Finally, the Pt-Mo₂N/SBA-15 catalyst was obtained by controlling the growth of Pt NPs on Mo₂N/SBA-15 using a NaBH₄ method (step 4). A series of characterizations were carried out for the Pt-Mo₂N/SBA-15 samples.

The Mo₂N/SBA-15 and 3 wt% Pt-Mo₂N/SBA-15 samples were investigated by low-angle XRD (Fig. 1). SBA-15 and 3 wt% Pt/SBA-15 were also tested under the same conditions as the references. All the samples exhibited the typical (100), (110), and (200) diffraction peaks of SBA-15 in the region of $2\theta = 0.5-2^{\circ}$, characteristic of a highly ordered hexagonal mesostructure, which remained intact during post-grafting. In contrast to SBA-15 (Fig. 1a), the diffraction peaks of the Mo₂N/SBA-15 (Fig. 1b) and 3 wt% Pt-Mo₂N/SBA-15 (Fig. 1c) samples shifted to a high-angle region and the intensity of the (100) reflection peak was reduced, indicating that some Mo₂N and Pt NPs were scattered inside the pore channels of SBA-15.

The textural properties of the samples were investigated by N₂ adsorption–desorption isotherm measurement. As shown in Fig. 2A, the isotherms of the $Mo_2N/SBA-15$, 3 wt% Pt– $Mo_2N/SBA-15$ and 3 wt% Pt/SBA-15 samples exhibited



Scheme 2 Procedure for the synthesis of the $\ensuremath{\text{Pt-Mo}_2N}\xspace{\text{NSBA-15}}$ sample.



Fig. 1 Low-angle XRD patterns of (a) SBA-15, (b) $Mo_2N/SBA-15,$ (c) 3 wt% Pt-Mo_2N/SBA-15 and (d) 3 wt% Pt/SBA-15.



Fig. 2 (A) Nitrogen adsorption-desorption isotherms and (B) the corresponding pore size distributions calculated from the desorption isotherms using the BJH method for (a) SBA-15, (b) $Mo_2N/SBA-15$, (c) 3 wt% Pt-Mo₂N/SBA-15 and (d) 3 wt% Pt/SBA-15 samples.

representative type IV curves with an obvious hysteresis loop at a relative pressure (P/P_0) of 0.60–0.75 according to the IUPAC classification. It is very similar to that of pure silica SBA-15, having a narrow pore size distribution of the cylindrical channels.⁴⁶ The main part of the hysteresis loops remained in the same relative pressure range. The P/P_0 position of the inflection points is clearly related to the diameter in the mesoporous range, and the sharpness of the step indicates the uniformity of the mesoporous size distribution. However, the desorption branch extends to a lower relative pressure for the Mo₂N/SBA-15 and 3 wt% Pt–Mo₂N/SBA-15 samples, suggesting a partial loss of structural organization and the formation of some narrower pores by the introduction of Mo₂N and Pt one by one. Meanwhile, the porosity parameters, such as the BET specific surface area and cumulative pore volume, are listed in Table 1, and the pore size distributions are displayed in Fig. 2B. The BET surface areas of SBA-15 and Mo₂N/SBA-15 were 758 and 370 m² g⁻¹, respectively. The cumulative pore volumes for the SBA-15 and Mo₂N/SBA-15 samples were 1.05 and 0.68 cm³ g⁻¹. The mesoporous size distribution in Fig. 2B showed that the pore diameters of the above two samples were 9.4 and 8.0 nm. It's worth noting that the specific surface area, pore volume and pore size of the Mo₂N/SBA-15 sample decreased compared with those of the SBA-15 host, because the introduced Mo₂N occupied the mesopore space leading to the decrease in pore width. Moreover, the ordered channel of SBA-15 was not destroyed or blocked by the Mo₂N NPs, which indicates that Mo₂N may be well dispersed on the channel surface of SBA-15. For the 3 wt% Pt-Mo₂N/SBA-15 sample, the corresponding physicochemical parameters were further reduced. For the 3 wt% Pt-Mo₂N/SBA-15 sample, the BET surface area, cumulative pore volume and pore size distribution decreased to 350 m² g⁻¹, 0.59 cm³ g⁻¹ and 7.5 nm, respectively, suggesting that Pt loaded on the Mo₂N/SBA-15 composite also occupied the surface and channel of the SBA-15 support.

The TEM and elemental micrographs were obtained to investigate the morphology, metal distribution and particle size of the Mo₂N/SBA-15 and 3 wt% Pt-Mo₂N/SBA-15 samples, as displayed in Fig. 3. The TEM images of Mo₂N/SBA-15 (Fig. 3a), 3 wt% Pt-Mo₂N/SBA-15 (Fig. 3d) and 3 wt% Pt/SBA-15 (Fig. 3h) showed a highly ordered 2-D hexagonal mesostructure, the same as that of pure silica SBA-15 (Fig. S4⁺), which were in good agreement with the results of the smallangle XRD and N2 adsorption-desorption isotherm measurements. From Fig. 3a, it can be seen that the small Mo₂N NPs were highly dispersed on the SBA-15 support with uniform size ($<d> = 3.8 \pm 0.1$ nm). It was also confirmed by the corresponding elemental micrograph for Si, Mo and N (Fig. 3b). The formation of the small-sized Mo₂N by our strategy should be attributed to the following factors: the high surface area and the restriction effect resulting from the mesoporous structure of the SBA-15 support, the small size and stable structure of the HPM precursor, and the anchoring function of APTES to HPM clusters. The ethoxy groups of APTES could react with the surface Si-OH of SBA-15 to form SBA-15-NH₂. This leaves the functional groups (-NH₂) available on the surface. The -NH2 groups on SBA-15-NH2 can combine with the proton to form a cation $(-NH_3)^+$, and the HPM cluster can easily ionize to form a discrete, negatively charged heteropolyanion $[PO_4(Mo_3O_9)_4]^{3-}$. Thus, this anion can combine with the -NH2 groups on SBA-15-NH2 to obtain the HPM/SBA-15-NH₂ complex by electrostatic interaction. Followed by the nitridation in pure NH₃, the small-sized Mo₂N NPs on SBA-15 were gained without aggregation due to the intensive interaction of HPM clusters with SBA-15-NH₂. After loading of Pt, the TEM image of 3 wt% Pt-Mo₂N/SBA-15 (Fig. 3d) showed high metal dispersion, but the particle size ($\langle d \rangle = 8.2 \pm 0.3 \text{ nm}$) was larger than that of the Mo₂N/SBA-15 composite. Although it is difficult to distinguish Pt from Mo₂N due to their similar

Table 1 Relevant physicochemical parameters of the different samples

Sample	$S_{\rm BET}^{a} \left({ m m}^2 \ { m g}^{-1} ight)$	$V_{\text{pore}}^{a} (\text{cm}^{3} \text{g}^{-1})$	Pore size ^{<i>a</i>} (nm)	$\bar{\mathrm{d}}\mathrm{XRD}^{b}\left(\mathrm{nm}\right)$	$\bar{d}TEM^{c}$ (nm)	Pt loading ^d (wt%)
SBA-15	758	1.05	9.4	_	_	_
Mo ₂ N/SBA-15	370	0.68	8.0	4.2/Mo ₂ N	3.8	_
3 wt% Pt-Mo ₂ N/SBA-15	350	0.59	7.5	5.4/Pt	8.2	2.95
3 wt% Pt/SBA-15	625	0.96	8.5	8.3/Pt	10.8	2.89
3 wt% Pt–Mo ₂ N/SBA-15- r^{e}	390	0.62	7.5	6.2/Pt	20.7	2.80

^{*a*} Derived from N₂ adsorption–desorption isotherms. ^{*b*} Average particle sizes calculated from XRD patterns of Mo₂N or Pt based on Scherrer's equation. ^{*c*} Average particle sizes calculated from at least 100 individual crystallites in TEM images. ^{*d*} The loading content of Pt determined by ICP-OES. ^{*e*} 3 wt% Pt-Mo₂N/SBA-15 sample after four consecutive catalytic runs.

dark points in Fig. 3d, it can be seen that the Pt NPs would also be highly dispersed on the Mo₂N/SBA-15 composite without agglomeration as shown in the corresponding element maps in Fig. 3g. Furthermore, the HRTEM image of the 3 wt% Pt-Mo₂N/SBA-15 sample in Fig. 3e exhibited the small-sized particles in close contact with each other on SBA-15. The larger particles were typical Mo₂N with a size of about 8.0 nm, whereas the relatively small ones located around the Mo₂N grains can be recognized as Pt particles with the (111) crystal plane. A similar nanostructure was also observed in different regions of the 3 wt% Pt-Mo₂N/SBA-15 sample (Fig. S5†), which demonstrates that this contact of Pt with Mo₂N is common in the sample. The particle size of Pt in the 3 wt% Pt-Mo₂N/SBA-15 sample was about 5–6 nm which was consistent with the value of 5.4 nm calculated from XRD data by



Fig. 3 (a) TEM image, (b) element maps and (c) size distribution of particles for the $Mo_2N/SBA-15$ sample; (d) TEM image, (e) HRTEM image, (f) size distribution of the particles and (g) element maps of the 3 wt% Pt- $Mo_2N/SBA-15$ sample; (h) TEM image and (i) size distribution of particles for the 3 wt% Pt/SBA-15 sample. Panels (c), (f) and (i) are the size histogram of the particle distribution and the average size of the particles determined by statistical analysis of the TEM images; at least 100 individual crystallites were analyzed.

Scherrer's equation (Table 1). Thus, the images reveal the coexistence of Pt and Mo2N in the 3 wt% Pt-Mo2N/SBA-15 sample. Significantly, it shows distinctly the intimate contact of Pt with Mo₂N, which could lead to an intensive interaction between them. Besides, in the case of 3 wt% Pt/SBA-15, it exhibited polydispersity with average particle sizes of about 12.6 nm (Fig. 3i); even some much larger Pt aggregations (25 nm) could be seen, implying the sintering or aggregation of Pt NPs on SBA-15. Chen and Zhu et al.48,49 reported that the Pt particles of Pt/SBA-15 prepared by an impregnation method were severely sintered and showed a particle size of about 18 nm, in agreement with our results. The observations demonstrate that the dispersion of Pt NPs could be controlled effectively by the addition of homogeneous Mo₂N on the surface of SBA-15. The results also reflect the intensive interaction between Mo₂N and Pt NPs owing to their similar electronic structures,^{25,31} which may improve the properties of Pt in the catalysis field. In our earlier works, this similar effect was also observed for Pt-WC (WN) nanostructures on graphene, and the DFT calculations revealed that Pt particles preferentially grow on WC rather than on graphene when Pt attaches to the pre-existing WC/graphene hybrid.39,50 Thus, according to the above results, it's reasonable to conclude that the Pt NPs preferentially grow on the highly dispersed Mo₂N grains anchored on SBA-15 in view of the similar structure and properties of Mo₂N and WC (WN).^{39,50} Therefore, the universal particles in 3 wt% Pt-Mo₂N/SBA-15 became much larger than those of the Mo₂N/SBA-15 composite. This indicates that the Mo₂N NPs help to disperse Pt NPs and effectively prevent agglomeration of Pt NPs.

The samples were also characterized using wide-angle XRD. As shown in Fig. 4, all samples displayed a diffuse peak of amorphous SiO₂ around 22.5°. For Mo₂N/SBA-15 (Fig. 4b), it exhibited characteristic diffraction lines of γ -Mo₂N (JCPDS#25-1366) at 36.9 and 43.6°, although they were broad diffraction peaks. The grain size of Mo₂N NPs on the Mo₂N/SBA-15 sample was about 4.2 nm according to Scherrer's equation, consistent with the observation from the TEM image ($<d> = 3.8 \pm 0.1$ nm), which indicates that Mo₂N NPs are well dispersed on the SBA-15 support. Meanwhile, the diffraction peaks of the 3 wt% Pt-Mo₂N/SBA-15 sample (Fig. 4c) located at 39.7 and 45.9° can be identified as the (111) and (200) reflections of Pt with a face-centered cubic structure. However, the peaks belonging to Mo₂N disappeared for



Fig. 4 Wide-angle XRD patterns of (a) SBA-15, (b) $Mo_2N/SBA-15$, (c) 3 wt% Pt-Mo_2N/SBA-15 and (d) 3 wt% Pt/SBA-15.

3 wt% Pt-Mo₂N/SBA-15. The results are in line with other reports.^{23,51–53} It can be explained by the intensive interaction of Pt with Mo₂N NPs and the epitaxial growth of Pt on Mo₂N, due to their similar electronic structures. In addition, by comparing the wide-angle XRD pattern of 3 wt% Pt-Mo₂N/ SBA-15 (Fig. 4c) with that of 3 wt% Pt/SBA-15 (Fig. 4d), it can be seen that the intensity of the diffraction peak of Pt (111) at 39.7° is much weaker than that of 3 wt% Pt/SBA-15, although their Pt loading amount was similar (2.95 wt% and 2.89 wt%, respectively, determined by ICP-OES and shown in Table 1). Based on the calculation using Scherrer's equation, the Pt particle size of the 3 wt% Pt/SBA-15 sample (8.3 nm) was larger than that of 3 wt% Pt-Mo₂N/SBA-15 (5.4 nm), which implies that the addition of Mo₂N is able to improve the dispersion of Pt on the SBA-15 support. The results are consistent with the TEM images.

To investigate the surface electronic state of Pt species and the interaction between Pt and Mo₂N NPs, the 3 wt% Pt-Mo₂N/SBA-15 sample was further analyzed by XPS. The Pt 4f XPS spectra of the 3 wt% Pt/SBA-15 and 3 wt% Pt-Mo₂N/SBA-15 samples are shown in Fig. 5, together with their deconvolution obtained by fitting Gaussian peaks after Shirley background subtraction. In Fig. 5a, the Pt $4f_{7/2}$ binding energy (BE) of 3 wt% Pt-Mo2N/SBA-15 at 70.8 eV was assigned to platinum in the metallic state (Pt⁰); the Pt $4f_{7/2}$ peak at 72.5 eV could be attributed to the Pt²⁺ species.^{15,54} For the 3 wt% Pt/SBA-15 sample, it can be observed that there were three Pt 4f7/2 peaks located at 70.5, 72.0 and 74.8 eV, which were ascribed to the Pt⁰, Pt²⁺ and Pt⁴⁺ species, respectively. As far as the Mo 3d spectrum of Mo₂N/SBA-15 (Fig. 6a) is concerned, the peaks of Mo 3d were located at 229.5, 233.2 and 236.2 eV. The peak at 229.5 eV was typical of Mo^{δ^+} (2 $< \delta$ < 4) and assigned to Mo₂N species; the BE values of 233.2 and 236.2 eV were typical of Mo4+ and Mo6+, and ascribed to Mo oxynitrides.^{55,56} The corresponding Mo 3d BE values for 3 wt% Pt-Mo₂N/SBA-15 (Fig. 6b) were 229.2, 232.6 and 235.5 eV. This indicates that Mo₂N and Mo oxynitrides coexist on the surface of these samples. Interestingly, the peak of Mo from Mo-N was located at 229.5 eV for Mo₂N/SBA-15;



Fig. 5 Pt 4f XPS spectra of (a) 3 wt% Pt–Mo_2N/SBA-15 and (b) 3 wt% Pt/SBA-15.

however, it was at 229.2 eV for 3 wt% Pt-Mo₂N/SBA-15. It is noticed that there is a negative shift relative to that of Mo₂N/ SBA-15. This shift should be attributed to the electron transfer between Pt and Mo₂N via their intimate contact. This transfer is also reflected by comparing the Pt XPS of 3 wt% Pt-Mo₂N/SBA-15 with that of 3 wt% Pt/SBA-15. As shown in Table 2, the Pt $4f_{7/2}$ peaks of Pt⁰ and Pt²⁺ species for 3 wt% Pt/SBA-15 were located at 70.5 and 72.0 eV, respectively. However, the Pt 4f_{7/2} BE values of the metallic Pt⁰ and Pt²⁺ species for 3 wt% Pt-Mo2N/SBA-15 were 70.8 and 72.5 eV, respectively, having positive shifts of about 0.3 and 0.5 eV to higher energy than that for 3 wt% Pt/SBA-15. Similar results were also found in our previous work.^{36,38,39} This shift also indicates the acquisition of the electron of Mo₂N after Pt growth. The above results confirm the intensive interaction between Pt and Mo₂N combined with the TEM and XRD results for 3 wt% Pt-Mo₂N/SBA-15.

On the other hand, in terms of the quantitation of the surface Pt species, the fractions of the Pt^0 and Pt^{2+} species in 3 wt% Pt-Mo₂N/SBA-15 were estimated to be 71% and 29%, respectively (Table 2). Attractively, the amounts of the Pt^0 ,



Fig. 6 Mo 3d XPS spectra of (a) Mo_2N/SBA-15 and (b) 3 wt% Pt–Mo_2N/SBA-15.

Table 2 XPS data of the Pt 4f levels for the different samples

		Pt spec (eV)	Content of Pt	
Sample	Pt species	4f _{7/2}	$4f_{5/2}$	species (%)
3 wt% Pt-Mo ₂ N/SBA-15	Pt ⁰	70.8	74.1	71
	Pt^{2+}	72.5	76.0	29
3 wt% Pt/SBA-15	Pt ⁰	70.5	73.8	53
	Pt^{2+}	72.0	75.5	32
	Pt^{4+}	74.8	78.1	15
3 wt% Pt-Mo ₂ N/SBA-15-r	Pt ⁰	71.0	74.4	62
	Pt^{2+}	72.5	76.0	25
	Pt ⁴⁺	75.2	78.5	13

 Pt^{2+} and Pt^{4+} species in 3 wt% Pt/SBA-15 without Mo₂N NPs were about 53%, 32% and 15%. It's notable that the amount of Pt^{0} species in 3 wt% Pt-Mo₂N/SBA-15 is more than that in 3 wt% Pt/SBA-15, and almost no Pt^{4+} species is observed in the 3 wt% Pt-Mo₂N/SBA-15 sample. This is due to the fact that the presence of nitrides (carbides) could largely improve the crystallinity of Pt NPs because of the intensive interaction of nitrides (carbides) with Pt NPs.^{39,50}

Briefly, the highly ordered mesoporous structure is kept for SBA-15 with the loading of Mo₂N and Pt confirmed by the low-angle XRD, N2 adsorption-desorption isotherms and TEM results. Furthermore, the TEM images and elemental micrograph show that the Mo₂N and Pt NPs are well dispersed on SBA-15, but after loading of Pt, the particles grow much larger for the 3 wt% Pt-Mo₂N/SBA-15 sample. And the HRTEM images show that there is an intimate contact between Pt and Mo₂N grains, which suggests that the Pt NPs prefer to grow on the highly dispersed Mo₂N grains. In addition, the dispersion of Pt is better on the 3 wt% Pt-Mo₂N/ SBA-15 sample than that on the 3 wt% Pt/SBA-15 sample. It's also clarified by the wide-angle XRD results. For the 3 wt% Pt-Mo₂N/SBA-15 sample, the diffraction peaks of γ -Mo₂N disappear with the introduction of Pt to Mo₂N/SBA-15, and the intensity of the Pt peak becomes much weaker than that of 3 wt% Pt/SBA-15, which also demonstrates that there is an intensive interaction between Pt and Mo_2N . It results in the improvement of the dispersion of Pt. Moreover, the XPS results illustrate the electron transfer from Pt to Mo_2N and the increase in the amount of Pt^0 species on the surface of 3 wt% Pt-Mo₂N/SBA-15, which further confirms the interaction.

3.2. Catalytic performance

The catalytic performance was evaluated in the liquid-phase selective hydrogenation of CAL over the 3 wt% Pt-Mo₂N/SBA-15 catalyst. The 3 wt% Pt/SBA-15 and Mo₂N/SBA-15 catalysts were also tested as references. Table 3 displays the main results. It can be seen that the Mo₂N/SBA-15 catalyst showed negligible activity (5.8% conversion of CAL) and selectivity to COL (9.4%), and CAL was mainly converted to side products (90.6%), which indicates that Mo₂N possesses much lower catalytic activity for selective hydrogenation of CAL. The 3 wt% Pt/SBA-15 catalyst exhibited 47.7% conversion of CAL and 29.6% selectivity to COL, while the selectivities to HALD, HALC and other side products were 21.2%, 18.1% and 31.1%, respectively. In the case of the 3 wt% Pt-Mo₂N/SBA-15 catalyst, the conversion of CAL attained was 85.8% and the selectivity to COL was 78.0%; the selectivity to HCAL, HCOL and other side products were 7.9%, 10.7% and 3.4%, respectively. Therefore, it's clear that Mo₂N could markedly enhance the activity of Pt NPs on 3 wt% Pt-Mo₂N/SBA-15 for the conversion of CAL. Compared with other catalysts including the 3 wt% Pt/SiO₂ and 5 wt% Pt/C commercial catalysts (Table 3), the 3 wt% Pt-Mo₂N/SBA-15 catalyst exhibits the best activity. This can be attributed to the improvement of the dispersion of Pt NPs and the intensive interaction between Pt and Mo₂N revealed by TEM and XRD characterizations. As we know, small nanoparticle size and high dispersion of metals are beneficial to high activity in the selective hydrogenation.^{57,58} The smaller the nanoparticles, the more the active sites for Pt to absorb the reactants.¹⁵ What's more, the main product over the 3 wt% Pt-Mo2N/SBA-15 catalyst was COL via C=O bond hydrogenation with more than 78.0% selectivity, which

Table 3 Hydrogenation of cinnamaldehyde over different catalysts ^a									
Sample	Conversion (%)	$\operatorname{TOF}^{b}(\operatorname{h}^{-1})$	Selectivity (%)						
			COL	HALD	HALC	Others ^c			
Mo ₂ N/SBA-15	5.8		9.4	0	0	90.6			
3 wt% Pt/SBA-15	47.7	238	29.6	21.2	18.1	31.1			
2 wt% Pt/SBA-15	14.1	102	35.2	33.8	9.8	20.6			
1 wt% Pt/SBA-15	5.5	80	46.0	30.7	20.9	2.4			
3 wt% Pt-Mo ₂ N/SBA-15	85.8	423	78.0	7.9	10.7	3.4			
2 wt% Pt-Mo ₂ N/SBA-15	70.8	521	76.9	6.7	8.4	8.0			
1 wt% Pt-Mo ₂ N/SBA-15	16.3	239	80.2	11.8	8.0	0			
3 wt% Pt/SiO ₂	36.8	224	27.2	20.5	12.7	39.6			
5 wt% Pt/C	90.0	328	40.6	11.2	38.4	9.8			

^{*a*} Reaction conditions: 50 mg of the catalyst, 1.00 g of CAL, 30 mL of isopropanol, 10 bar H₂, 80 °C, 2 h. ^{*b*} Turnover frequency (TOF) = [moles of cinnamaldehyde reacted]/[(moles of Pt loading) × (reaction time)]. ^{*c*} Includes 1-(3-propoxyprop-1-enyl)benzene, cinnamyl formate, cinnamic acid, benzyl, cinnamate, 4,4-diphenylcyclohexa-1,5-dienyl acetate, and other condensation products that could be identified by GC-MS because of their large molecular weights.

was much higher than that of the 3 wt% Pt/SBA-15, 3 wt% Pt/ SiO₂ and commercial 5 wt% Pt/C catalysts. Consequently, it is evident that the addition of Mo₂N also could promote the selectivity for the hydrogenation of CAL to COL. The enhanced performance of the 3 wt% Pt-Mo₂N/SBA-15 catalyst is even superior to the reported Pt supported on new carbonaceous materials under similar reaction conditions.14-16,47 It is found that the cinnamaldehyde adsorption through its C=O bond becomes more favorable with the increase of the metallic character of the Pt clusters, and the large fraction of Pt⁴⁺ atoms is responsible for the high-molecular-weight secondary products obtained by experiments and DFT calculations.⁴⁷ In this work, the interaction between Pt and Mo₂N increases the fraction of Pt⁰ species and lessens the fraction of Pt⁴⁺ species on the surface of 3 wt% Pt-Mo₂N/SBA-15. Therefore, it suggests that the high selectivity to the COL product over the 3 wt% Pt-Mo₂N/SBA-15 catalyst is attributed to the higher amounts of Pt⁰ species on its surface. In other words, Mo₂N could be used as a highly effective co-catalyst of Pt NPs for the liquid-phase hydrogenation of CAL to COL.

The catalytic performances were also investigated over the Pt-Mo₂N/SBA-15 catalysts with different Pt contents (Table 3). As shown in Table 3, the TOF was 239 h^{-1} for 1 wt% Pt-Mo₂N/SBA-15 with 16.3% conversion of CAL. However, when the loading of Pt increased to 2 times (2 wt%), the conversion of CAL for 2 wt% Pt-Mo2N/SBA-15 increased to 70.8%, 4.3 times that for 1 wt% Pt-Mo₂N/SBA-15. Thus, the TOF for 2 wt% Pt-Mo₂N/SBA-15 (521 h^{-1}) is higher than that for 1 wt% Pt-Mo₂N/SBA-15 (239 h^{-1}). Furthermore, for 3 wt% Pt-Mo₂N/ SBA-15, the conversion of CAL slightly increased to 85.8%. Then, the TOF decreased to 423 h^{-1} for 3 wt% Pt-Mo₂N/SBA-15. This demonstrates that the Pt NPs on the 2 wt% Pt-Mo₂N/ SBA-15 catalyst were the most active in the conversion of CAL due to the synergistic effect of Pt and Mo₂N NPs, which leads to the sharp increase in the CAL conversion and TOF. Moreover, comparing the binary Pt/SBA-15 with the ternary Pt-Mo₂N/SBA-15 with the same Pt content, the ternary ones displayed more outstanding catalytic performance in the conversion of CAL and the selectivity to COL than the binary ones. When the Pt content decreased from 3 wt% to 1 wt% for the Pt/SBA-15 catalyst, the TOF decreased from 238 to 80 h⁻¹. However, the TOF over 1 wt% Pt-Mo₂N/SBA-15 could attain 239 h⁻¹, which was close to that over the 3 wt% Pt/SBA-15 catalyst. Simultaneously, the selectivity to COL over 1 wt% Pt-Mo₂N/SBA-15 was 80.2%, 2.5 times that over 3 wt% Pt/SBA-15. Herein, it is further proved that the intensive interaction between Pt and Mo₂N is beneficial to the promotion of the catalytic performance of Pt, and Mo₂N as a co-catalyst could lessen the usage of Pt for the selective hydrogenation of CAL to some extent. However, this effect of Mo₂N on Pt is closely related to the particle size of Mo₂N. As references, large Mo₂N NPs supported on SBA-15 were also prepared by impregnating SBA-15 without APTES modification as the support (denoted as Mo₂N/SBA-15-1), and after loading 3 wt% Pt on Mo₂N/SBA-15-1, the catalyst was denoted as Pt-Mo₂N/SBA-15-1. The TEM images of Mo₂N/SBA-15-1 (Fig. S6[†]) showed

that the Mo₂N NPs were about 20 nm in size with worse uniformity than those in Mo₂N/SBA-15 prepared by using SBA-15-NH₂ as the support (Fig. 3a). The XRD patterns of Mo₂N/SBA-15-1 (Fig. S7†) showed that the γ -Mo₂N phase was formed, and its size was about 7.5 nm according to Scherrer's equation. Besides, the peaks of the MoO₂ were observed, indicating the important role of APTES in obtaining the phase-pure and small-sized Mo₂N NPs. The conversion of CAL over 3 wt% Pt-Mo₂N/SBA-15-1 was 53.5%, and the selectivity to COL was 47.2% (Fig. S8†). This indicates that it's essential to support small-sized Mo₂N NPs on SBA-15 as the promoter, because there is more exposed surface of Mo₂N NPs for Pt NPs to be in contact with. Thus, the intensive interaction between them could be fully exploited.

The stability of 3 wt% Pt-Mo₂N/SBA-15 was also examined based on its excellent catalytic activity for the selective hydrogenation of CAL. The catalyst was reused directly without any treatment after precipitation and separation from the reaction solution. It is noteworthy that the 3 wt% Pt-Mo₂N/SBA-15 catalyst presented relative stabilization under the reaction conditions; a slight decrease in the conversion and selectivity appeared after the catalyst was reused three times, and the conversion of CAL and the selectivity to COL still reached about 80% and 70%, respectively (Fig. 7). However, after four catalytic cycles, the conversion and selectivity decreased to 60% and 50%, respectively. Obviously, the reusability of the 3 wt% Pt-Mo₂N/SBA-15 catalyst is superior to that of the 3 wt% Pt/SiO₂ catalyst (Fig. S9[†]), but it's slightly inferior to the 5 wt% Pt/C commercial catalyst (Fig. S10[†]) that displayed low selectivity to COL. In order to investigate the reason for the decrease in activity, the 3 wt% Pt-Mo₂N/SBA-15 catalyst after four cycles was characterized by ICP-OES, XRD, XPS and TEM, and the results are shown in Table 1 and Fig. 8. The ICP-OES analysis showed that the Pt content was about 2.80 wt% for the 3 wt% Pt-Mo2N/SBA-15 catalyst after four cycles, which indicates that there is slight leaching of Pt in the process compared to the fresh 3 wt% Pt-Mo₂N/SBA-15 catalyst (2.95 wt%). Thus, the slight leaching of Pt should not



Fig. 7 Stability test for 3 wt% Pt-Mo₂N/SBA-15 shown as performance versus number of recycling runs. Reaction conditions: 50 mg of 3 wt% Pt-Mo₂N/SBA-15, 1.00 g of CAL, 30 mL of isopropanol, 10 bar of H₂, 80 °C, 2 h.



Fig. 8 (a) Wide-angle XRD patterns, (b) Pt 4f XPS spectra, (c) TEM image and (d) particle size distribution of the 3 wt% Pt-Mo₂N/SBA-15 catalyst after four catalytic cycles.

be the main reason for the decrease in the activity. According to the XRD result of 3 wt% Pt-Mo₂N/SBA-15 after recycling runs (Fig. 8a), the intensity of Pt (111) and (200) diffraction peaks became stronger and sharper, as well as the appearance of Pt (220) diffraction peak at 67.8°. Moreover, the TEM image of the 3 wt% Pt-Mo2N/SBA-15 catalyst after four cycles showed that there was a remarkable particle aggregation on the catalyst surface (Fig. 8c), and the average particle size increased from 8.2 nm for the fresh 3 wt% Pt-Mo₂N/SBA-15 catalyst to 20.7 nm after the fourth catalytic cycle. In addition, as shown in Fig. 8b and Table 2, the other significant changes were the presence of Pt species on the surface of the used catalyst, the fraction of Pt⁰ species decreased from 71% to 62%, and the Pt^{4+} species appeared (15%) that contributed to the increase in the high-molecular-weight secondary products. Thus, it's clear that the reduced amount of Pt⁰ species means the reduction of the possibility for CAL adsorption through its C=O bond, which isn't favourable to the generation of COL, and the increase in the amount of Pt⁴⁺ species is beneficial to the increase of the secondary products. As a consequence, the main reason for the decrease in activity for the 3 wt% Pt-Mo₂N/SBA-15 catalyst can be attributed to the aggregation of particles and the reduced amount of Pt⁰ species on the surface. It also confirmed that the Pt⁰ species play a key role in the selectivity to COL in the selective hydrogenation of cinnamaldehyde.

Conclusions

The ternary Pt-Mo₂N/SBA-15 catalyst with uniform Pt NPs was obtained by loading Pt on Mo_2N modified SBA-15. The intimate contact and intensive interaction between Pt and Mo_2N were observed in the ternary Pt-Mo₂N/SBA-15 catalyst,

which resulted in the difference of Pt species on the surface from the Pt/SBA-15 catalyst and the electron transfer between Pt and Mo₂N. The Pt-Mo₂N/SBA-15 catalyst exhibited a remarkably enhanced catalytic performance for the liquidphase hydrogenation of cinnamaldehyde. The selectivity to COL over the 1 wt% Pt-Mo₂N/SBA-15 catalyst is 2.5 times that over the 3 wt% Pt/SBA-15 catalyst at the same TOF. It illustrates that Mo₂N could be a new kind of co-catalyst of Pt promoting its catalytic efficiency in selective hydrogenation. This promotion can be ascribed to the synergistic effect between Pt and Mo₂N: the first one, the presence of Mo₂N NPs favours the dispersion of the Pt NPs; the second one, the Mo₂N NPs increase the amount of Pt⁰ species on the surface of the Pt-Mo₂N/SBA-15 catalyst. The present study opens up a new way for preparing robust Pt-based catalysts for a wide range of interesting and industrial reactions.

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