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# Surface synergistic effect in well-dispersed Cu/MgO catalysts for highly efficient vapor-phase hydrogenation of carbonyl compounds<sup>†</sup>

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The highly efficient vapor-phase selective hydrogenation of carbonyl compounds (e.g. furfural (FAL) and dimethyl 1,4-cyclohexane dicarboxylate (DMCD)) to corresponding alcohols was achieved excellently over well-dispersed MgO-supported copper catalysts (Cu/MgO), which were prepared by an alternative separate nucleation and aging step method. The characterization results revealed that the structure and catalytic performance of as-formed Cu/MgO catalysts were profoundly affected by the Cu loading. Especially, the results confirmed that the decrease in the Cu loading could lead to the improvement of metal dispersion and the formation of more surface strong Lewis basic sites. In the vapor-phase selective hydrogenation of FAL to furfuryl alcohol (FOL) and DMCD to 1,4-cyclohexane dimethanol (CHDM), two Cu/MgO catalysts with the Cu loadings of 27.6 wt % and 70.9 wt % exhibited superior catalytic performance with the higher conversions (> 97.3%) and selectivities to alcohols (>96.0 %) to other supported ones. The high efficiency of as-formed Cu/MgO catalysts was mainly attributed to the surface synergistic catalytic effect between catalytically active metallic copper species and Lewis basic sites, which held the key to hydrogenation reaction related to the hydrogen dissociation and the activation of carbonyl groups.

#### Introduction

Nowadays, a series of hydrogenation processes of carbonyl compounds to corresponding alcohols have been successfully developed in industry,<sup>1-6</sup> due to their academic and commercial value. For instance, 1,4-cyclohexane dimethanol (CHDM), which is preferred over ethylene glycol as a stepping stone for producing various high-quality and nontoxic resins and fibers in the polymer industry,<sup>7</sup> can be normally produced by catalytic hydrogenation of dimethyl 1,4-cyclohexane dicarboxylate (DMCD).<sup>8,9</sup> In addition, due to increasingly serious energy and environmental issues, efficient utilization and conversion of natural biomass resources are attracting considerable interest. In this respect, furfural (FAL), an important biomass-derived platform molecule, is employed extensively for the production of a variety of non-petroleum based chemicals and biofuels.<sup>10-13</sup> Typically, catalytic hydrogenation conversion of FAL by using metal-based catalysts can generate high-value-added furfuryl

alcohol (FOL),<sup>14</sup> which is widely used for the production of a great number of chemicals.<sup>15,16</sup> In industry, these important alcohols usually are produced by the catalytic hydrogenation of corresponding carbonyl compounds over  $Cr_2O_3$  promoted copper-based (Cu-Cr<sub>2</sub>O<sub>3</sub>) catalysts with moderate activity and selectivity at high temperatures and pressures.<sup>8,9, 17-20</sup> The high toxicity of  $Cr^{6+}$  ion, however, causes severe pollution to environment and humans during the preparation and operation. Therefore, the development of nontoxic green Cr-free catalysts is crucial for the efficient production of alcohols from the viewpoint of sustainable development of resources and economy.

Over the past decade, a large number of new catalysts have been explored for selective hydrogenation of carbonyl compounds in either liquid phase or vapor phase. For example, supported bimetallic RuSn-based catalysts are found to be active in liquid-phase hydrogenating DMCD into CHDM.<sup>21,22</sup> Meanwhile, various supported metals (e.g. Cu, Ni, Co, Pt, Ru, Pd, and Rh)<sup>16, 20, 23-30</sup> and amorphous alloys<sup>31</sup> catalysts are employed to catalyze the hydrogenation of FAL. Especially, low-cost Cu-based catalysts, as the most employed catalysts in industry, can preferentially catalyze the hydrogenation of C=O bond in carbonyl compounds. In some cases, surface Cu<sup>+</sup>-Cu<sup>0</sup> synergy in Cu-based catalysts can remarkably control the

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catalytic performance in the hydrogenation of carbonyl compounds.<sup>29, 32, 33</sup> However, the main disadvantages are that most of the above catalysts cannot be reused due to severe deactivation of active species and liquid-phase hydrogenation requires high hydrogen pressures. In contrast, vapor-phase hydrogenation of carbonyl compounds may be generally conducted under more mild conditions, i.e., lower hydrogen pressures and reaction temperatures. In addition, it is well known that the surface acid-base nature of catalysts may greatly influence the way that the reactions go. Recently, we found preliminarily that surface basic sites on copper-based catalysts derived from Cu-Mg-Al layered double hydroxide precursors could promote the catalytic performance in the hydrogenation of DMCD.<sup>34</sup>

On the other hand, although the preparation approaches for supported metal catalysts (*e.g.* deposition-precipitation and incipient wetness impregnation) have been intensively explored in order to make full use of their catalytic properties,<sup>35</sup> it is difficult to obtain well-dispersed metal nanopaticles (NPs) with uniform size and good thermal stability in most cases, especially at high loadings, which mainly originates from inhomogeneous distribution of active precursors on supports as well as weak interactions between them. Therefore, various high-specific-surface-area supports, such as MgO <sup>36-38</sup>, have been adopted to disperse active metal sites and enhance interactions between them. Up to now, however, highly active and stable simple metal oxides supported Cu-based catalysts suitable for industrial applications have not been developed yet.

Inspired by the above results, in this work, new environment-friendly well-dispersed MgO supported Cu nanocatalysts (Cu/MgO) for the vapor-phase selective hydrogenation of representative carbonyl compounds (e.g. FAL and DMCD) were prepared by an alternative separate nucleation and aging step method, which was developed previously in our group.<sup>39</sup> In combination with systematic characterizations, the effects of the copper loading on the metal dispersion, surface basicity and catalytic performance of Cu/MgO catalysts were elucidated. It was found that the high conversions (> 97.3%) and selectivities to alcohols (>96.0 %) were achieved over two Cu/MgO catalysts with a low Cu loading of 27.6 wt % or a high Cu loading of 70.9 wt % in the vapor-phase selective hydrogenation. This could be attributed to the surface synergistic catalytic effect between metallic copper species and Lewis basic sites, which mainly held the key to hydrogenation reaction related to hydrogen dissociation and the activation of carbonyl groups. More importantly, the obtained catalyst achieved a stable catalytic performance up to 200 hours. To the best our knowledge, such highly efficient and stable simple metal oxide supported Cu-based catalysts for the hydrogenation of carbonyls have not been reported until now.

# **Results and discussion**

# Structural analysis

In the course of synthesis for Cu/MgO catalyst precursors, two solutions of metal salts and bases were rapidly mixed and nucleation process could occur in a colloid mill within a quite short time of 3 min. The resultant hydroxide slurry was

subsequently aged. In this way, all the particles precipitated out at almost the same time, and the following growth time was the same. As a result, metal ions precipitated more uniformly and integrated better with each other to form uniform catalyst precursor particles.

Fig.1A shows the XRD patterns of calcined catalyst precursors. In the cases of the Cu loadings of < 55.0 wt%, the XRD patterns of samples only exhibit the characteristic diffractions of poorly crystalline MgO-like phase. However, no diffraction peaks related to crystalline CuO are found in the XRD patterns, as a consequence of its high dispersion nature. As the Cu loading increases to 55 wt%, the weak characteristic diffractions of CuO (JCPDS No. 05-0661) begin to appear. The diffraction intensities for CuO phase increase gradually with the Cu loading, whereas those for MgO phase decrease. The above results demonstrate that the well-dispersed CuO phase is successfully formed in calcined samples.



Fig. 1 XRD patterns of calcined samples (A) and reduced catalysts (B). Inset in (B) shows the detail XRD patterns of Cu-40 and Cu-55 samples in the 2  $\theta$  range of 38°–48°.

Fig.1B presents the XRD patterns of reduced Cu/MgO samples. In the cases of Cu-10 and Cu-25 samples, only three broad (111), (200), and (220) diffractions of crystalline MgO phase are observed. As for Cu-40 and Cu-55 samples, the broad asymmetric peak at about 43° can be deconvoluted into two peaks with their maxima at about 42.5 and 43.2° (inset in Fig.2B), corresponding to the (200) diffraction of MgO and the (111) diffraction of the face-centered cubic (*fcc*) metallic copper (JCPDS no. 04-0836), respectively. Noticeably, with the further increase in the Cu loading, Cu-70 and Cu-90 samples present a strong (111) diffraction peak of metallic copper at 20 of 43.2° along with the (200) one at 50.4°, besides weak diffractions of MgO phase. However, the diffractions of metallic copper phase can not be detected in the cases of Cu-10 and Cu-25 samples, mainly due to the lowered crystallinity.

The average crystallite sizes of metallic copper particles calculated by the Scherrer formula according to the (111) diffraction are listed in Table 1. It is noted that the crystallite size of copper particles increases gradually from about 5.2 to 33.8 nm when the Cu loading increases from 38.6 to 82.7 wt %. As shown in Table 1, the copper dispersion measured by  $H_2$ -N<sub>2</sub>O titration decreases monotonically from 0.283 to 0.016 with the Cu loading, well consistent with the change in the average size of copper

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particles determined by the XRD patterns. As a result, the introduction of a large amount of Cu is not helpful for retarding the growth of metallic copper crystallites. Usually, the high specific surface area can result in the good metal dispersion.<sup>40,41</sup> In the present catalyst system, the BET specific surface area of Cu/MgO samples decreases gradually with the Cu loading (Table 1), which is associated mainly with the decrease in the component of MgO support, as well as the enlarged sizes of Cu particles. Meanwhile, Cu surface areas exhibit an increasing trend with the Cu loading from 8.5 to 70.9 wt %, indicative of the increase in the surface metallic copper sites. However, Cu-90 sample has a smallest Cu surface area (8.2 m<sup>2</sup>g<sup>-1</sup>), which should be ascribed to the agglomeration of large Cu particles.

 Table 1
 Structural and textural data of different Cu/MgO samples.

Sample	Cu <sup>a</sup>	S <sub>BET</sub> <sup>b</sup>	D <sub>111</sub> °	$S_{Cu}^{d}$	D <sub>dis</sub> <sup>e</sup>	Basic sites <sup>f</sup>	SB sites <sup>g</sup>
	(wt%)	$(m^2/g)$	(nm)	(m2/g)	(%)	(mmol/g)	(mmol/g)
Cu-10	8.5	74		8.3	28.3	1.136	0.424
Cu-25	27.6	71		13.9	15.8	1.188	0.686
Cu-40	38.6	63	5.2	16.4	8.1	0.856	0.405
Cu-55	48.5	56	6.0	16.4	6.9	0.719	0.242
Cu-70	70.9	54	18.8	17.5	5.0	0.439	0.168
Cu-90	82.7	44	33.8	8.2	1.6	0.075	0

<sup>a</sup> determined by ICP-AES; <sup>b</sup> specific surface area calculated by the BET method; <sup>c</sup> average crystallite size of metallic copper particles based on XRD patterns; <sup>d</sup> Metallic copper surface area determined by H<sub>2</sub>-N<sub>2</sub>O titration; <sup>e</sup> Copper dispersion degree; <sup>f</sup> the density of total basic sites determined by CO<sub>2</sub>-TPD; <sup>g</sup> the density of strong basic (SB) sites determined by CO<sub>2</sub>-TPD.



Fig. 2 TEM and HRTEM images of Cu-25 (a,b) and Cu-70 (c,d) samples.

Typical TEM images of representative Cu/MgO samples (Cu-25 and Cu-70) are presented in Fig. 2. It can be found that small Cu clusters without agglomeration of particles are well dispersed on the support in the Cu-25. However, the clear interface between the Cu phase and the support matrix is difficult to be identified,

due to poor contrast between metal and support. Further, the HAADF-STEM image of Cu-25 sample (Fig.S1<sup>†</sup>) depicts a large quantity of small bright spots in the image corresponding to Cu NPs supported on the matrix. The presence and distribution of the Mg and Cu elements within several particles were further verified by means of the STEM-EDS line scan spectrum. Noticeably, the intensity of Mg element in the EDS line spectrum appears to be higher than that of Cu element, suggesting that Cu NPs are probably surrounded by the MgO phase, thus leading to the formation of a strong interfacial contact between Cu NPs and MgO phase. In the case of Cu-70 sample, a large number of approximately spherical Cu NPs with the average diameter of about 15 nm undergo a little agglomeration, due to its high Cu loading of 70.9 wt% (Fig.2c). This is in good agreement with the above N2O titration results. Furthermore, HRTEM images of Cu-25 and Cu-70 depict the lattice fringes with an interplanar spacing of approximately 0.21 nm within a single nanoparticle (Fig.2b, d) corresponding to the (111) plane of the metallic Cu phase. In the present synthetic system for Cu/MgO samples, homogeneous precipitation of all metal ions can guarantee the formation of uniform catalyst precursor particles, which provides a favourable dispersing effect for copper species thus preventing agglomeration of metallic copper particles, although the Cu loadings are pretty high in some cases.

#### **Redox behaviors**



Fig. 3 H<sub>2</sub>-TPR profiles of calcined samples.

H<sub>2</sub>-TPR measurement was carried out to study the redox properties of calcined samples and the interaction between the copper species and the support. As shown in Fig. 3, the total hydrogen consumption corresponds to the reduction of Cu<sup>2+</sup> species. Obviously, two kinds of copper species exist in the Cu-10 sample. The broad low-temperature reduction peak at *ca*. 235 °C is assigned to the reduction of isolated highly-dispersed CuO species, <sup>42</sup> while the small high-temperature one at *ca*. 310 °C is associated with the reduction of Cu<sup>2+</sup> species having a strong interaction with the matrix.<sup>43</sup> With the Cu loading increasing to 27.6 %, two reduction peaks all shift to the lower temperatures. Further, as the Cu loading increases, the high-temperature peak disappears; while the low-temperature one continues to shift to the lower temperatures and becomes broader. In the case of Cu-90, besides the main peak at 183 °C, a shoulder peak related to the reduction of large bulk CuO particles appears at 197 °C. The above results demonstrate that the increase in the Cu loading leads to the weakened interactions between the Cu-containing species and the MgO matrix and thus the improved reducibility of copper species, in spite of the enlarged particle size.

#### Surface chemical states



Fig. 4 Cu 2p XPS of calcined samples.

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It is well known that the catalytic performance of catalysts is greatly related to their surface chemical states. The surface/near-surface chemical states of calcined catalyst precursors were analyzed by XPS (Fig. 4). Usually, the binding energy (BE) for the main Cu 2p3/2 peak related to  $Cu^{2+}$  species is about in the range of 932.0–935.0 eV, <sup>44,45</sup> whereas its shake-up satellite line lies between 940 and 945 eV. As for C-10 sample, the peak at about 933.6 eV is attributed to highly dispersed  $Cu^{2+}$  species present in metal oxide  $(Cu_A^{2+})$ , while the one at about 935.0 eV may be associated with covalent  $Cu^{2+}$ -O bond polarized by Mg<sup>2+</sup> ions  $(Cu_B^{2+})$  thereby decreasing the effective charge of  $Cu^{2+}$  species rather than  $Cu_B^{2+}$  species, due to the formation of more CuO phase, indicative of the weakened interactions between Cu-Mg species.



Fig. 5 Cu 2p XPS of reduced Cu/MgO samples. Inset is the Cu LMM XAES of

#### Cu-25 sample.

Further, the reduced samples were characterized by XPS to obtain more information about the surface chemical states of copper (Fig.5). In all cases, the Cu 2p3/2 signal at ca. 932.6 eV is due to the presence of metallic copper species.47, 48 The solid evidence of the copper reduction stems from the absence of XPS signals of Cu<sup>2+</sup> at 933–935 eV. <sup>47</sup> Clearly, the appearance of a single peak at kinetic energy of 918.2 eV in the Cu LMM XAES depicts the sole presence of Cu<sup>0</sup> species on the surface of Cu-25 sample.<sup>49</sup> Further analysis on the surface copper species was performed by in situ FT-IR spectra of CO absorption on the Cu-25. Usually, the band of CO absorption on the surface  $Cu^{2+}$  site is above 2140 cm<sup>-1</sup>, while the bands of CO absorption on surface Cu<sup>0</sup> and Cu<sup>+</sup> sites are below 2110 cm<sup>-1</sup> and between 2110 and 2135 cm<sup>-1</sup> respectively.<sup>50</sup> As shown in the inset in Fig. 6, a single symmetric peak is found at *ca*. 2100 cm<sup>-1</sup> after saturating the Cu-25 with CO at room temperature. Upon heating, the adsorbed CO is totally removed at 100 °C, which is a typical feature of weakly bound CO on Cu<sup>0</sup> sites.<sup>51</sup> Therefore, it can be deduced that there are only metallic Cu<sup>0</sup> species in reduced catalysts.



Fig. 6 In situ FT-IR spectra of CO absorption on the Cu-25 sample. CO under 500 Pa (a), followed by evacuation at 30  $^{\circ}$ C (b) and 100  $^{\circ}$ C (c)

#### Surface basicity

As for as-formed Cu/MgO samples, basic sites are mainly related to O<sup>2-</sup> ions on the surface.<sup>52</sup> CO<sub>2</sub>-TPD measurement was used to probe surface basicity of Cu/MgO samples. As shown in Fig.7, except for Cu-90 sample, all samples present three CO<sub>2</sub> desorption peaks including weak Brønsted basic sites centered at 83-142 °C, medium-strength Lewis basic sites centered at 196-265 °C, and strong Lewis basic sites centered at 509-566 °C,53 which are related to surface OH groups, Mg-O-Mg groups or  $Mg^{2+}-O^{2-}$  pairs, and coordinatively unsaturated  $O^{2-}$  ions, respectively. However, Cu-90 sample does not shows a desorption peak above 350 °C, indicative of the absence of strong basic (SB) sites. According to a quantitative analysis on the densities of basic sites on Cu/MgO samples (Table 1), the densities of total basic sites and SB sites increase from 1.136 and 0.424 for Cu-10 to 1.188 and 0.686 and mmol/g for Cu-25, then drop gradually with the continuous increase in the Cu loading. Among them, Cu-25 sample possesses the highest densities of

total basic sites and SB sites.

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Fig. 7  $CO_2$ -TPD profiles of different reduced samples. (a) Cu-10, (b) Cu-25, (c) Cu-40, (d) Cu-55, (e) Cu-70 and (f) Cu-90.



Fig. 8 O1s XPS of reduced Cu/MgO samples. (a) Cu-10, (b) Cu-25, (c) Cu-40, (d) Cu-5, (e) Cu-70, (f) Cu-90.

Considering that the origin of basic sites is related to the surface oxygen species, O1s XPS of Cu/MgO samples also were analysed. From the O 1s spectra (Fig.8), it is seen that there are four fitted peaks in all cases, except for Cu-90 sample, representing four different kinds of surface oxygen species. The peak with the BE around 531.7 eV belongs most likely to oxygen species of hydroxyl groups on the surface, while the peaks at lower BE of about 530.6 and 529.3 eV are the characteristic of lattice oxygen bound to metal cations of the structure, *i.e.*, Mg-O-Mg groups and Mg<sup>2+</sup>-O<sup>2-</sup> pairs.<sup>54,55</sup> In addition, the peak located at 528.2 eV can be attributed to the coordinatively unsaturated O<sup>2-</sup> species strongly bound to Mg<sup>2+</sup> cations  $(O^{\delta})$ , which should be related to the reduction of the Cu-O-Mg parts in calcined precursors during the catalyst activation procedure, leading to the formation of Cu NPs in strong interfacial contact with MgO phase. As for Cu-90 sample, however, there are not  $O^{\delta}$  species on the surface. It indicates the presence of SB sites on the surface of Cu/MgO samples (not including Cu-90 sample), in good agreement with the CO<sub>2</sub>-TPD results. Furthermore, it is worthy to note that the proportion of  $O^{\delta}$  species in the total oxygen species presents a decreasing trend with the Cu loading, indicative of the decrease in the proportion of surface SB sites.

### Vapor-phase hydrogenation

Firstly, the catalytic performance of Cu/MgO catalysts was investigated in the vapor-phase hydrogenation of DMCD. In the course of hydrogenation, CHDM product can be further dehydrated to 4-methyl-cyclohexanemethanol (MCHM). In addition, methyl 4-hydroxymethylcyclohexane carboxylate (MHMCC) intermediate and incomplete hydrogenation product, 4-(hydroxymethyl)-1-cyclohexanecarboxaldehyde (HMCCA), can be detected.

The catalytic activity and selectivity for DMCD hydrogenation on different Cu/MgO catalysts are listed in Table 2. Interestingly, the catalytic activity and selectivity to CHDM present a bimodal distribution with the Cu loading under the given reaction conditions. That is, Cu-25 and Cu-70 catalysts yield higher DMCD conversions (>97.0%) with the higher selectivities to CHDM (>96%), compared with other catalysts. In contrast, Cu-10 and Cu-90 catalysts show the worst catalytic performance for the DMCD hydrogenation. Additionally, different oxides (MgO, TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO) supported Cubased catalysts prepared by the conventional impregnation method were used here as comparison catalysts. Note from Table 2 that their catalytic efficiency is markedly lower than that of Cu-25 with the similar Cu loading.

In addition, the reactions under different LHSV values were conducted (Fig.9). The DMCD conversions over Cu-25 and Cu-70 catalysts remain above 97% between LHSVs of DMCD from 1.0 to 3.0 h<sup>-1</sup>, then decrease slowly with LHSV increasing from 3.0 to 4.0 h<sup>-1</sup>. Subsequently, the conversions over other four Cu/MgO catalysts decline continuously at a LHSV of 1.0 h<sup>-1</sup>. Despite the gradual decrease in selectivity to CHDM with the further increase in LHSV, Cu-25 and Cu-70 catalysts continue to show higher selectivity than other catalysts. As a result, the

best catalytic performance, as well as high tolerance to the LHSV of DMCD ( $h^{-1}$ ) over different catalyst °C, H<sub>2</sub>/DMCD=220 (mol mol<sup>-1</sup>).

**Table 2** The catalytic performance of different catalysts in vaporphase hydrogenation of DMCD <sup>a</sup>.

Catalyst	TOF <sup>b</sup>	Conversion	Selectivity (%)			
	(h <sup>-1</sup> )	(%)	CHDM	MHMCC	MCHM	HMCCA
Cu-10	28.8	33.9	30.1	1.3	53.6	15.0
Cu-25	49.1	97.3	96.1	0.3	2.5	1.1
Cu-40	36.7	85.3	82.6	0.2	12.5	4.7
Cu-55	38.6	90.2	87.8	0.3	8.8	3.1
Cu-70	39.6	98.7	98.2	0.2	0.7	0.9
Cu-90	27.0	31.8	27.4	0.7	63.9	8.0
Cu/MgO <sup>c</sup>		67.4	75.1	0	23.4	1.5
Cu/TiO2 c		1.4	15.1	0	83.3	1.6
Cu/Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>		23.5	32.0	0	67.3	0.7
Cu/SiO <sub>2</sub> <sup>c</sup>		0.4	8.7	0	90.1	1.2
Cu/CaO <sup>c</sup>		45.3	60.0	0	39.5	0.5

<sup>a</sup> Reaction conditions: temperature, 220 °C; hydrogen pressure: 6 MPa, LHSV of DMCD, 3.0 h<sup>-1</sup>; H<sub>2</sub>/DMCD = 220 (mol mol<sup>-1</sup>). <sup>b</sup> calculated according to the moles of DMCD converted in the initial 1 h per mole surface metallic copper. <sup>c</sup> prepared by the conventional impregnation.



Fig. 9 DMCD conversion (A) and CHDM selectivity (B) versus LHSV of

DMCD (h<sup>-1</sup>) over different catalysts. Reaction conditions: P=6.0 Mpa, T=220  $^{\circ}$ C, H<sub>2</sub>/DMCD=220 (mol mol<sup>-1</sup>).

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As to hydrogenation catalyzed by metallic copper, one important key to high performance is a large accessible Cu surface area, because higher copper surface area can supply more catalytically active sits for hydrogen dissociation and thus higher conversion.<sup>56</sup> However, in the present catalyst system, the change in the activity of the catalysts does not change monotonically with the metallic copper surface area. Cu-70 catalyst with the largest active Cu surface area exhibits superior catalytic performance to others. Interestingly, when Cu-25 catalyst with the largest amounts of total basic sites and SB sites is used to catalyze the hydrogenation, similar conversion and selectivity to those over the Cu-70 catalyst are obtained, although Cu-25 catalyst presents lower copper surface area. Furthermore, Cu-25 exhibits higher catalytic activity than Cu-40 and Cu-55 catalysts with the larger Cu surface areas. Therefore, in order to rigorously compare the intrinsic nature of catalytically active copper sites on different Cu/MgO catalysts, the DMCD conversion data limited to less than 30 % by adjusting the LHSV of DMCD were used to calculate the initial turnover frequency (TOF), according to the moles of DMCD converted by each mole of the surface copper on the catalyst surface in the initial 1h. As shown in Table 2, the TOF value reaches the maximum (49.1 h<sup>-1</sup>) in the case of Cu-25. Cu-70, however, possesses a relatively small TOF of 39.6 h<sup>-1</sup>. The aforementioned results indicate that the Cu surface area alone cannot explain the differences in catalytic performance of catalysts, and some complicated interactions on catalytically active sites for the hydrogenation should occur. It is suggested that the surface basic nature of as-formed Cu/MgO catalysts probably plays an important role in the hydrogenation of DMCD. In this regard, the fact that acidic  $TiO_2$  and  $SiO_2$ supported Cu-based catalysts showed much lower catalytic hydrogenation performance than basic MgO and CaO supported ones (See Table 2) also suggests the promotional effect of surface basicity on the catalytic performance.

 Table 3 The catalytic performance of Cu/MgO catalysts in vapor-phase hydrogenation of FAL <sup>a</sup>.

Catalyst	Conversion	Selectivity (%)	
	(%)	FOL	1-MF
Cu-10	45.7	96.2	3.8
Cu-25	97.2	97.4	2.6
Cu-40	95.5	95.6	4.4
Cu-55	92.5	96.0	4.0
Cu-70	98.1	97.6	2.4
Cu-90	36.7	94.3	5.3

<sup>a</sup> Reaction conditions: temperature, 180 °C; LHSV of FAL, 1.0 h<sup>-1</sup>;  $H_2/FAL =$  16 (mol mol<sup>-1</sup>); atmospheric pressure.

Secondly, the vapor-phase hydrogenation of FAL to FOL was performed on as-formed Cu/MgO catalysts. Here, a side reaction, hydrogenolysis of FOL to 2-methylfuran (MF), also can occur. As shown in Table 3, Cu-25 and Cu-70 catalysts also show superior catalytic performance to other catalysts,

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indicating that Cu/MgO catalysts follow a similar regulation of catalytic performance to that in the hydrogenation of DMCD. It means that as for as-formed Cu/MgO catalysts, the catalytic mechanism is the same in two kinds of hydrogenation reactions.



**Fig. 10** Catalytic performance as a function of reaction time over Cu-25 catalyst: (A) hydrogenation of DMCD, P = 6 MPa, reaction temperature = 220 °C, H<sub>2</sub>/DMCD = 220 (mol mol<sup>-1</sup>), LHSV = 3.0 h<sup>-1</sup> and (B) hydrogenation of FAL, reaction temperature = 180 °C, LHSV = 1.0 h<sup>-1</sup>, H<sub>2</sub>/FAL = 16 (mol mol<sup>-1</sup>), atmospheric pressure.

Thirdly, the long-term stability of catalysts is very significant for practical applications. Generally, the activity loss for metalbased catalysts can be attributed to surface transmigration and aggregation of metal NPs. Fig.10 presents the catalytic hydrogenation performance as a function of time on stream over Cu-25 catalyst. It is noted that Cu-25 exhibits high stability for the hydrogenation of DMCD and FAL up to 200 hours and no decrease in either the conversions of DMCD and FAL or the selectivities to CHDM and FOL can be observed. XRD analyses further confirm that no obvious structural change of Cu-25 catalyst is observed after 200 h of hydrogenation reaction (Fig.S2†). In addition, a weak diffraction related to quartz (JCPDS No. 46-1045) appears at 26.6°, because a small amount of quartz filled in the reactor is dragged into the catalyst during the long time reaction. After 200 h of catalytic test, no obvious agglomeration and accumulation of the Cu NPs on the support surface can be observed from HRTEM images of used Cu-25 catalyst (Fig.S3†), and the crystallite size of used Cu NPs is about 4.5 nm. Due to the confinement effect of MgO phase, active copper species are surrounded by the MgO phase and stabilized on the support surface, thereby leading to the stable activity of asformed Cu/MgO catalyst.



Scheme 1 Proposed possible mechanism of the hydrogenation of aldehyde over as-formed Cu/MgO catalyst.

At last, based on the above experimental results, it can be deduced that the Cu<sup>0</sup> species should be the effective catalytically active centres for dissociating hydrogen in the hydrogenations of DMCD and FAL. Additionally, surface basic sites, especially SB sites in intimate contact with metallic Cu<sup>0</sup> sites, can easily interact with the  $\pi^*$  acceptor orbital of the C=O group, thus improving the reactivity of the carbonyl group in substrate molecules.<sup>57</sup> Therefore, a synergistic effect mechanism for hydrogenation reaction between surface Cu<sup>0</sup> and basic sites over as-formed Cu/MgO catalysts is tentatively proposed to rationalize the experimentally observed structure-performance relation (Scheme 1). Here, the C=O group may form a zwitterionic, tetrahedral intermediate with enhanced nucleophilic reactivity at the oxygen atom on the surface basic sites of catalysts. Consequently, the  $\pi$ bond of C=O activated by basic sites become easy to be attacked by dissociative hydrogen on the surface of Cu<sup>0</sup> particles. Therefore, the carbonyl group gets two H atoms from Cu<sup>0</sup> and parts from basic sites.

As a result, in our case, a uniform distribution of Cu and Mg species in catalyst precursors facilitates high dispersion of active Cu species, as well as the formation of strong interfacial contact between active copper NPs and MgO support. Correspondingly, the conversion rate of carbonyl compounds increases significantly owing to the facile dissociation of H<sub>2</sub> molecules on catalytically active Cu<sup>0</sup> sites and activation of carbonyl groups by adjacent basic sites. In particular, such formed surface synergistic catalytic effect between metallic copper species and basic sites in the Cu-25 catalyst with the highest amount of basic sites and the appropriate amount of Cu<sup>0</sup> sites can highly efficiently promote the hydrogenation reaction related to the carbonyl groups. As for Cu-

70 catalyst, the high efficiency mainly relies on its largest copper surface area, due to relatively weaker surface basic nature.

In general, the current study can be more advantageous over previous studies because of the two following merits. Firstly, the synthesis of catalyst precursors was performed by a separate nucleation and aging step method, which resulted in excellent stability of the resultant Cu/MgO catalysts due to the strong confinement effect of MgO phase. Secondly, unlike the Cu<sup>+</sup>–Cu<sup>0</sup> synergy reported in the literature that mainly holds the key to hydrogenation reactions and is easily weakened due to deep reduction of Cu<sup>+</sup> species under real reaction conditions, in our case, Lewis basic sites synergistically promote the hydrogenation activity of Cu<sup>0</sup> sites, which results in significantly enhanced catalytic performance in the hydrogenation of carbonyl compounds.

#### Conclusions

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In summary, well-dispersed Cu/MgO catalysts were prepared by an alternative separate nucleation and aging step method. Asformed Cu/MgO catalysts with the largest amount of basic sites or the largest amount of copper surface area exhibited superior catalytic performance in the vapor-phase hydrogenation of DMCD and FAL, which could be tentatively ascribed to the synergistic effect between the metallic copper species and surface basic sites (especially SB sites). The Cu<sup>0</sup> sites contributed to the activation of H<sub>2</sub> molecule, while surface basic sites favored the activation of substrate molecules. From both academic and industrial viewpoints, this work is very meaningful to guide the preparation of low-cost and highly-efficient supported Cu-based catalysts for the selective hydrogenation of carbonyls to alcohols.

#### Experimental

#### Synthesis of catalysts

Supported Cu/MgO catalyst precursors were prepared by a separate nucleation and aging step method developed in our group.<sup>39</sup> Solution A: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O salts with the theoretical Cu/(Cu+MgO) mass ratios of x in wt.% (x =10, 25, 40, 55, 70 and 90) were dissolved in 100 mL of deionized water to give a solution with a total cationic concentration of 0.4 M. Solution B: NaOH and Na<sub>2</sub>CO<sub>3</sub> were dissolved in 100 mL of deionized water to form a mixed base solution ( $[CO_3^{2^-}] = 0.4 \text{ M}$ , [OH<sup>-</sup>] =0.8M). Solutions A and B were simultaneously added to a colloid mill with the rotor speed set at 6000 rpm and mixed for 3 min. The resulting suspension was washed several times with deionized water, aged at 60 °C for 12 h, and finally dried at 70 °C over night. The catalyst precursor was calcined in static air at 450 <sup>o</sup>C for 6 h, pelletized, crushed, sieved to 40-60 mesh, and denoted as C-x. Before the hydrogenation reaction, the calcined samples were in situ reduced in 10 %  $H_2/N_2$  atmosphere at 300 °C for 2 h at a ramp rate of 2 °C min<sup>-1</sup>, and the obtained reduced catalysts were denoted as Cu-x.

For comparison, different commercial supports (MgO, CaO,  $Al_2O_3$ , TiO<sub>2</sub>, SiO<sub>2</sub>) also were used to synthesize supported Cubased catalysts with the same Cu loading of about 25.0 wt.% by impregnation method.<sup>58</sup>

X-ray diffraction (XRD) data were collected at room temperature on Shimadzu XRD-6000 diffractometer with graphite-filtered Cu  $K\alpha$  source ( $\lambda$ = 0.15418 nm), 40 kV and 40 mA.

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Elemental analysis was carried out using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscopy (ICP-AES) after the samples were dissolved in dilute hydrochloric acid (1:1).

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL 2100 operated at an accelerating voltage of 200 kV.

High-angle annular dark-field scanning TEM-energydispersive X-ray spectroscopy (HAADF-STEM) image was recorded on a JEOL2010F instrument combined with X-ray energy dispersive spectroscopy (EDS) system.

 $N_2$  adsorption-desorption isotherms of samples were obtained on a Micromeritics ASAP 2020 sorptometer apparatus at -196 °C. The specific surface areas were obtained by the multipoint Brunauer–Emmett–Teller (BET) method.

X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger spectra (XAES) were recorded on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer at a base pressure of  $2 \times 10^{-9}$  Pa using Al K $\alpha$  X-ray radiation (1486.6 eV photons).

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) was performed using Micromeritics ChemiSorb 2720 instrument. Sample (0.1g) was placed in a quartz U-tube reactor and degassed at 200 °C for 2 h under argon flow (40 mL/min). Then TPR was conducted in a stream of 10% v/v H<sub>2</sub>/Ar (40 mL/min) with a heating rate of 5 °C /min up to 800 °C. The effluent gas was analyzed by a thermal conductivity detector (TCD).

The copper surface areas and copper dispersions were determined according to  $H_2$ -N<sub>2</sub>O titration.<sup>59</sup> Firstly, calcined sample underwent a H<sub>2</sub>-TPR process in 10% H<sub>2</sub>/Ar mixture from 50 to 400 °C and held the temperature until no more H<sub>2</sub> consumption. After cooling down, the gas was switched to 10% N<sub>2</sub>O/N<sub>2</sub>, and the sample was oxidized at a flow rate of 50 ml/min at 60 °C for 1 h, followed by Ar purging and cooling the sample bed down to room temperature. Finally, H<sub>2</sub>-TPR was carried out again with a gas mixture of 10 % H<sub>2</sub>/Ar to 400 °C. Copper dispersion was calculated by dividing the amount of surface copper sites by the total number of Cu atoms; copper surface area was calculated by assuming spherical shape of the Cu metal particles and a surface concentration of 1.47 × 10<sup>19</sup> Cu atoms/m<sup>2</sup>.

Temperature-programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) was conducted on a ChemiSorb 2720 instrument equipped with a TCD. 0.1 g sample was heated at a rate of 10 °C/min to 600 °C under He flow (40ml/min) and maintained at this temperature for 1 h in order to remove the surface impurities. Then the sample was reduced with 10% H<sub>2</sub>/Ar mixture at 300 °C for 1 h. After cooling down to room temperature under He flow, the sample was exposed to pure CO<sub>2</sub> (20 ml/min) for 1 h. Subsequently, the sample was purged with He (40 ml/min) for 1 h and then heated to 800 °C at a rate of 5 °C /min.

In situ FT-IR spectra of CO adsorption were recorded on a Thermo Nicolet 380 FT-IR spectrometer. The sample powder was pressed into a self-supporting wafer (50 mg) and mounted into the IR cell. The sample was first reduced with  $H_2$  (10 ml/min) at 300

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°C for 1 h, followed by evacuating for 1 h at 400 °C and then cooling the sample wafer down to room temperature. After acquisition of the background spectrum, the sample was exposed to CO with increasing pressure (500 Pa) at room temperature. Then the cell was evacuated and heated from room temperature to 100 °C. The FT-IR spectra of CO adsorption on the catalyst were obtained by subtracting the background spectrum.

## Catalytic hydrogenation

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The hydrogenation of DMCD was carried out in a stainlesssteel fixed-bed tubular reactor with the inner diameter of 12 mm. The calcined Cu-based sample (2.0 g) was loaded into tubular reactor with quartz powders packed in both sides of the catalyst bed, and then were reduced in a 10%  $H_2/N_2$  atmosphere at 300 °C for 2 h at a heating rate of 2 °C min<sup>-1</sup>. After activation of catalysts, 20.0 wt. % DMCD (purity >99.9 %) in methanol and H<sub>2</sub> were fed into the reactor at a H<sub>2</sub>/DMCD molar ratio of 220 at a certain temperature. During hydrogenation, the total pressure was kept at 6.0 MPa, and the room-temperature liquid hourly space velocity (LHSV) of DMCD changed from 1.0 to 4.0  $h^{-1}$ . In addition, the hydrogenation of FAL was also carried out using the same instrument. After activation of catalysts, 100 wt. % FAL (purity > 99.0%) without solvent and H<sub>2</sub> were fed into the reactor at a H<sub>2</sub>/FAL molar ratio of 16. Hydrogenation was performed at atmospheric pressure, and LHSV of FAL was set at 1.0 h<sup>-1</sup>. Finally, liquid products were analyzed by an Agilent GC7890B gas chromatograph equipped with flame ionization detector and DB-wax capillary column. The injector temperature was set at 230 °C, and the detector temperature was set at 240 °C. As for products from DMCD hydrogenation, the column temperature was increased from 150 to 180 °C with a ramp rate of 10 °C/min and then to 240 °C with a ramp rate of 20 °C/min. As for products from FAL hydrogenation, the column temperature was increased from 55 to 100 °C with a ramp rate of 20 °C/min and then to 230 °C with a ramp rate of 30 °C/min. The conversions were calculated by the change in molar number before and after the reaction. The selectivities of all products were calculated by the equation: selectivity (mol.%) = (moles of product)/(the sum of themoles of all products)  $\times$  100 %. The average conversions and selectivities with the experimental errors less than 3 % were obtained based on at least 3 parallel experiments.

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