View Article Online View Journal

# Green Chemistry

# **Accepted Manuscript**

This article can be cited before page numbers have been issued, to do this please use: S. Zhang, G. Fan and F. Li, *Green Chem.*, 2013, DOI: 10.1039/C3GC40658J.

### **Green Chemistry**



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

## **RSC**Publishing

www.rsc.org/greenchem Registered Charity Number 207890 Published on 16 July 2013. Downloaded by Queens University - Kingston on 28/07/2013 18:18:42.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxx

# Lewis-base-promoted copper-based catalyst for highly efficient hydrogenation of dimethyl 1,4-cyclohexane dicarboxylate <sup>†</sup>

Shaoyan Zhang, Guoli Fan, Feng Li\*

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

<sup>1</sup>The gas-phase hydrogenation of dimethyl 1,4-cyclohexane dicarboxylate to 1,4-cyclohexane dimethanol was performed on a well-dispersed Cr-free supported copper-based catalyst derived from Cu-Mg-Al layered double hydroxide precursor, <sup>10</sup> and achieved a lasting 100 % conversion with 99.8 % selectivity up to 200 hours. The unprecedented catalytic performance is ascribed to the synergistic effect between surface active Cu<sup>0</sup> sites and Lewis base sites.

Nowadays, 1,4-cyclohexane dimethanol (CHDM), а 15 commercially important diol, is preferred over ethylene glycol as a stepping stone in the production of high-quality and nontoxic polyester fiber materials with high melting point and excellent transparency for extensive use in photography and in other applications involving polycarbonates and polyurethanes.<sup>1</sup> In 20 industry, CHDM is produced normally by the catalytic hydrogenation of dimethyl 1,4-cyclohexane dicarboxylate (DMCD) over traditional CuCr-based catalysts.<sup>2</sup> In spite of the high yield of desired product, the toxicity of such type of Crcontaining catalysts, however, can cause quite serious 25 environmental pollutions, and thus limits their large-scale practical applications. Therefore, it is imperative to look for Crfree and highly efficient catalysts for the hydrogenation of DMCD.

It is well known that supported copper-based catalysts exhibited excellent activity and selectivity in some vapour-phase <sup>30</sup> hydrogenation reactions.<sup>3</sup> The preparation optimization of catalytically active copper-based catalysts, however, is far more advanced than the fundamental understanding of their catalytic activity. Therefore, approaches to prepare Cu-based catalysts (*e.g.* deposition-precipitation and incipient wetness impregnation) <sup>35</sup> have been intensively explored in order to make full use of their

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, P. O. BOX 98, Beijing, 100029, P. R. China.

E-mail: lifeng@mail.buct.edu.cn; Fax: +8610-64425385;

unique catalytic properties. In most cases, however, it is difficult to obtain well-dispersed metal nanopaticles (NPs) with uniform size and good thermal stability, especially at high loadings, which originates from inhomogeneous distribution of active precursors 40 on supports as well as weak interaction between them.

Layered double hydroxides (LDHs,  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ [A<sub>x/n</sub>]<sup>n-</sup>·mH<sub>2</sub>O) belong to a family of highly ordered twodimensional layered materials, where different  $M^{2+}$  and  $M^{3+}$ metal cations uniformly distribute and orderly prearrange in the 45 brucite-like sheets.<sup>4</sup> Correspondingly, well-dispersed supported metal catalysts can be obtained by reducing calcined LDHs with desired active metal species.<sup>5</sup> This kind of structural transformation endows LDH materials with extraordinary capability as catalyst precursors in various metal-catalyzed <sup>50</sup> reactions.<sup>6</sup> In comparison with other metal-supported catalysts, LDH-derived supported metal catalysts have two advantages: (i) a uniform distribution of active metal cations on the atomic level without a segregation of "lakes" of separate cations within the brucite-like layers, which ensures the high homogeneity in a LDH 55 precursor, facilitates the formation of highly dispersed metal species upon calcination; (ii) metal nanoparticles with tunable particle size can be formed in a controllable manner. Recently, considerable attempts have been made on using LDHs containing Cu, Zn and Al with different metal ratios as catalyst precursors 60 for a variety of industrially important reactions including methanol steam reforming, methane synthesis, and so on.'

Herein, we conduct a facile single-source precursor route to achieve green, well-dispersed supported Cr-free Cu-based catalysts from CuMgAl-LDH precursors and use them for the <sup>65</sup> vapour-phase hydrogenation of DMCD. It is found that, in our case, the synergistic effect between surface active Cu<sup>0</sup> sites and Lewis base (LB) sites controls the hydrogenating capability, unlike the Cu<sup>+</sup>-Cu<sup>0</sup> synergy reported in the literature that mainly hold the key to hydrogenation reactions related to <sup>70</sup> ester groups.<sup>8</sup> More importantly, the obtained catalyst achieves a lasting 100 % conversion of DMCD with 99.8 % selectivity to CHDM up to 200 hours. To the best our knowledge, such ultra highly active, efficient and stable Cr-free Cu-based catalyst for hydrogenation of DMCD has not been reported <sup>75</sup> until now.

The preparation procedure of supported Cu-based catalysts with different Cu/Mg/Al atomic ratios (Table 1) invoked the formation of single-source CuMgAl-LDH precursors and controllable calcination and reduction[see SI†]. CuMgAl-LDH <sup>80</sup> precursors were prepared by separate nucleation and aging steps

Tel.: +8610-64451226

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental section, XRD patterns of Cu-3 catalysts obtained at different calcination temperature (Fig.S1), XRD patterns of different Cu-based catalysts (Fig.S2), H2-TPR profiles of different calcined CuMgAl-LDH precursors (Fig. S3), TEM and HRTEM images of Cu-3 sample (Fig.S4), the elemental mapping of Cu, Mg and Al atoms over the Cu-3 sample (Fig. S5). See DOI: 10.1039/b000000x

method developed in our laboratory.9 The powder XRD patterns of the representative LDH precursor with the Cu/Mg/Al atomic ratio of 6:6:6 (Fig. 1a) show the characteristic diffractions of hydrotalcite-like materials (JCPDS no. 37-0630) with good 5 crystallinity. After calcination at 600 °C, a broad diffraction

- observed at 2 $\theta$  of about 36° is obviously different from those of crystalline simple metal oxides (e.g. CuO, MgO and Al<sub>2</sub>O<sub>3</sub>), suggestive of the formation of mixed metal oxide solid-solution phase. Additonally, diffraction peaks belonging to MgO and CuO
- 10 with poor crystallinity are detectable in the XRD patterns. After reduction, a strong diffraction appears at 20 of about 43.3° along with a weak one at 50.4°, which is characteristic of fcc copper phase (JCPDS 04-0836). With the increasing calcination temperature, the diffraction intensities of metallic Cu and MgO 15 phases are enhanced gradually (Fig.S1†).No diffractions related
- to alumina phase are observed, indicative of the presence of amorphous aluminia. With the increasing Mg content, the broader and weaker characteristic diffractions of metallic copper (Fig. S2<sup>†</sup>) can be attributed to the dilution effect of MgO component in 20 reduced samples, thus leading to the reduced particle size of Cu NPs (Table 1).  $H_2$ -TPR results (Fig. S3<sup>†</sup>) further confirm that the addition of Mg can improve the the reducibility of Cu species in the calcined CuMgAl-LDHs, due to the increase in the metal dispersion degree (Table 1).
- TEM images give a direct insight into the microstructure of 25 representative Cu-3 sample. As shown in Fig.1b-c and Fig.S4<sup>†</sup>, a large number of approximately spherical Cu NPs of a size around 4-6 nm are well-dispersed on the support, in good agreement with the elemental mapping observation of relatively homogeneous 30 distributions of Cu, Mg and Al atoms over the sample (Fig. S5<sup>†</sup>). It is believed that benefiting from the uniformly distributed

cations in the brucite-like layers of LDH precursor,<sup>5</sup> the resulting MgO and amorphous Al<sub>2</sub>O<sub>3</sub> phases may function as supports or dispersing agents between Cu-containing phases to form porous <sup>35</sup> aggregates exposing a large Cu surface area of up to  $\sim$ 35 m<sup>2</sup> g<sup>-1</sup>.



Fig. 1 XRD patterns (a) of different samples, TEM (b,c) and HRTEM (d) images of representative Cu-3 sample.

DMCD

conversion

<sup>g</sup> (%) 92.3

96.5

100

96.9

63.8(14.1)

CHDM

86.2

93.1

99.8

94.3

Selectivity (%)

MCHM

2.3

1.2

0.2

0.2

MHMCC

6.6

3.2

0.0

1.9

40			-		-				
	Table 1 Physico-chemical properties and catalytic hydrogenation performance of								
_	Catalysts	Atomic ratios of Cu/Mg/Al	Cu loadings <sup>a</sup> (wt.%)	${S_{BET}}^{b}$ (m <sup>2</sup> /g)	$\frac{S_{Cu}}{(m^2/g)}$	Di <sup>d</sup> (%)	D <sub>Cu</sub> <sup>e</sup> (nm)	Specific basicity <sup>f</sup> (µmolCO <sub>2</sub> /g)	Total LB site (SLB sites) <sup>4</sup> (µmolCO <sub>2</sub> /g)
	Cu-1	12:0:6	70.5	29.6	21.9	4.6	14	30.8	23.1(0)
	Cu-2	9:3:6	56.8	51.3	35.7	9.3	7	39.5	26.8(1.8)
	Cu-3	6:6:6	40.3	67.3	34.9	12.8	6	108.9	96.2(44.1)

24.2

12.8

76.6

of different Cu-based catalysts

<sup>a</sup> determined by ICP-AES analysis. <sup>b</sup> BET surface area. <sup>c</sup>Cu surface area determined by N<sub>2</sub>O titration. <sup>d</sup>Cu dispersion degree determined by N<sub>2</sub>O titration. crystal size of Cu NPs estimated by XRD patterns.<sup>f</sup> determined by CO<sub>2</sub>-TPD.<sup>g</sup> reaction conditions: liquid hour space velocity (LHSV) = 1.0 h<sup>-1</sup>,  $H_2/DMCD = 203$ , reaction temperature = 220 °C and reaction pressure = 6 MPa.

76.1

4



27.9

4:8:6

Cu-4

45

Fig. 2 (A) Cu 2p XPS and Cu LMM XAES of Cu-3; (B) In situ FT-IR spectra of CO absorption on Cu-3 sample. CO pressure of 500 Pa (a), followed by evacuation at 30  $^{\circ}$ C (b) and 100  $^{\circ}$ C (c).

As to hydrogenation catalyzed by metallic copper, the surface nature of Cu species in the Cu-based catalysts was investigated by XPS measurements. As shown in Fig. 2A, the disappearance of the Cu 2p satellite peak at binding energy (BE) of 942-944 eV in the XPS and the appearance of a single peak at kinetic energy 55 of 918.3 eV in the Cu LMM XAES dipict clearly the sole presence of Cu<sup>0</sup> species on the surface of Cu-3 sample.<sup>10</sup> Further evidence can be obtained from the in situ FT-IR spectrum of CO absorption on the Cu-3 sample. As shown in Fig. 2B, a single symmetric peak is observed at about 2100 cm<sup>-1</sup> after saturating 60 the sample 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>11</sup>

CO2-TPD measurements were used to probe surface basicity

of the as-synthesized Cu-based catalysts. As shown in Fig.3, Cu-3 sample presents four kinds of CO<sub>2</sub> desorption peaks. The three peaks at lower temperatures are assigned to weak Brønsted basic sites centered at 100 °C, moderate LB sites centered at 150 °C, <sup>5</sup> and strong LB sites centered at 400 °C, respectively.<sup>12</sup> The intensive desorption peak centered at 510 °C should be associated with the large amount of super LB (SLB) sites existing on the surface of Cu-3 sample. From the O 1s spectrum of Cu-3 sample (Fig.4), it is seen that there are four fitted peaks, representing four

10 different kinds of surface oxygen species. There is a general agreement between the literature and the present results such that the peak with the BE around 530.9 eV belongs most likely to oxygen species of hydroxyl groups at surface, while the peaks at lower BE of about 530.1 and 529.3 eV are the characteristic of 15 lattice oxygens bound to metal cations of the structure, *i.e.*, M-O-M groups and Mg-O<sup>2-</sup> pairs.<sup>13</sup> Interestingly, the peak located at 528.3 eV can be attributed to the coordinatively unsaturated  $O^{2-}$ species strongly bound to  $Mg^{2+}$  cations ( $O^{\delta-}$ ), which should be related to the reduction of the Cu-O-Mg parts in mixed metal 20 oxide solid-solution phase during the catalyst activation procedure, leading to the formation of Cu NPs in strong interfacial contact with MgO phase. It also indicates the presence of SLB sites on the surface of Cu-3 sample, in good agreement with the CO<sub>2</sub>-TPD result. As listed in Table 1, Cu-3 possesses the 25 largest amount of total LB sites as well as that of SLB sites among the Cu-based samples.



Fig. 3 CO<sub>2</sub>-TPD profile of Cu-3 sample.

Published on 16 July 2013. Downloaded by Queens University - Kingston on 28/07/2013 18:18:42.



Fig.4 O 1s XPS of Cu-3 sample.

It is well documented that the catalytic hydrogenation of DMCD to CHDM usually goes through a consecutive multi-step <sup>35</sup> reaction pathway (Scheme 1), and that CHDM product can be further dehydrated to 4-methyl-cyclohexanemethanol (MCHM). Meanwhile, the accumulation of the reaction intermediate, methyl 4-hydroxymethylcyclohexane carboxylate (MHMCC), can not be neglected.



Scheme 1 Reaction pathway for the hydrogenation of DMCD to CHDM

Table 1 summarizes the results of catalytic hydrogenation of 45 DMCD over as-synthesized Cu-based catalysts with different Cu/Mg/Al atomic ratios, which were obtained under industrial conditions. The yield of CHDM decreases in the following order for the catalysts: Cu-3 > Cu-4  $\approx$  Cu-2 > Cu-1. Especially, a 50 complete DMCD conversion with 99.8% selectivity was achieved over the Cu-3 catalyst, which is the most efficient catalyst for this reaction reported to date. As to hydrogenation catalyzed by metallic copper, one important key to high performance is a large accessible Cu surface area. The Cu-1 catalyst with the smallest 55 active Cu surface area exhibits lower catalytic activity than the other catalysts, because of smaller copper surface area supplying less catalytically active sits for hydrogen dissociation and thus lower DMCD conversion.<sup>14</sup> However, the change in the activity of the catalysts does not change monotonically with the metallic 60 copper surface area. It is worthy to note that the Cu-3 catalyst with the largest amount of surface LB sites exhibits superior catalytic performance to others, in spite of slightly lower copper surface area than that of the Cu-2 catalyst. Furthermore, when the Cu-4 catalyst with relatively more surface LB sites is used to 65 catalyze the hydrogenation, similar DMCD conversion and selectivity of CHDM to those of the Cu-2 catalyst are found, though it presents much lower copper surface area than the Cu-2 catalyst. The aforementioned results indicate that the Cu surface area alone cannot explain the differences in catalytic performance 70 for catalysts, and the surface basic nature also should play an important role in the hydrogenation of DMCD. In contrast, traditional Cu-Cr<sub>2</sub>O<sub>3</sub> catalyst with the Cu loading of 40.3 % exhibits much lower conversion of DMCD (89.0%) and selectivity to CHDM (90.0 %), compared with the Cu-3 catalyst. Based on the above experimental results, it is deduced that 75

effect mechanism for hydrogenation reaction between surface  $Cu^0$  and LB sites over as-formed Cu-based catalysts is tentatively proposed to rationalize the experimentally observed structureperformance relation (Scheme 2). The first step is the dissociation s of H<sub>2</sub> on the surface of Cu<sup>0</sup> particles and the activation of DMCD

by surface LB sites. On the surface LB sites of catalyst, the C=O group may form a zwitterionic, tetrahedral intermediate with enhanced nucleophilic reactivity at the oxygen atom. Consequently, the π-bond of C=O become easy to be attacked by dissociative hydrogen. Therefore, the ester carbonyl gets two H atoms from Cu<sup>0</sup> and parts from LB sites. Due to the hydrogenation of C=O bond, DMCD transforms gradually to MHMCC by eliminating a CH<sub>3</sub>OH, which can be confirmed by the incompletely hydrogenation product. In the proposed nechanism, only one of the ester group hydrogenation is shown, while the other ester group is supposed to undergo the same hydrogenation path. As a result, the extremely high and effective hydrogenation activity of Cu-3 catalyst may rely on the active Cu<sup>0</sup> particles and the surface LB nature.



Published on 16 July 2013. Downloaded by Queens University - Kingston on 28/07/2013 18:18:42.

20

25

Scheme 2 Schematic representation of over as-synthesized Cubased catalyst.



Fig. 5 Hydrogenation performance of Cu-3 catalyst as a function of time on stream at 220  $^{\circ}$ C (a); DMCD conversion and product selectivities as a function of reaction temperature (b) over Cu-3 catalyst.

As a result, due to the highly dispersed nature of Cu nanoparticles, metallic Cu may interact closely with neighboring MgO component at the interface in the Cu-based catalysts. Such interaction facilities the occurrence of synergistic effect between surface active Cu<sup>0</sup> sites and LB sites for hydrogenation of DMCD.

Remarkably, it is interesting to find that the excellent catalytic performance of the most efficient Cu-3 catalyst in the gas-phase hydrogenation of DMCD stays nearly unchanged over a 200 h reaction time when the other reaction conditions are kept constant (Fig.5a). Furthermore, even though at the higher teating 100 % over the Cu-3 catalyst and the selectivity to CHDM reaches as high as 98.0% (Fig. 5b). These results indicate that the catalyst derived from CuMgAl-LDH precursor is very stable, due to the stabilization effect of MgO and Al<sub>2</sub>O<sub>3</sub> phases in the scatalyst preventing the Cu NPs from aggregation.

In summary, we have presented that the introduction of Mg into Cu-based catalysts from LDH precursor provides a significant route to modify the structural and surface properties of catalysts. The Cu-3 catalyst possessing the largest amount of LB so sites and relatively high copper surface area exhibited the best catalytic performance, which could be tentatively ascribed to the synergistic effect between the metallic copper species and surface LB sites (especially SLB sites). Furthermore, the Cu-based catalyst showed a good stability with a lasting 200-hour ultrahigh sactivity and selectivity to CHDM. We believe that such low-cost and environment-friendly Cr-free Cu-based catalysts are of great industrial importance for the gas-phase successive production of CHDM, although further investigation of the reaction mechanism and catalytic stability still remains to be done.

### 60 Acknowledgment

We gratefully acknowledge the financial support from 973 Program (2011CBA00506) and the National Natural Science Foundation of China.

#### Notes and references

75

85

- 5 1 T. S. Richard, J. Polym. Sci. part A, 2004, 42, 5847.
  - 2 (a) Schlossman and L. Mitchell, US pat., 4 301 046, 1981; (b) G. A. Akin, Marl, H. J. Lewis and T. F. Reid, US pat., 3 334 149, 1967.
  - 3 (a) J. H. Schlander and T. Turek, *Ind. Eng. Chem. Res.*, 1999, 38, 1264; (b) T. Sodesawa, M. Nagacho, A. Onodera and F. Nozaki, *J. Catal.*, 1986, 102, 460; (c) H. Kobayashi, N. Takezawa and C. Minochi, *J. Catal.*, 1981, 69, 487.
  - 4 (a) P. S. Braterman, Z. P. Xu, F. Yarberry, In Handbook of Layered Materials, S. M. Auerbach, K. A. Carrado and P. K. Dutta, ed. Marcel Dekker, New York, 2004; (b) D. G. Evans and R. C. T. Slade, in *Layered double hydroxides*.ed. X. Duan and D. G. Evans, springer, Struct. Bond., 2006, **119**, 1.
  - 5 (a) A. I. Tsyganok, T. Tsunoda, S. Hamakawa, K. Suzuki, K. Takehira and T. Hayakawa. J. Catal., 2003, 213, 191; (b) C. Gérardin, D. Kostadinova, N. Sanson, B. Coq and D. Tichit, Chem. Mater., 2005, 17, 6473; (c) C. Gérardin, D. Kostadinova, B. Coq and D. Tichit, Chem. Mater., 2008, 20, 2086.
  - 6 (a) C. Resini, T. Montanari, L. Barattini, G. Ramis, G. Busca, S. Presto, P. Riani, R. Marazza, M. Sisani, F. Marmottini and U. Costantino, *Appl. Catal.*, *A*, 2009, 355, 83; (b) A. Olafsen, Å. Slagtern, I. M. Dahl, U. Olsbye, Y. Schuurman and C. Mirodatos. *J Catal.*, 2005, 229, 163; (c) Z. Yu, D. Chen, M. Rønning, B. Tøtdal, T. Vrålstad, E. Ochoa-Fernández and A. Holmen, *Appl. Catal.*, A, 2008, 338, 147; (d) N. Barrabes, D. Cornado, K. Foettinger, A. Dafinov, J. Llorca, F. Medina and G. Rupprechter, *J. Catal.*, 2009,

15

20

25

30

35

40

Published on 16 July 2013. Downloaded by Queens University - Kingston on 28/07/2013 18:18:42.

**263**, 239; (e) J. T. Feng, Y. J. Lin, D. G. Evans, X. Duan and D. Q. Li, *J. Catal.*, 2009, **266**, 351; (f) L. Zhang, F. Li, X. Xiang, M. Wei and D. G. Evans, *Chem. Eng. J.*, 2009, **155**, 474; (g) X. Xiang, H. I. Hima, H. Wang, and F. Li. *Chem. Mater.*, 2008, **20**, 1173.

- <sup>5</sup> 7 (a) S. R. Segal, K. B. Anderson, K. A. carrado and C. L. Marshall, *Appl. Catal. A*, 2002, **231**, 215; (b) P. Kurr, I. Kasatkin, F. Girgsdies, A. Trunschke, R. Schlögl and T. Ressler, *Appl. Catal. A*, 2008, **348**, 153; (c) S. Tanasoi, N. Tanchoux, A. Urdă, D. Tichit, I. Săndulescu, F. Fajula, and I. C. Marcu, *Appl. Catal. A*, 2009, **363**,
- 135; (d) S. Velu, K. Suzuki, M. P. Kapoor, F. Ohashi and T. Osaki. Appl. Catal. A, 2001, 213, 47; (e) G. Busca, U. Costantino, F. Marmottini, T. Montanari, P. Patrono, F. Pinzari and G. Ramis, Appl. Catal. A, 2006, 310, 70; (f) U. Costantino, Fmarmottini, M. Sisani, T. Montanari, G. Ramis, G. Busca, M. Turco and G.
  - Bagnasco, Solid State Ionics, 2005, **176**, 2917. g) M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. Kniep, M. Tovar, R. W. Fischer, J.K. Nørskov, R. Schlögl, Science, 2012, **336**, 893.
  - 8 J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang and X. Ma, J. Am. Chem. Soc., 2012, 134, 13922.
  - 9 Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater.*, 2002, **14**, 4286.
  - 10 (a) L. F. Chen, P. J. Guo, M. H. Qiao, S. R. Yan, H. X. Li, W. Shen, H. L. Xu and K. N. Fan, *J. Catal.*, 2008, **257**, 172; (b) A. Y. Yin, X.
  - Y. Guo, W. L. Dai, H. X. Li and K. N. Fan, *Appl. Catal. A*, 2008, 349, 91; (c) A. Y. Yin, X. Y. Guo, W. L. Dai and K. N. Fan, *J. Phys. Chem. C*, 2009, 113, 11003.
  - 11 (a) R. Shi, F. Wang, Tana, Y. Li, X. Huang and W. Shen, *Green Chem.*, 2010, **12**, 108; (b) V. Z. Fridman and A. A. Davydov, *J. Catal.*, 2000, **195**, 20.
  - (a) J. I. Di Cosimo, V. K. Díez, M. Xu, E. Iglesia and C. R. Apesteguia, J. Catal., 1998, **178**, 499; (b) P.Unnikrishnan and D. Srinivas, Ind. Eng. Chem. Res., 2012, **51**, 6356
  - (a) M. Tamura, T. Tonomura, K. Shimizu and A. Satsuma, *Green Chem.*, 2012, 14, 717; (b) S. V. Jaime, L. Enrique, A. T. A. Jose, A. C. J. Maria, L. R. Luis, M. Ramon and P. Julia, *J. Phys. Chem. C*, 2010, 114, 2089.
  - 14 L. Shi, K. Tao, R. Yang, F. Z. Meng, C. Xing and N. Tsubaki, *Appl. Catal. A*, 2011, **401**, 46.
  - 15 S. E. Denmark and G. L. Beutner, Angew. Chem. Int. Ed., 2008, 47, 1560.

### Graphical and textual abstract

Synthesis of 1,4-cyclohexane dimethanol was conducted over an efficient lewis-base-promoted Cr-free supported copper-based catalyst.

