

Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Q. Hu, G. Fan, L. Yang, X. Cao, P. Zhang, B. Wang and F. Li, *Green Chem.*, 2016, DOI: 10.1039/C5GC02924D.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/greenchem

Green Chemistry

DOI: 10.1039/C5GC02924D



Journal Name

COMMUNICATION

Received 00th January 20xx,

Gas-phase coupling process for simultaneous production of γ butyrolactone and furfuryl alcohol without external hydrogen over bifunctional base-metal heterogeneous catalysts

Accepted 00th January 20xx

Qi Hu^a, Guoli Fan^a, Lan Yang^a, Xinzhong Cao^b, Peng Zhang^b, Baoyi Wang^b and Feng Li^a*

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 25 January 2016. Downloaded by Gazi Universitesi on 28/01/2016 04:19:38.

A solvent-free gas-phase coupling process through hydrogen transfer without external hydrogen supply over novel bifunctional base-metal heterogeneous catalysts was developed for the simultaneous production of γ -butyrolactone and furfuryl alcohol with high yields of 95.0 % from bimass-derived compounds. Such practical, unparalleledly efficient and environment-benign process make it promising in terms of both green sustainable chemistry and industrial perspective.

With the increasing concern about energy and environment issues originating from increasing greenhouse gas emission and the shortage of fossil resources, the conversion from sustainable and renewable raw biomass to fuel and chemicals is attracting more and more attention.¹ As one of the most promising biomass-derived platform chemicals, furfuryl alcohol (FOL), which is widely transformed into various useful chemicals including functional resins, lysine, lubricants, and plasticizers,² can be produced industrially by gas-phase hydrogenation of furfural (FL) over copper chromite catalysts.³ However, Cr⁶⁺ species with the high toxicity can cause severe environmental pollution. Therefore, exploring environmentally friendly Cr-free metal catalysts for FL hydrogenation is attracting enormous concerns. For example, a large number of supported noble metal catalysts (i.e. Pt, Pd, Ru) can show excellent catalytic hydrogenation performance.⁴ Further, electronic or structural promoters like Re also are incorporated into catalysts to improve the affinity toward carbonyl group.⁵ Their high cost, however, limits practical application. Recently, heterogeneous nonnoble-metal catalysts (i.e. Ni, Co, Cu) have been employed for FL hydrogenation.⁶ The main disadvantage is that these catalysts are less active compared with noble-metal-based catalysts.

Conventionally, hydrogenating FL always consumes

external hydrogen produced by non-renewable substances such as coal and other natural gas. Very recently, liquid-phase hydrogenation of FL using different alcohols as hydrogen sources has been investigated.⁷ The demand for large amounts of hydrogen donators and solvents, however, limits its practical application. Therefore, gas-phase solvent-free hydrogenation using equal moles of organic hydrogen donators would be greener alternative.⁸ Due to low efficiency of catalysts, external hydrogen supply or hydrogen recycle is still prerequisite to achieve products with high yields, which renders hydrogen transfer process economically and environmentally undesirable.

As an important chemical intermediate, γ -butyrolactone (GBL) has been employed widely for the production of pyrrolidone derivatives, herbicides, and rubber additives in fine and petroleum industries.⁹ In industry, the major production route for GBL involves gas-phase dehydrogenation of 1, 4-butanediol (1,4-BDO) over supported metal catalysts, especially copper chromite catalysts.¹⁰ Recently, supported Cu/SiO₂ catalyst with 80 wt % metal loadings has been reported to exhibit excellent catalytic performance with a 98 % yield of GBL.¹¹ However, decreasing Cu loadings to 12 wt % led to a rapid deactivation, due to the sintering of active species. And, it was found that surface acid sites on catalysts could induce the formation of tetrahydrofuran (THF) in the 1,4-BDO dehydrogenation.¹² Therefore, high selectivity to GBL can be achieved on alkaline metals modified Cu-based catalyst.¹³

At present, 1,4-BDO can be easily obtained on a large scale by highly efficient, low-cost, commercially realized fermentation of renewable biomass (i.e. glucose).¹⁴ Recently, combining 1,4-BDO lactonization with transfer hydrogenation of FL has been reported over a Cu-based catalyst. However, the whole reaction system still was operated under external hydrogen (16 bar).¹⁵ From the viewpoint of sustainable development of resources and economy, if equal moles of 1,4-BDO and FL can be converted simultaneously to GBL and FOL via in situ the coupling between hydrogenation and dehydrogenation over recyclable and selective catalysts in the absence of any external hydrogen, such synthetic route would become the most sustainable and

^a State key laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, P.O.BOX 98, Beijing, 100029, P. R. China.

^b Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China Email: <u>lifeng@mail.buct.edu.cn</u>; Fax:+8610 64425385; Tel : +8610 64451226 †Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Published on 25 January 2016. Downloaded by Gazi Universitesi on 28/01/2016 04:19:38.

Herein, we reported new Ca-Al mixed metal oxide supported copper catalysts prepared via a two-step procedure based on layered double hydroxide precursors (LDHs, $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ $[A_{x/n}]^{n-}$ mH₂O),¹⁶ and then employed them as bifunctional basemetal heterogenous catalysts for gas-phase solvent-free coupling between dehydrogenation and hydrogenation without external hydrogen to produce GBL and FOL from bimass-derived 1,4 BDO and FL (Fig.1). It was found that the surface Lewis base (LB) sites, defective Cu nanoparticles (NPs) and Cu⁺ species on catalysts could create a cooperative nanoenvironment for holding the dehydrogenation of hydroxyl group in 1,4 BDO and the hydrogenation of carbonyl group in FL. More importantly, assynthesized bifunctional base-metal catalyst achieved lasting high yields of GBL and FOL (> 95.0 %) up to 100 hours under the mild reaction conditions. To the best our knowledge, such practical, unparalleledly efficient and environment-benign gasphase coupling between 1,4-BDO dehydrogenation and FL hydrogenation for simultaneous production of GBL and FOL without the use of any solvent and external hydrogen supply or recycle has not been reported until now.



Fig. 1 Reaction coupling for the production of GBL and FOL from biomass.

The preparation of supported copper-based catalysts over Ca-Al mixed metal oxide (CaAlO) (Table 1) includes the preparation of CaAlO from CaAl-LDH precursors, followed by further impregnation, calcination and reduction (see ESI[†]). As shown in Fig 2a, XRD patterns of representative CaAl-LDH precursor with the Ca/Al atom ratio of 4.0 exhibit the characteristic diffractions of hydrotalcite-like materials (JCPDS no. 37-0630) with good crystallinity. However, a small amount of calcium carbonate phase (JCPDS no. 47-1743) can be observed, due to the reaction between Ca2+ cations in the brucite-like layers of CaAl-LDH precursor and interlayer carbonate anions upon heating. In the case of reduced Cu-4 sample, a major diffraction at 2θ of about 43.07° can be indexed to the (111) plane of face cubic centered (fcc) metallic copper (JCPDS 04-0836), besides CaCO₃ phase. No diffractions related to crystalline CaO and Al₂O₃ are observed, implying that CaAlO or Al₂O₃ may exist in the amorphous form. In the present catalyst system, this kind of Al³⁺-containing amorphous phase as a support can improve the interaction between metal NPs and support, ¹⁷ thus enhancing the dispersion of Cu NPs. Moreover, as the Ca content increases, the diffractions for metallic copper become broader and weaker (Fig.S1), indicating the dispersion effect of CaAlO component in samples, leading to the reduced particle size of Cu NPs (Table 1).

Table 1 The structural data of Cu-based catalysts

Samples	Ca/Al ratio	Cu ^a (wt %)	$\frac{S_{Cu}{}^{b}}{(m^{2}/g)}$	D _{av} ^c (nm)	Specific SLB sites ^d (mmol CO ₂ /g)	Cu ⁺ /(Cu ⁰ +Cu ⁺) ratio ^e
Cu-3	3:1	27.6	7.9	19.8	1.58	0.38
Cu-4	4:1	24.3	10.8	11.7	2.61	0.52
Cu-5	5:1	25.6	11.0	10.9	2.82	0.37

^a Determined by ICP-AES. ^b Copper surface area. ^c Average crystal size of Cu NPs determined by XRD patterns. ^d Determined by CO₂-TPD. ^e Determined by XPS.

In the case of Ca/Al atom ratio of 3.0, a broad reduction region for Cu²⁺ species in H₂-TPR profiles of calcined precursors can be fitted into three peaks at about 200, 237 and 288 °C (Fig.S2), which are assigned to the reduction of isolated highly-dispersed CuO (Cu_A^{2+}) , small CuO particles (Cu_B^{2+}) and large bulk CuO species (Cu_{C}^{2+}) , respectively.¹⁸ With increasing Ca/Al molar ratio to 4.0, two reduction peaks for CuA2+ and CuB2+ species shift to lower temperatures, and the reduction peak for Cu_C²⁺ species disappears. In the case of Ca/Al atom ratio of 5.0, in turn, the reduction peaks slightly shift to higher temperatures, due to strong metal-support interaction. It demonstrates that the addition of an appropriate amount of Ca^{2+} can greatly improve the reducibility of Cu^{2+} species. Further, Cu XAES analysis was performed to determine the chemical states of copper species on Cu-x catalysts (Fig.S3). Obviously, broad and asymmetric Auger kinetic energy peak can be fitted into two peaks around 916.6 eV and 918.8 eV, corresponding to Cu^+ and Cu^0 species, respectively.¹⁹ The surface $Cu^+/(Cu^0+Cu^+)$ ratio can be quantitatively calculated by the ratio of the peak area of Cu⁺ to total peak area.²⁰ Notably, Cu-4 sample possesses the largest $Cu^+/(Cu^0+Cu^+)$ ratio (0.52).

The morphology and microstructure of Cu-4 sample were characterized by TEM. It is interesting to note that a large number of highly dispersed cuboctahedron or truncated octahedron Cu NPs of around 11 nm in size are embedded in the support matrix (Fig 2b,c), suggestive of the presence of strong metal-support interaction (SMSI). This result is in good agreement with the HAADF-STEM-EDS observation showing relatively homogenous distributions of Cu, Ca and Al elements on the sample (Fig.S4). As the best approximations for the geometry of a metallic particle, both cuboctahedron and octahedron may bring about the surface to intrinsically contain a large number of steps, thereby leading to the formation of defects.²¹ In addition, in the case, the fast Fourier transform (FFT) lattice-fringe image of an individual copper particle (Fig. 2d) depicts spots at 2.0 and 1.8 Å, which correspond to the (111) and (200) planes of metallic copper, respectively, further reflecting the presence of cuboctahedron Cu NPs in a fcc structure.22

Published on 25 January 2016. Downloaded by Gazi Universitesi on 28/01/2016 04:19:38.

Green Chemistry

Journal Name



Fig. 2 XRD patterns of different samples (a), TEM (b), HRTEM (c), and FFT (d) images of Cu-4 sample.

As an extremely sensitive probe of defects in solids, positron annihilation spectroscopy (PAS) can provide an excellent means to investigate relative density of various defects. Positron lifetime components and relative intensities of components for Cu-4 and pristine CaAlO support are listed in Table S1.It is well-known that the shortest-survived component (τ_1) of sample is usually ascribed to small size defects mostly in the bulk section of NPs,²³ while the moderate one (τ_2) results from positrons trapped by large size defects located on the surface, boundary, or interface of NPs.²⁴ Correspondingly, the higher relative intensity of τ_2 to τ_1 for Cu-4 (0.48) than that for CaAlO support (0.42) indicates that the concentration of defect sites is higher in the Cu-4 than in the CaAlO, which is in good accordance with the HRTEM results. Therefore, it can be deduced that the SMSI can promote the formation of a large number of well-dispersed defective Cu NPs on the CaAlO support.

CO2-TPD measurement was used to probe the surface basicity of copper catalysts. In the case of Cu-4, there are four kinds of CO₂ desorption peaks (Fig.3A). A tiny peak at about 100 °C is assigned to weak Brønsted base sites, while a small peak in the range from 440 °C to 580°C is associated with moderate strength LB sites. Noticeably, large desorption peak above 580 °C can be assigned to strong LB (SLB) sites.²⁵ To gain a deeper insight into SLB sites, the O 1s XPS was further analyzed (Fig.3B). Obviously, four fitted XPS peaks should correspond to different surface oxygen species. The small peak at about 531.0 eV can be attributed to oxygen species in hydroxyl groups, while another small peak at 530.2 eV is related to M-O-M groups in the CaAlO structure.²⁶ Notably, two large peaks at 529.3 and 528.1 eV belong to Ca-O²⁺ pairs and coordinatively unsaturated O2- species bound to Ca2+ cations (O^{δ}), respectively. Specially, O^{δ} species are probably formed by the reduction of Cu²⁺-O-Ca²⁺ parts upon activation.²⁷ It demonstrates that strong interfacial contact exists between Cu NPs and CaAlO support. As a result, a large number of SLB sites and highly dispersed defective Cu NPs intimately contacting with SLB sites can be formed on the catalyst surface after reduction. Moreover, according to the CO₂-TPD results, the density of SLB sites in Cu-*x* samples presents an increasing trend with the Ca content (Table 1). In addition, FT-IR spectra of CO₂ adsorption depict the presence of unidentate carbonate species at 1360 and 1590 cm⁻¹ (Fig.S5), which are associated with high strength basic absorption formed on surface Ca-O²⁺ pairs and O^{δ-} species, further reflecting the existence of a large amount of SLB sites on as-formed catalysts.²⁸



Fig. 3 CO2-TPD curve (A) and O 1s XPS (B) for Cu-4 sample.

 Table 2 Catalytic performance of different catalysts ^a

Catalysta	Convers	ion (%)	Selectiv	vity (%)	TOF ^b
Catalysis	FL	BDO	FOL	GBL	(h ⁻¹)
Cu-3	63.0	63.1	100	100	43.8
Cu-4	96.0	95.3	100	100	50.9
Cu-5	90.1	91.2	100	100	47.2
Cu/CaO	30.3	30.6	100	100	16.2
Cu/MgO	23.2	22.4	100	100	14.7
Cu/Al_2O_3	14.3	14.7	99 °	99 ^d	9.2
Cu/SiO ₂	10.4	12.6	99 °	99 ^d	5.5
CaAlO	1.0	2.1	100	100	

^a Reaction condition: LHSV(FL+1,4-BDO)=1.8h⁻¹, n(FL):n(1,4-BDO)=1, n(N₂):n(FL+1,4-BDO) = 13, temperature = 210 °C and reaction pressure = 1 atm.
 ^b Calculated based on the moles of FL converted per mole surface metallic copper in the initial 1 h. °2-MF as by products. °THF as by products.

Under nitrogen atmosphere, the hydrogen transfer goes through a consecutive two-step reaction pathway: dehydrogenation of 1,4-BDO to produce hydrogen and GBL and hydrogenation of FL to produce FOL using the hydrogen produced by dehydrogenation. Table 2 summarizes the results of catalytic hydrogenation of FL and dehydrogenation of 1,4-BDO over different Cu-based catalysts without external hydrogen supply or recycle. And, gas chromatogram spectra of some typical experiments are shown in Figs.S6-S9. It is found that the yields of GBL and FOL decrease in the following order for catalysts: Cu-4 > Cu-5 > Cu-3. Especially, high GBL and FOL yields (> 95.0%) are achieved over the Cu-4 under the high LHSV value. For comparison, such coupling process was also conducted over other oxides (CaO, MgO, Al₂O₃, SiO₂)-supported Cu

COMMUNICATION

Published on 25 January 2016. Downloaded by Gazi Universitesi on 28/01/2016 04:19:38.

catalysts with the similar Cu loadings to Cu-4, which were synthesized by conventional impregnation method. Noticeably, these catalysts exhibit remarkably lower catalytic performance, compared with the present Cu-4. Among these comparison catalysts, basic oxides-supported catalysts (Cu/CaO and Cu/MgO) are more active than neutral and acidic oxides-supported ones (Cu/Al₂O₃ and Cu/SiO₂), indicating the significant promotional effect of LB sites on the couple between dehydrogenation and hydrogenation. Notably, Cu-4 attains a highest turnover frequency (TOF) value of 50.9 h⁻¹, demonstrating the excellent catalytic efficiency of Cu-4 catalyst. On the other hand, such excellent catalytic performance of Cu-4 stays nearly unchanged over 100 hours (Fig.S10). And, TEM image (Fig.S11) gives the evidence that no aggregation or growth of Cu NPs is found after reaction, arising from the stabilization effect of CaAlO support on Cu NPs.

Further, NH₃-TPD profiles of Cu-x samples (Fig.S12) only reveal one broad peak at 113 °C, which originates from desorption of NH₃ from weak Brønsted acid sites.²⁹ In addition, FT-IR spectra of pyridine adsorption (Fig.S13) present two weak bands at 1450 and 1584 cm⁻¹ associated with adsorption of pyridine by H-bonding, besides a weak band at 1435 cm⁻¹ assigned to physical adsorption of pyridine.³⁰ As it was reported, surface Lewis acid sites could facilitate the formation of 2-methyl furan (2-MF) in the FL hydrogenation or the formation of THF in the 1,4-BDO dehydrogenation.^{12,31} Therefore, the high selectivities to both FOL and GBL over Cu-x catalysts also are related to the lack of surface Lewis acid sites.

In addition, 1,4-BDO dehydrogenation under N2 atmosphere was conducted over Cu-x, Cu/CaO and CaAlO samples (Table S2). A relatively high 1,4-BDO conversion of 89.2% can be achieved over the Cu-4 catalyst. However, compared with the results in Table 2, the conversions of 1,4-BDO over catalysts are reduced, indicating that FL hydrogenation can drive reaction equilibrium of 1,4-BDO dehydrogenation toward GBL. Further, FL hydrogenation and 1,4-BDO dehydrogenation over different catalysts was simultaneously conducted under 50% H₂/N₂ mixture atmosphere (Table S3). Noticeably, with the introduction of external hydrogen, the FL conversion is increased in each case, whereas the FOL selectivity is greatly decreased due to the formation of 2-MF. However, the conversion of 1,4-BDO is significantly decreased, because external hydrogen can inhibit the dehydrogenation reaction.

Previously, it was reported that the surface basicity of catalysts imposes a significant effect on the dehydrogenation of alcohols.³² In the course of dehydrogenation, a negatively charged alkoxide intermediate can form through the abstraction of hydroxyl group in alcohols by surface nucleophilic base sites.³³ To further investigate the effect of surface basicity on the dehydrogenation, FT-IR spectra of butanol adsorption on Cu-4 and CaAlO samples were obtained (Fig.4). As for pristine CaAlO, the band at 1032 cm⁻¹ is associated with alkoxide species (Ca-O-CH₂-R) formed through the interaction between basic Ca-O pairs on the catalyst surface and hydroxyl group in butanol.³⁴ Interestingly, after loading Cu NPs, the band related to Ca-O-CH2-R species disappears, but another new band at 1072 cm⁻¹ representing Cu-O-CH₂-R like species can be observed. $^{\rm 35}$ Meanwhile, the stretching bands of -CH_2 groups blue-shifts by about 5 cm⁻¹. The above results demonstrate that CaAlO support may activate hydroxyl group in butanol, while

defective Cu NPs may capture another hydrogen atom from the





Fig. 4 FT-IR spectra of butanol absorption on CaAlO and Cu-4 samples.

According to the above results, it can be concluded that surface SLB sites in intimate contact with defective Cu NPs can interact strongly with the hydroxyl group in 1,4-BDO for abstracting hydrogen, while the highly dispersed defective Cu NPs can further abstract and transfer hydrogen. Cu-3 catalyst with smaller specific SLB sites and copper surface area shows a lower catalytic performance than other Cu-x catalysts, due to the insufficiency of catalytically active sites supplying for transfer hydrogenation. However, the catalytic activity does not change monotonically with the copper surface area or the amount of SLB sites. Specially, compared with Cu-4, Cu-5 exhibits a lower catalytic activity, in spite of the larger number of SLB sites or slightly higher copper surface area. Therefore, there should be other factors affecting the catalytic process. As it is well reported, surface electrophilic Cu⁺ species may promote the hydrogenation of carbonyl compounds to some extent by polarizing the C=O bond via the interaction with the lone pair electron on the O atom.³⁶ Thus, Cu⁺ species on catalysts also may play an important role in further enhancing the catalytic efficiency during the FL hydrogenation, thus promoting the reaction equilibrium toward the production of GBL (Table 1).

Journal Name



Fig. 5 Proposed simplified dehydrogenation-hydrogenation coupling process for production of GBL and FOL on Cu/CaAlO catalysts.

As a result, a mechanism for dehydrogenation-hydrogenation coupling process through hydrogen transfer over as-formed Cu/CaAlO catalysts is proposed tentatively (Fig.5). Firstly, the hydroxyl group in 1,4-BDO interacts with SLB sites on the surface of CaAlO matrix. Subsequently, a hydrogen atom is abstracted to form a negatively charged alkoxide intermediate, which can further bond to adjacent defective Cu NPs to form another adsorbed alkoxide intermediate. Then, Cu NPs capture another α -hydrogen atom from alcoholic group to produce GBL product. Finally, hydrogenation of FL is triggered on Cu NPs using the attracted hydrogen produced from 1,4-BDO and promoted by Cu⁺ species, driving the reaction equilibrium toward the production of GBL. As a result, extremely high and effective hydrogen transfer activity of Cu-4 catalyst can be reasonably attributed to a cooperative nanoenvironment composed of surface SLB sites, defective Cu NPs and Cu⁺ species, which efficiently hold the dehydrogenation of hydroxyl group in 1,4 BDO and the hydrogenation of carbonyl group in FL through hydrogen transfer.

Conclusions

In summary, we reported the fabrication of CaAlO-supported copper catalysts with strong base sites via a two-step procedure based on CaAl-LDH precursor route. The resulting catalyst exhibited superior catalytic performance for gas-phase solvent-free coupling between dehydrogenation and hydrogenation without external hydrogen supply or recycle to simultaneously produce GBL and FOL. The HRTEM, PAS, XPS, CO2-TPD, in situ IR of butanol adsorption confirmed the existence of defective Cu NPs, abundant SLB sites and Cu⁺ species on the catalyst surface, which created a cooperative nanoenvironment for the highly efficient dehydrogenation of hydroxyl group in 1,4 BDO and hydrogenation of carbonyl group in FL. More importantly, a good stability with a lasting 100 h for the high yields of GBL and FOL (>95.0%) could be attained. Our present strategy can hold significant promise for new bifunctional base-metal heterogeneous catalyst toward highly efficient gas-phase dehydrogenation-hydrogenation coupling process, which may be an eco-friendly and economical alternative to the already established processes to manufacture GBL and FOL.

Acknowledgment

We gratefully thank the financial support from National Natural Science Foundation of China (21325624) and the Fundamental Research Funds for the Central Universities (buctrc201528).

Notes and references

- (a) P. P. Upare, D. W. Hwang, Y. K. Hwang, U. -H. Lee, D. -Y. Hong and J. -S. Chang, *Green Chem.*, 2015, **17**, 3310; (b) X. -Y. Li, R. Shang, M. -C. Fu and Y. Fu, *Green Chem.*, 2015, **17**, 2790.
- (a) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411;
 (b) B. M. Nagaraja, A. H. Padmasri, B. D. Raju and K. S. R. Rao, *J. Mol. Catal.*, *A*, 2007, **265**, 90.
- 3. G. Seo and H. Chon, J. Catal., 1987, 67, 424.
- 4. (a) P. D. Vaidya and V. V. Mahajani, *Ind. Eng. Chem. Res.*, 2003, 42, 3881; (b) J. Kijenski, P. Winiarek, T. Paryjczak, A. Lewicki and A. Mikołajska, *Appl. Catal. A.*, 2002, 233, 171; (c) S. Sitthisa, T. Sooknoi, Y. Ma, P. B. Balbuena, D. E. Resasco, *J. Catal.*, 2011, 277, 1; (d) S. Sitthisa and D. E. Resasco, *Catal. Lett.*, 2011, 141, 784.
- (a) Y. Nakagawa, Y. Shinmi, S. Koso and K. Tomishige. J. Catal., 2010, 272, 191; (b) Y. Amada, Y. Shinmi, S. Koso, T. Kubota and Y. Nakagawa. Appl. Catal., B, 2011, 105, 117.
- (a) B. M. Nagaraja, V. S. Kumar, V. Shasikala, A. H. Padmasri, B. Sreedhar, B. D. Raju and K. S. R. Rao, *Catal. Commun.*, 2003, 4, 287; (b) X. Chen, H. Li, H. Luo and M. Qiao, *Appl. Catal. A.*, 2002, 233, 13; (c) R. S. Rao, R. T. Baker and M. A. Vannice, *Catal. Lett.*, 1999, 60, 51; (d) R. Rao, A. Dandekar, R. T. K. Baker and M. A Vannice, *J. Catal.*, 1997, 171, 406; (e) B. M. Nagaraja, A. H. Padmasri, P. Seetharamulu, K. H. P. Reddy, B. D. Raju and K. S. R. Rao, *J. Mol. Catal. A.*, 2007, 278, 29.
- (a) P. Panagiotopoulou, N. Martin and D. G. Vlachos, *J. Mol. Catal., A,* 2014, **392**, 223; (b) P. Panagiotopoulou, D. G. Vlachos, *Appl. Catal., A,* 2014, **480**, 17; (c) D. Scholz, C. Aellig and I. Hermans, *Chemsuschem,* 2014, **7**, 268; (d) M. J. Gilkey, P. Panagiotopoulou, A. V. Mironenko, G. R. Jenness, D. G. Vlachos and B. Xu, *ACS Catal.,* 2015, **5**, 3988.
- Y. L. Zhu, H. W. Xiang, Y. W. Li, H. Jiao, J. S. Wu, B. Zhong and G. Q. Guo, *New J. Chem.*, 2003, 27, 208.
- 9. (a) A. C. Albertsson, I. K. Varma, *Biomacromolecules*, 2003,
 4, 1466; (b) H. Lee, F. Zeng, M. Dunne and C. Allen, *Biomacromolecules*, 2005, 6, 3119.
- 10. H. E. Bellis and W. Del, US Pat., 5110954, 1992.
- D.W. Hwang, P. Kashinathan, J. M. Lee, J. H. Leea, U. H. Lee, J. S. Hwang and Y. K. Hwang, *Green Chem.*, 2011, 13 1672.
- (a) N. Ichikawa, S. Sato, R. Takahashi, T. Sodesawa and K. Inui, *J. Mol. Catal. A.*, 2004, **212**, 197; (b) H. Inoue, S. Sato, R. Takahashi, Y. Izawa, H. Ohno and K.Takahashi, *Appl. Catal.*, *A*, 2009, **352**, 66.
- (a) H. J. Mercker, F.-F. Pape, J. Simon, A. Henne, M. Hesse, U. Koehler, R. Dostalek, C.F. Erdbruegger and D. Kratz, US Pat., 6093677, 2000; (b) B. Zhang, Y. Zhu, G. Ding, H. Zheng and Y. Li, *Appl. Catal.*, A, 2012, 443–444, 191.
- (a) O. Robin and S. Jun, US Pat., 7858350, 2010; (b) H. Yim, R. Haselbeck, W. Niu, C. Pujol-Baxley, A. Burgard, J. Boldt, J. Khandurina, J. D. Trawick, R. E. Osterhout, R. Stephen, J. Estadilla, S. Teisan, H. B. Schreyer, S. Andrae,

DOI: 10.1039/C5GC02924D Journal Name

T. H. Yang, S. Y. Lee, M. J. Burk and S. Van Dien, Nat. Chem.Biol., 2011, 7, 445.

- 15. (a) D. G. Evans, R. C. T. Slade, Struct. Bond., 2006, 119, 1; (b) G. Fan, F. Li, D. G. Evans and X. Duan, Chem. Soc. Rev., 2014, 43, 7040; (c) J. Feng, Y. Lin, D. G. Evans, X. Duan and D. Li, J. Catal., 2009, 266, 351.
- 16. C. Aellig, F. Jenny, D. Scholz, P. Wolf, I. Giovinazzo, F. Kollhoff and I. Hermans, Catal. Sci. Technol., 2014, 4, 2326.
- 17. (a) Y. Zhu, X. Kong, X. Li, G. Ding, Y. Zhu and Y. W. Li, ACS Catal., 2014, 4, 3612; (b) W. Wang, S Wang, X. Ma and J. Gong, Chem. Soc. Rev., 2011, 40, 3703; (c) M. Behrens, S. Zander, P. Kurr, N. Jacobsen, J. Senker, G. Koch, T. Ressler, R. W. Fischer and R. Schlögl, J. Am. Chem. Soc., 2013, 135, 6061.
- 18. (a) S. Zhang, Q. Hu, G. Fan and F, Li, Catal. Commun., 2013, 39, 96; (b) Y. Tang, Y. Liu, P. Zhu, Q. S. Xue, L. Chen and Y. Lu, AIChE J. 2009, 55, 1217.
- 19. Q. Hu, G. Fan, S. Zhang, L. Yang and F. Li, J. Mol. Catal. A: Chem., 2015, 397, 134.
- 20. (a) Z. He, H. Lin, P. He and Y. Yuan, J. Catal. 2011, 277, 54; (b) A. Yin, X. Guo, W. L. Dai and K. Fan, J. Phys. Chem. C, 2009, 113, 11003.
- 21. (a) T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa and K. Kaneda, Chem. Commun., 2008, 4804; (b) W. Fang, O. Zhang, J. Chen, W. Deng and Y. Wang, Chem. Commun., 2010, 46, 1547; (c)W. Fang, J. Chen, Q. Zhang, W. Deng and Y. Wang, Chem. Eur. J., 2011, 17, 1247.
- 22. (a) K. Mori, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, J. Am. Chem. Soc., 2004, 126, 10657; (b) M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, Patrick. Kurr, B. L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, Science, 2012, 336, 893; (c) N. Scotti, M. Dangate, A. Gervasini, C. Evangelisti, N. Ravasio and F. Zaccheria, ACS Catal., 2014, 4, 2818.
- 23. (a) C. Ma, Y. Du, J. Feng, X. Cao, J. Yang and D. Li, J. Catal., 2014, 317, 263; (b) M. Kong, Y. Li, X. Chen, T. Tian, P. Fang, F. Zheng and X. Zhao, J. Am. Chem. Soc., 2011. 133. 16414.
- 24. S. Ghosh, G. G. Khan, K. Mandal, A. Samanta and P. M. G. Nambissan, J. Phys. Chem. C., 2013, 117, 8458.
- 25. S. Zhang, G. Fan and F. Li, Green Chem., 2013, 15, 2389.
- 26. 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
- 27. H. Liu, Q. Hu, G. Fan, Y. Lan and F. Li, Catal. Sci. Technol., 2015, 5, 3960.
- 28. J. I. Di Cosimo, V. K. Díez, M. Xu, E. Iglesia and C. R. Apesteguia, J. Catal., 1998, 178, 499.
- 29. (a) J. Zuo, Z. Chen, F. Wang, Y. Yu, L. Wang and X. Li, Ind. Eng. Chem. Res., 2014, 53, 2647; (b) H. Xu, Q. Zhang, C. Qiu, T. Lin, M. Gong and Y. Chen, Chem. Eng. Sci., 2012, 76, 120.
- 30. (a) G. Busca, Phys. Chem. Chem. Phys., 1999, 1, 723; (b) Q. Hu, G. Fan, L. Yang and F. Li, ChemCatChem, 2014, 6, 3501; (c) B. Tang, W. Dai, G. Wu, N. Guan, L. Li and M. Hunger, ACS Catal., 2014, 4, 2801.
- 31. (a) G. R. Jenness and D. G. Vlachos, J. Phys. Chem. C. 2015, 119, 5938; (b) M. J. Taylora, L. J. Durndellb, M. A.

Isaacsb, C. M. A. Parlettb, K. Wilsonb, A. F. Leeb and G. Kyriakoua, Appl. Catal., B, 2016, 180, 580.

- 32. (a) U. R. Pillai and E. Sahle-Demessie, Green Chem., 2004, 6, 161; (b) G. Colón, J. A. Navío, R. Monaci and I. Ferino, Phys. Chem. Chem. Phys., 2000, 2, 4453.
- 33. (a) T. Ishida, M. Nagaoka, T. Akita and M. Haruta, Chem. Eur. J., 2008, 14, 8456; (b) K. I. Shimizu, K. Sugino, K. Sawabe and A. Satsuma, Chem. Eur. J., 2009, 15, 2341; (c) K. Kaneda, T. Mitsudome, T. Mizugaki and K. Jitsukawa, Molecules, 2010, 15, 8988
- 34. W. C. Wu, C. C. Chuang and J. L. Lin, J. Phys. Chem. B, 2000, 104, 8719.
- 35. V. Z. Fridman, A. A. Davydov and K. Titievsky, J. Catal., 2004, 222, 545.
- 36. (a) H. Yue, Y. Zhao, S. Zhao, B. Wang, X. Ma and Gong J. Nat. Commun., 2013, 4, 2339; (b) J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang and X. Ma, J. Am. Chem. Soc., 2012, 134, 13922.

Published on 25 January 2016. Downloaded by Gazi Universitesi on 28/01/2016 04:19:38.

Graphical and textual abstract

A solvent-free gas-phase coupling process through hydrogen transfer without external hydrogen was conducted over novel bifunctional base-metal heterogeneous catalysts.

