



Hydrogenation of CO for Alcohol Over Cu-ZnO-Al₂O₃ Catalysts Prepared by Completely Liquid-Phase Technology and Sol-Gel Methods: A Comparative Study

S.R. YU^{1,2}, Y.G. CHEN¹, S.S. GAO², X.D. WANG¹ and W. HUANG^{1,*}

¹Key Laboratory of Coal Science and Technology of Education Ministry and Shanxi Province, Taiyuan University of Technology, Taiyuan, Shanxi Province, P.R. China

²School of Chemistry and Chemical Engineering, Guizhou University, Guiyang, Guizhou Province, P.R. China

*Corresponding author: Tel./Fax: +86 351 60180733; E-mail: huangwei@tyut.edu.cn; weihuang74@hotmail.com

(Received: 15 December 2012;

Accepted: 5 June 2013)

AJC-13587

Cu-ZnO-Al₂O₃ catalysts for alcohol by hydrogenation of CO were prepared using completely liquid-phase (CZA-L) and sol-gel methods (CZA-T). Characterization showed that there are difference in structure and catalytic performance between CZA-L and CZA-T. Amorphous ZnO, Cu⁺ and Cu⁰ coexist in CZA-L, whereas crystal ZnO and Cu⁰ exist in CZA-T. Compare with CZA-T, the C₂⁺OH selectivity in CZA-L was increased 4 times and provided a CO conversion rate of 33 %, C₂⁺OH selectivity of up to 20.9 % with a total alcohol selectivity of 67 %, meanwhile C₂⁺OH selectivity of 4 % and total alcohol selectivity of 86.5 % with CZA-T under the reaction conditions of 5.0 MPa, 250 °C, H₂/CO = 1 and a gas hourly space velocity of 360 mL/(g_{cat} h). Experimental results showed that the synergy of various valence copper was responsible for improving the selectivity to C₂⁺OH from syngas over Cu-ZnO-Al₂O₃ catalysts.

Key Words: CO hydrogenation, Completely liquid-phase method, Cu-ZnO-Al₂O₃ catalysts, Alcohol, Sol-gel method.

INTRODUCTION

Cu-ZnO-Al₂O₃ catalysts are used widely in many catalytic reactions, such as CO shift at low temperature¹, methanol synthesis^{2,3}, production of γ -butyrolactone and 2-methylfuran⁴, cinnamaldehyde hydrogenation⁵ and hydrogen production from alcohols⁶⁻¹³. Limited availability of fossil fuels and rising oil prices have motivated years of research on alternative energy. Higher alcohols can be used pure unleaded fuels or as fuel additives in unleaded fuels^{14,15} and be regarded as the most promising environment friendly alternative energy sources. Higher alcohol synthesis from CO hydrogenation have attracted the interest of C1 chemistry researcher. The reaction of higher alcohol from syngas is thermodynamically more feasible than methanol synthesis. Thus, Cu-ZnO/Al₂O₃ catalysts have been extensively studied for this purpose, since Cu-ZnO/Al₂O₃ catalysts have proved very efficient and low cost for methanol synthesis. The alkali-promoted and nonalkali-promoted Cu-ZnO/Al₂O₃ catalysts¹⁶⁻²⁰ have been extensively studied to enhance higher alcohol selectivity. The production is a mixture of linear and branched alcohols which includes a large proportion of methanol and hydrocarbon together with a small amount of other oxygenates. As a result, unmodified and modified Cu-ZnO/Al₂O₃ catalysts suffer from low selectivity

for C₂-C₆ alcohols, though substantial efforts have been devoted in this respect²¹.

It is well-known that the performance of a catalyst depends on the chemical composition, morphology and size of metal nanoparticles, acid-base strength on the catalytic surface. Meanwhile a small variation in the preparation process can induce evident changes of surface structure and bring about different catalytic performances. Currently, heterogeneous catalysts are generally prepared using several conventional methods, such as coprecipitation, impregnation and sol-gel techniques²²⁻²⁷. The preparation method comprises the following processes in turn: precursor preparation, crystallization, molding and calcination. The common characteristic of conventional methods is that metal oxides are obtained by calcination of a catalyst precursor using a muffle furnace or tube furnace under different ambient gases. A novel method named liquid-phase technology invented by us has been applied to prepare slurry catalysts. The main innovation being the preparation of catalysts from the raw material solution to slurry catalyst formation are in liquid-solid-gas three-phase environment²⁸⁻³⁰ all the time. The Cu-ZnO/Al₂O₃ catalysts prepared by sol-gel method showed higher Brunauer Emmett Teller area and smaller particle size than those by the other methods and it also showed the highest activity and methanol selectivity³¹,

while Cu-ZnO/Al₂O₃ catalysts for dimethyl ether prepared by completely liquid-phase technology exhibited higher activity and dimethyl ether selectivity and it also showed the good stability. In this paper, our study about the effect of preparation method on performance of CuO-ZnO-Al₂O₃ catalysts for mix alcohol from CO hydrogenation is reported.

EXPERIMENTAL

Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O and (C₃H₇O)₃Al were purchased from Tianjin Kernel Chemical Reagent Co., Ltd. Polyethylene glycol 600 (PEG-600) and polyvinyl-pyrrolidone (PVP) were obtained from Tianjin Damao Chemical Reagent Factory. All chemicals were of analytical reagent grade and were used without further purification. Deionized double-distilled water was used to make the solutions.

General procedure: An appropriate amount of aluminum isopropylate [(C₃H₇O)₃Al] was dissolved in a mixture of surfactant PVP, PEG-600 and deionized water and kept at 80 °C for 1.5 h in a water bath. After that, a certain amount of nitric acid was added to the solution with vigorous stirring for 1 h at 95 °C, then another solution was added which was prepared by dissolving Cu(NO₃)₂ and Zn(NO₃)₂ salts in an appropriate amount of ethanol. The mixture obtained was stirred under reflux at 95 °C for 10 h and then kept in a beaker at 25 °C for 10 days to obtain a gel. The gel was then heated in liquid paraffin from room temperature to 280 °C with a heating rate of 10 °C/min and held for 8 h at this temperature. The Cu-ZnO/Al₂O₃ slurry catalyst prepared by completely liquid-phase method resulted from this process. The sol-gel method is that the gel was heated from room temperature to 280 °C with a heating rate of 10 °C/min and held for 8 h in a muffle furnace. For convenience, the catalysts prepared by completely liquid-phase technology and traditional sol-gel method are hereafter designated by the abbreviation CZA-L and CZA-T, respectively. CZA-L_f and T_f denotes fresh catalysts, CZA-L_s and T_s denotes spent catalysts.

Detection method: Powder X-ray diffraction (XRD) analysis was performed with a Rigaku D/max-2500 powder diffractometer. X-Ray photoelectron spectroscopy (XPS) analysis was employed to study the chemical composition and oxidation state of catalytic surface. The instrument was a VG ESCALAB 250 spectrometer (VG Scientific Ltd., UK) using focused monochromatic AlK α (h ν = 1486.6 eV), the degree of vacuum was 7 \times 10⁻⁸ mbar and C1s (284.6 eV) was used as calibration. The reducibility of the catalysts was studied using temperature programmed reduction (TPR). H₂-TPR was carried out in a laboratory-made microreactor. Temperature-program-desorption (NH₃-TPD and CO-TPD) were performed on a TP-5000 instrument. The desorbed molecules were detected with a mass spectrometer (MS) by monitoring the signal at m/z = 17 (NH₃) or 28 (CO). The CO hydrogenation reaction was carried out in a 500 mL slurry-phase reactor. The reaction condition: H₂/CO = (1:1), P = 5.0 MPa, t = 250 °C and gas hourly space velocity of 360 mL/g_{cat} h⁻¹. The products were analyzed using a gas chromatograph equipped with flame ionization and thermal conductivity detectors, using GDX-502 and TDX-01 columns, respectively.

RESULTS AND DISCUSSION

The catalytic performances test for higher alcohol synthesis are summarized in Figs. 1 and 2. It is obvious that the CZA-L catalyst exhibits a better higher alcohol selectivity and CZA-T catalyst shows a higher methanol selectivity. The stabilities of catalysts are evaluated for 100 h. Under the same reaction conditions, CZA-L catalyst has a good stability, while the CZA-T catalyst activity decrease gradually with the reaction time. Two catalysts vary in product distribution result from difference in catalyst structure and surface property.

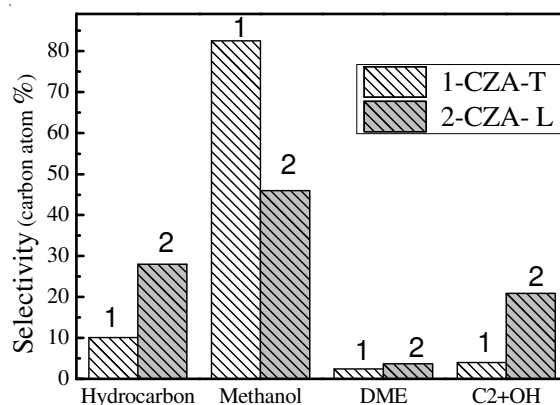


Fig. 1. Selectivity for the catalysts: 1. CZA-T 2. CZA-L (reaction conditions: 5.0 MPa, 250 °C, GHSV = 360 mL/g_{cat} h⁻¹, H₂/CO = 1.0)

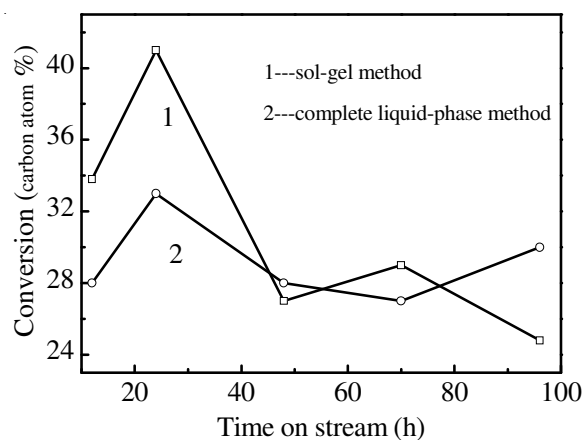


Fig. 2. The change of conversion with time for catalysts: 1. CZA-T 2. CZA-L (Reaction conditions: 5.0 MPa, 250 °C, GHSV = 360 mL/g_{cat} h⁻¹, H₂/CO = 1.0)

The XRD patterns of the Cu-Zn-Al catalysts after heat treatment and reaction are presented in Fig. 3a-b. For the CZA-T_f samples, peaks are identified as the diffraction lines of ZnO and CuO species, no metallic Cu and Cu₂O phase are found, which is related to calcinating process in the air. For the CZA-T_s samples, peaks are identified as the diffraction lines of ZnO and Cu species which showed CuO was reduced completely and the ZnO could not be reduced under the reaction conditions. For CZA-L_f samples, most peaks are identified as the diffraction lines of Cu metal and only a small peak at 2 θ = 36.5° is assigned to Cu₂O. The presence of Cu metal and Cu₂O could be due to the decomposition of the paraffin by heat to produce a reductive compound, causing CuO reduction. The

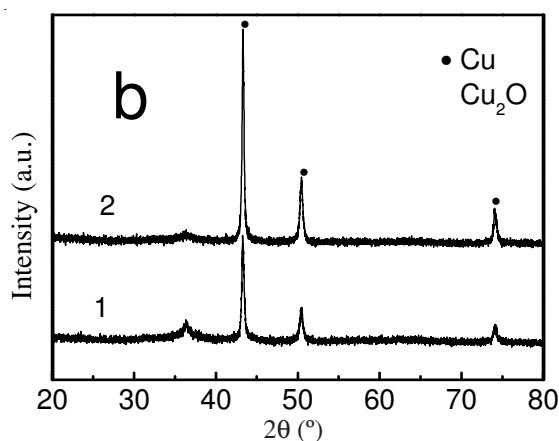
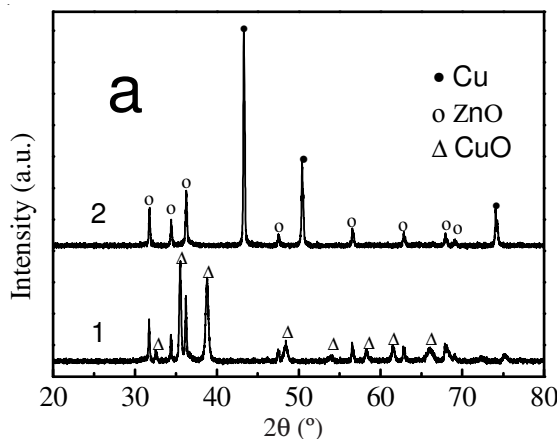


Fig. 3. XRD patterns of catalysts for a₁, CZA-T_f; a₂, CZA-T_s; b₁, CZA-L_f; b₂, CZA-L_s.

disappearance of diffraction peaks of ZnO may be thought that ZnO exists in amorphous form or minor crystals that could not be detected by XRD. For CZA-L_s samples, the diffraction peaks are similar with that of the CZA-L_f. This showed that the catalysts prepared by completely liquid-phase technology are quite stable under the reaction conditions. Comparing the peak shape of Cu species in CZA-L_f and CZA-L_s, the peaks are acute in CZA-L_s, but diffuse in CZA-L_f. The mean crystal size of Cu₂O and Cu is estimated by using Scherrer equation. The Cu crystal size of CZA-T_s is *ca.* 51.2 nm, while that of CZA-L is from 28.7 (before reaction) to 31.5 nm (after reaction) and Cu₂O crystal size from 16.8 (before reaction) to 24.5 nm (after reaction). Thereby, the dispersity of Cu in CZA-L is higher than that of CZA-T. The catalytic activity decrease result from aggregation effect of copper particles, since the CZA-L has a good stability to resist sintering in a slurry reactor under experimental conditions. For the post-reaction samples, the diffraction lines of copper species and zinc oxide are vary in CZA-T_s and CZA-L_s catalysts under the same reaction conditions and shows that the surface element distribution and constitution are determined by the preparation method.

The XPS spectra for as prepared catalysts and for spent catalysts are displayed in Fig. 4. It can be noticed that the spectral feature of CZA-L_f and CZA-L_s catalysts are very similar. The Cu2P_{3/2} XPS of CZA-L_f and CZA-L_s catalysts exhibit a sharp asymmetric peak at 932.4 eV, indicating that the copper species are Cu⁰ and Cu⁺³²⁻³⁵. Since the binding energy value

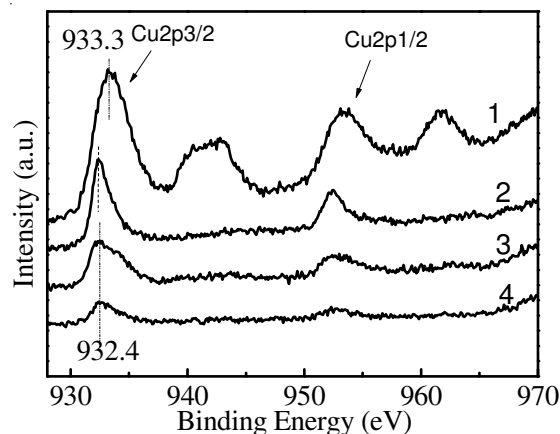
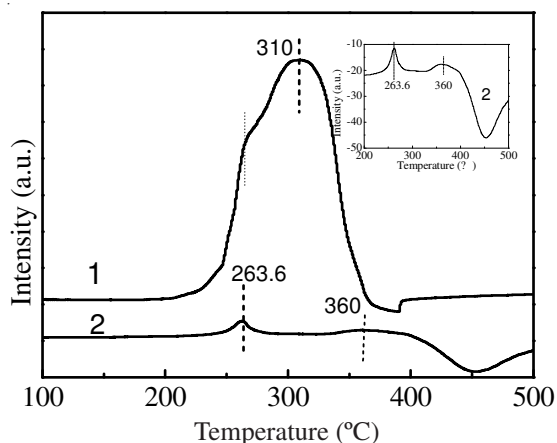


Fig. 4. Cu 2p core level spectra of catalysts for 1. CZA-T_f 2. CZA-T_s 3. CZA-L_f 4. CZA-L_s.

and widths for Cu2P_{3/2} peaks in Cu⁺ are almost identical to those of Cu⁰, it is difficult to distinguish them on the basis of the Cu2p level. The modified Auger parameter has been generally used to further confirm the chemical state of copper. It is defined as $\alpha_A = BE(Cu2P_{3/2}) + KE(CuL_{3VV})$ where BE(Cu2p_{3/2}) is binding energy of Cu(2P_{3/2}) core level photoelectron and KE CuL₃VV is kinetic energies of Cu L₃VV Auger electron^{35,36}. The XPS results show the presence of Cu⁺ and Cu⁰ in CZA-L_f and CZA-L_s. This is consistent with XRD results. For the CZA-T_s sample, the 2P_{3/2} spin-orbital photoelectron of Cu is located at the binding energies of 933.3 eV and with a satellite peak at *ca.* 941–944 eV assigned to Cu²⁺. Velu *et al.*³⁷ reported that the satellite-intensity-to-main-line-intensity ratio (I_S/I_M) should be larger than 0.5 for pure CuO. While I_S/I_M for CZA-T_f is 0.55 for the Cu2P_{3/2} band is in good agreement with the values for the CuO-ZnO mixed oxides reported by Okamoto *et al.*³⁸. That is to say, copper element is bivalent in CZA-T_f catalysts. Meanwhile, the CuL₃VV Auger spectra show a sharp peak of CZA-T_s catalyst at 918 eV with $\alpha_A = 1851.3$ eV, which is close to that of metallic Cu, indicating CuO are reduced as Cu⁰. These are consistent with XRD results. The BE of Zn 2P_{3/2} is insensitive to the chemical states, we turn to the help of the information from its XAES (X-ray excited Auger electron spectroscopy) peak. Because the extra-atomic relaxation energy of Auger process involving two-hole is higher than that of the photo-electronic process consisting of one-hole states, the Auger shift between Zn²⁺ and Zn⁰ is more than 4.6 eV³⁹. The Auger KE of Zn⁰ is at *ca.* 992.1 eV while ZnO is at 987.4–988.2 eV⁴⁰. Four catalysts show a main feature at *ca.* 987.5–988.1 eV which can be assigned to ZnO. The result implies that ZnO in catalysts can not be reduced to Zn⁰ under typical reduction or reaction conditions.

From above the characterization, the production distribution was influenced with catalysts structure and surface properties. Combining catalytic activity test, it may postulated that the synergy with Cu and Cu⁺ is favorable to carbon chain growth, since the C₂⁺OH selectivity in CZA-L is higher than CZA-T.

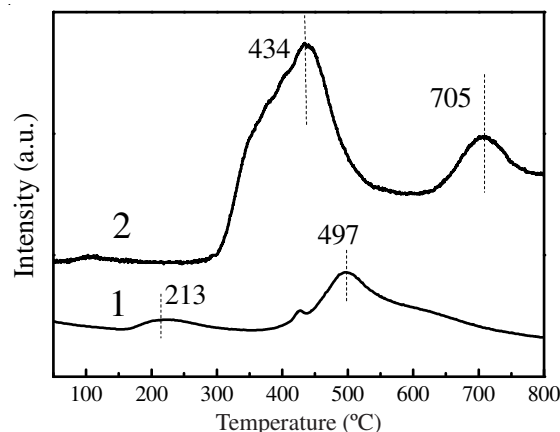
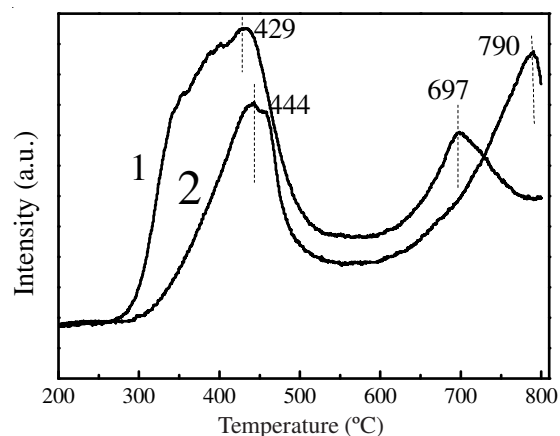
H₂-TPR profiles of catalysts after heat treatment are shown in Fig. 5. The CZA-T_f maxima reduction peak obtained is located at *ca.* 310 °C. A complete reduction to metallic copper for CZA-T_f was achieved according to XRD and XPS

Fig. 5. H₂-TPR profiles of catalysts for 1. CZA-T_f; 2. CZA-L_f

characterization. Pure CuO is reduced at *ca.* 370 °C, pure ZnO and alumina oxide are not reduced under experimental conditions. The CZA-T_f is completed at the lower reduction temperature, because ZnO around CuO influenced on the reducibility of H₂ on CuO. According to Fierro *et al.*³², the interaction between copper oxide and zinc oxide, leading to ZnO plays the role of H₂ activator and producing electronic coupling effect between the ZnO and the CuO particles, H₂ activation and spill-over would be improved between CuO and ZnO particles resulting in a promoting effect of the copper reduction. In addition, the apparent activation energy for the reduction of pure CuO higher than that found for the reduction of the CuO-ZnO catalysts. The reduction peaks of CZA-L_f catalyst are centered at 263.6 and 360 °C, which were assigned to the reduction of Cu₂O, since XRD and XPS characterization showed that there are only metallic copper and Cu⁺ existence in the CZA-L. Varying reduction peaks is resulting from the interaction with Cu₂O of varying sizes, promoter and supporter. The second Cu₂O reduction peak of the CZA-L_f catalyst was displaced by almost 96.4 °C towards higher temperature comparing with the first reduction this retardation effect is explained in terms of inter-particle mass transfer limitations⁴¹.

Fig. 6 displays NH₃-TPD profiles of both CZA-T_f and CZA-L_f catalysts. The CZA-T_f desorption peaks centered at 213 and 497 °C, corresponding to NH₃ eluted from the weak and medium-strong acid sites, respectively. Whereas reduced CZA-L_f exhibits two peaks around 434 and 705 °C, corresponding to NH₃ eluted from the medium-strong and strong acid sites, respectively. From the area of NH₃ desorption peaks, the concentration of medium-strong and strong acid in CZA-L_f are larger than that of CZA-T_f, but the weak acid quantity on the two catalytic surface are few. In general, hydrocarbon is result from medium and strong acid, the NH₃-TPD result is consistent with the catalytic activity results.

The CO-TPD profiles of the CuZnAl catalysts reduced at 280 °C for 1 h are exhibited in Fig. 7. As shown in the Fig. 7, the two CO-TPD peaks on the reduced CZA-T_f and CZA-L_f samples appear at around 429-444 and 697-790 °C, respectively, corresponding to the medium-strong and strong CO adsorption center. It is well known that alcohol synthesis is closely associated with medium-strongly or strongly adsorbed CO-species. The concentration of both medium-strongly and strongly adsorbed CO-species on the CZA-L_f is more than

Fig. 6. NH₃-TPD spectra for fresh catalysts: 1. CZA-T_f; 2. CZA-L_fFig. 7. CO-TPD spectra for fresh catalysts: 1. CZA-T_f; 2. CZA-L_f

those on the CZA-T_f catalyst. Apparently, the temperature of peak-II for the CZA-L_f catalyst increases by *ca.* 93 °C compared with that for the CZA-T_f sample, suggesting that the desorption of strongly adsorbed CO-species is enhanced. Simultaneously, the area of peak-II sharply increases for CZA-L_f, indicating that strongly adsorbed CO-species is obviously improved.

Based on the CO-TPD analysis, it is clear that the CZA-L_f catalyst is favorable for the adsorption/activation of CO molecules and the amount of strongly adsorbed CO-species increases correspondingly. The possibility for CO inserting into CH_x- forming formyl intermediate species will increase greatly according to the mechanism for higher alcohol synthesis from CO hydrogenation. It demonstrated that the CZA-L_f catalyst, being advantageous for CO activation, will considerably contribute to the higher-alcohol yield. In this work, those are well agree with the catalytic performance of CZA-L_f sample.

Conclusion

Characterization showed that there are distinctly distinguish with CuZnAl catalysts using sol-gel (CZA-T) and completely liquid-phase method (CZA-L). Cu⁰ and Cu⁺ coexist in CZA-L, whereas only Cu⁰ present in reduced CZA-T sample. ZnO exists in amorphous form or minor crystals that cannot be detected by XRD in CZA-L. The dispersity of Cu in CZA-L is higher than that of CZA-T. The CZA-L have a better C₂+OH selectivity and a better stability to resist sintering in a slurry reactor compare with CZA-T under the experimental conditions,

meanwhile CZA-T is favorable to methanol synthesis. It is concluded that the synergy of various valence copper is favourable to activation of CO molecules and carbon chain growth. In addition, the surface element distribution is determined by the preparation method.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation of China (21176167), the National Basic Research Program of China (2011CB21709), Science and Technology Foundation of Guizhou Province ([2012]2154), Doctoral Fund of Ministry of Education priority areas of development issues (2011140-2130002), Ministry of Education Science and Technology Key Project (212021).

REFERENCES

- M.J.L. Ginés, N. Amadeo, M. Laborde and C.R. Apesteguía, *Appl. Catal. A*, **131**, 283 (1995).
- G.C. Chinchén, P.J. Denny, D.G. Parker, M.S. Spencer and D.A. Whan, *Appl. Catal.*, **30**, 333 (1987).
- K.C. Waugh, *Catal. Today*, **15**, 51 (1992).
- J. Yang, H.Y. Zheng, Y.L. Zhu, G.W. Zhao, C.H. Zhang, B.T. Teng, H.W. Xiang and Y.W. Li, *Catal. Commun.*, **5**, 505 (2004).
- J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe and B.S. Clausen, *J. Catal.*, **194**, 452 (2000).
- A.J. Marchi, D.A. Gordo, A.F. Trasarti and C.R. Apesteguía, *Appl. Catal. A*, **249**, 53 (2003).
- M.N. Barroso, M.F. Gomez, J.A. Gambo, L.A. Arrúa and M.C. Abello, *J. Phys. Chem. Solid*, **67**, 1583 (2006).
- S. Velu, K. Suzuki and T. Osaki, *Catal. Lett.*, **62**, 159 (1999).
- S. Murcia-Mascarós, R.M. Navarro, L. Gómez-Sainero, U. Costantino, M. Nocchetti and J.L.G. Fierro, *J. Catal.*, **198**, 338 (2001).
- M. Turco, G. Bagnasco, U. Costantino, F. Marmottini, T. Montanari, G. Ramis and G. Busca, *J. Catal.*, **228**, 43 (2004).
- M.N. Barroso, M.F. Gomez, L.A. Arrúa and M.C. Abello, *Catal. Lett.*, **109**, 13 (2006).
- V. Agarwal, S. Patel and K.K. Pant, *Appl. Catal. A*, **279**, 155 (2005).
- P. Kurr, I. Kasatkin, F. Girgsdies, A. Trunschke, R. Schlögl and T. Ressler, *Appl. Catal. A*, **348**, 153 (2008).
- L.D. Schmidt and P.J. Dauenhauer, *Nature*, **447**, 914 (2007).
- S. Prasad, A. Singh and H.C. Joshi, *Resour. Conservat. Recycl.*, **50**, 1 (2007).
- S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki and F. Ohashi, *J. Catal.*, **194**, 373 (2000).
- J.P. Shen and C.S. Song, *Catal. Today*, **77**, 89 (2002).
- Y.L. Zhang, Q. Sun, J.F. Deng, D. Wu and S.Y. Chen, *Appl. Catal. A*, **158**, 105 (1997).
- W.S. Ning, H.Y. Shen and H.Z. Liu, *Appl. Catal. Gen.*, **211**, 153 (2001).
- A.E. Galetti, M.F. Gomez, L.A. Arrua, A.J. Marchi and M.C. Abello, *Catal. Commun.*, **9**, 1201 (2008).
- M.M. Yung, W.S. Jablonski and K.A. Magrini-Bair, *Energy Fuels*, **23**, 1874 (2009).
- K.P. Sun, W.W. Lu, F.Y. Qiu, S.W. Liu and X.L. Xu, *Appl. Catal. A*, **252**, 243 (2003).
- Q.J. Ge, Y.M. Huang, F.Y. Qiu and S.B. Li, *Appl. Catal. A*, **167**, 23 (1998).
- G.R. Moradi, S. Nosrati and F. Yaripor, *Catal. Commun.*, **8**, 598 (2007).
- J.L. Li, X.G. Zhang and T. Inui, *Appl. Catal. A*, **164**, 303 (1997).
- X.M. Zheng, J.H. Fei and Z.Y. Hou, *Chin. J. Chem.*, **19**, 67 (2001).
- J.L. Hu, Y. Wang, C.S. Cao, D.C. Elliott, D.J. Stevens and J.F. White, *Ind. Eng. Chem. Res.*, **44**, 1722 (2005).
- Z.H. Gao, L.F. Hao, W. Huang and K.C. Xie, *Catal. Lett.*, **102**, 139 (2005).
- Z.H. Gao, L.F. Hao, W. Huang and K.C. Xie, *Chin. J. Catal.*, **27**, 86 (2006).
- Z.H. Gao, W. Huang, L.H. Yin, L.F. Hao and K.C. Xie, *Catal. Lett.*, **127**, 354 (2009).
- Q. Sun, Y.L. Zhang, H.Y. Chen, J.F. Deng, D. Wu and S.Y. Chen, *J. Catal.*, **167**, 92 (1997).
- G. Fierro, M.L. Jacono, M. Inversi, P. Porta, F. Cioci and R. Lavecchia, *Appl. Catal. A: Gen.*, **137**, 327 (1996).
- B. Peplinski and W.E.S. Unger, *Appl. Surf. Sci.*, **62**, 115 (1992).
- C.C. Chusuei, M.A. Brookshier and D.W. Goodman, *Langmuir*, **15**, 2806 (1999).
- R.T. Figueiredo, A.M. Arias, M.L. Granados and J.L.G. Fierro, *J. Catal.*, **178**, 146 (1998).
- F. Márquez, A.E. Palomares, F. Rey and A. Corma, *J. Mater. Chem.*, **11**, 1675 (2001).
- S. Velu, K. Suzuki, V. Munusamy, S. Barman and C.S. Gopinath, *Appl. Catal.*, **55**, 287 (2005).
- Y. Okamoto, K. Fukino, T. Imanaka and S. Teranishi, *J. Phys. Chem.*, **87**, 3740 (1983).
- W.L. Dai, Q. Sun, J.F. Deng, D. Wu and Y.H. Sun, *Appl. Surf. Sci.*, **177**, 172 (2001).
- Z.H. Li, Z.J. Zuo, W. Huang and K.C. Xie, *Appl. Surf. Sci.*, **257**, 2180 (2011).
- L.M. Shi, W. Chu and S.Y. Deng, *J. Nat. Gas. Chem.*, **20**, 48 (2011).