Korean J. Chem. Eng., **26**(6), 1568-1573 (2009)
DOI: 10.1007/s11814-009-0258-8

Catalytic activity of Cu/MgO in liquid phase oxidation of cumene

Shuai Xu, Chongpin Huang†, Jie Zhang, and Biaohua Chen

State Key Laboratory of Chemical Resource Engineering,
Beijing University of Chemical Technology, Beijing 100029, China

(*Received 26 February 2009 • accepted 14 April 2009*)

Abstract−Cumene was oxidized with air as the oxidant and Cu/MgO as the catalyst. Cu/MgO with different compositions was prepared by co-precipitation and then characterized by X-ray diffraction (XRD), H_2-temperature programmed reduction (H_2-TPR) and X-ray photoelectron spectroscopy (XPS). The characterization results showed that CuO dispersed on MgO well in the cases that the Cu content in Cu/MgO was 1% by molar. In this catalytic system, MgO did not only act as the supporter, but also as the catalyst to activate the tertiary C-H of cumene. The conversion of cumene was increased by using CuO as the promoter on MgO catalyst. The cumene conversion and cumene hydroperoxide (CHP) selectivity were in a trade-off relationship because cumene oxidation was subject to the decomposition of CHP. Thus, the effects of the operating variables were investigated and the relevant mechanism was discussed.

Key words: Cumene, Oxidation, Catalysis, Cu/MgO, Cumene Hydroperoxide

INTRODUCTION

Phenol and its derivatives are important raw materials for phenol resins, polycarbonates, polyphenylene ethers, perfumes, medicines, agricultural chemicals, etc. The cumene-phenol process (Hock process), based on the decomposition of cumene hydroperoxide (CHP) with sulfuric acid to phenol and acetone, is currently used worldwide for phenol synthesis [1]. The chemical pathway of the phenol/acetone process starts with the alkylation of benzene using propylene to give cumene, continues with the oxidation of cumene to CHP and, ultimately produces phenol and acetone by the decomposition of CHP. Among the three steps, the cumene oxidation step affords the lowest efficiency [2].

In the past decades, many catalysts were investigated for the oxidation of cumene, especially transition metal compounds [3-6]. For all of the catalytic systems, copper compounds were excellent catalysts not only with regard to the reaction activity but also with regard to the CHP selectivity [2,7]. On the other hand, alkali solutions are used to neutralize the formic acid formed in the oxidation process in order to prevent the decomposition of hydroperoxide produced [8,9]. Considering these results, the system of CuO+$NaOH_{aq}$ was used as catalyst in the oxidation of 2-isopropylnaphthalene to 2-isopropylnaphthalene hydroperoxide (2-IPNHP), which is analogous to the cumene process [10,11].

With the increase in environmental consciousness, solid basic catalysts have attracted increasing interest in the context of green chemistry. Consequently, alkaline-earth compounds have been used as the catalysts for the oxidation of the alkylbenzenes to the corresponding hydroperoxides [12]. MgO is often chosen as the supporter to enhance the specific surface area of the catalyst [13]. In addition, MgO is also used as catalyst for different reactions [14-17]. It was reported that Fe/MgO activated C-H bonds at low temperature [18].

Considering the advantages of CuO and MgO mentioned above, the performance of Cu/MgO in the oxidation of cumene was investigated. The effects of the operating variables were also studied and the relevant mechanism was discussed.

EXPERIMENTAL

1. Catalyst Preparation

Cu/MgO catalysts were prepared by co-precipitation method using Na_2CO_3 as a precipitator. In a typical synthesis, copper nitrate and magnesium nitrate were mixed with various metal molar ratios in 100 mL deionized water. The precipitator (1 M Na_2CO_3 solution) was added dropwise into the as-prepared mixed-metal nitrate aqueous solution under vigorous magnetic stirring until the pH of mother liquor reached about 9.0. After aging in the suspension for 3 h at room temperature, precipitates were collected by filtration and thoroughly washed with the deionized water. The filter cake was dried at 373 K overnight and then calcined in air at 803 K for 5 h to derive the corresponding oxides. The copper loadings in Cu/MgO were designed to be 1%, 3%, 5%, 10% by molar. The Cu/MgO with different copper loadings was denoted as 1%Cu/MgO, 3%Cu/MgO, 5%Cu/MgO and 10%Cu/MgO, respectively.

2. Characterizations

The X-ray diffraction (XRD) patterns of samples were measured on a Bruker D8 Advance X-ray Diffractometer with Cu Kα radiation (λ=0.15406 nm). The operation voltage was 40 kV and the current was 40 mA. The XRD patterns were recorded with a step of 0.05° and a scan rate of 1 s/step.

H_2-temperature programmed reduction (H_2-TPR) measurements were performed on a TPD/R/O 1100 series apparatus (Thermo Electron Co.) to determine the reducibility of samples. About 20 mg of catalyst sample was placed in a quartz reactor and reduced by a 5% H_2/N_2 mixture in a flow rate of 50 ml/min. It was heated linearly at 20 °C/min from room temperature to 1,000 °C, and isothermal con-

---

†To whom correspondence should be addressed.
E-mail: huangcp@mail.buct.edu.cn

dition was maintained for further 30 min at 1,000 °C. Before reduction, the samples were purged with pure N_2 at 500 °C for 1 h.

And X-ray photoelectron spectroscopy (XPS) experiment was detected on an ESCALAB250 (Thermo Electron Co.) using Al Kα radiation source at the constant pass energy of 50 eV. The binding energy values were corrected by using the C1s peak at 285.0 eV.

3. Activity Test

Cumene (50 ml) was oxidized in 100 ml of a three-necked flask supplied with a mechanical stirrer with a rotation counter, the bubbler, reflux condenser and the oil bath. Cumene was placed in the reactor and heated to 90 °C. Then, 0.5 g of catalyst was added and air was passed through. The air flow was 160 ml/min. 1 g of CHP was added as the initiator. The stir speed was above 1,000 r/min. The reaction was carried out for 10 h. The oxidation products were analyzed on VARIAN PROSTAR 330 HPLC. HPLC analyses were conducted with a photo diode array (PDA) detector and 25 cm× 4.6 mm stainless-steel column filled with InterSil (5 μm). Compounds were detected at 257 nm. The mobile phases were n-hexane-isopropanol mixture (97 : 3, v/v) at a flow-rate of 1 ml/min.

RESULTS AND DISCUSSION

1. Characterization of the Catalysts

In Fig. 1, the X-ray powder diffraction patterns of the catalysts are shown. The diffraction peaks corresponding to copper-containing phases are not observed for Cu_1%, Cu_3% catalysts, in agreement with the high copper dispersion, while the most intense reflections corresponding to CuO (at 2θ values of 35.5° and 38.8°) are clearly visible for the catalysts Cu_5% and Cu_10%. The crystalline phase of MgO was confirmed from 2θ values (42.82°, 62.25°, and 78.30°). The absence of CuO diffraction peaks in some catalysts indicated the formation of finely dispersed copper species on the MgO surface that are not detectable by this technique.

The redox properties of copper were studied by H_2-TPR. The TCD signal profiles obtained in the H_2-TPR experiments with the set of copper catalysts are in Fig. 2. All the catalysts consumed H_2 in these tests because of the reduction of copper oxide. As expected, the H_2 consumption increased with the increase of the copper loading. The TCD signal profiles (Fig. 2) show two bands, indicating that copper oxide species with different redox behavior are present. The band at 210 °C can be attributed to the copper oxide species that can be easily reduced. This band is probably due to the reduction of the well-dispersed CuO phase. The other band at 262 °C is regarded as the less-reducible copper oxide. This high temperature band is able to be attributed to the reduction of the larger CuO particles. In the case of 1%Cu/MgO, only the low temperature band was found. In the cases of 3% Cu/MgO, the high temperature peak appears with relative lower intensity. With the Cu content increasing, the intensity of the high temperature band increases remarkably. This result reveals that the copper dispersion was lower with higher copper loading content, which is consistent with the XRD characterization. In the studies about the other different copper catalysts (CuO/Al_2O_3, CuO/CeO_2-Al_2O_3), Similar H_2-TPR profiles of CuO materials and trend were reported [19,20].

The surface of the catalysts was also characterized by XPS fol-

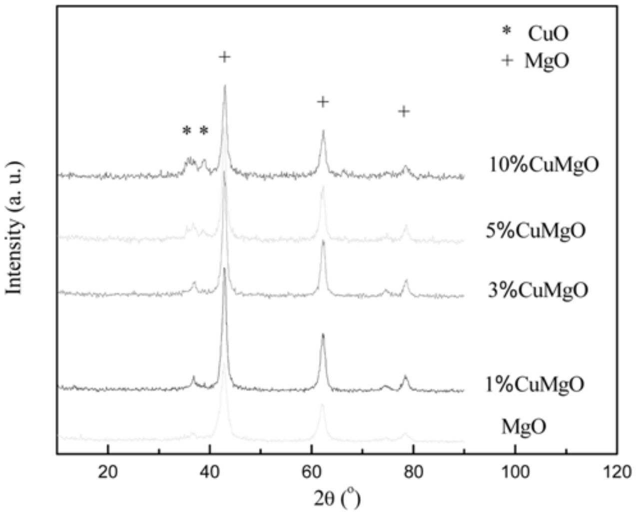


Fig. 1. XRD patterns of Cu/MgO catalyst.

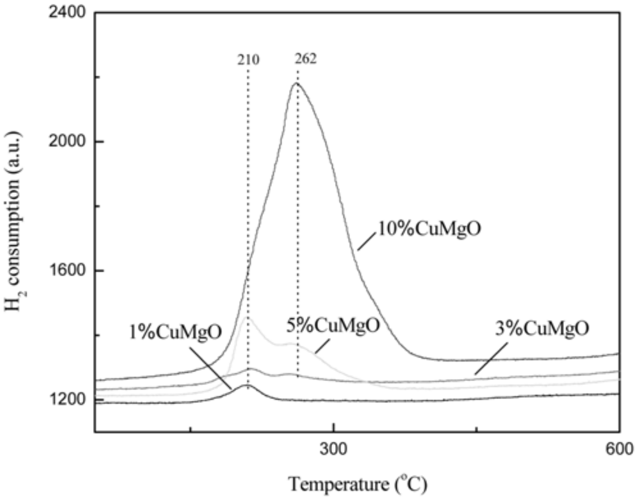


Fig. 2. Catalyst characterization by H_2-TPR.

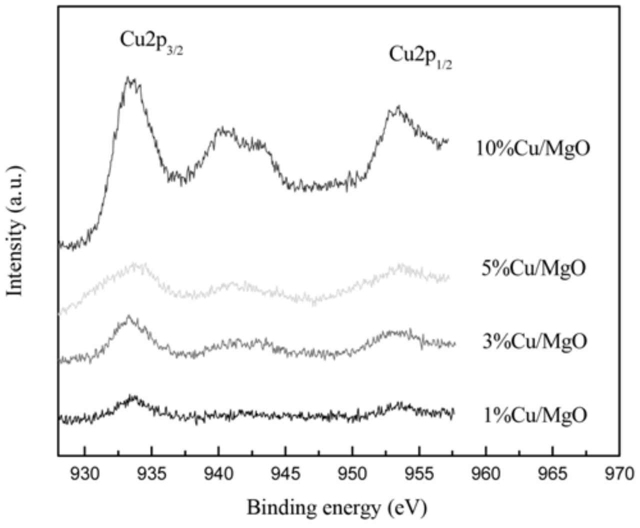


Fig. 3. XPS characterization of the Cu2p transition for the catalysts.

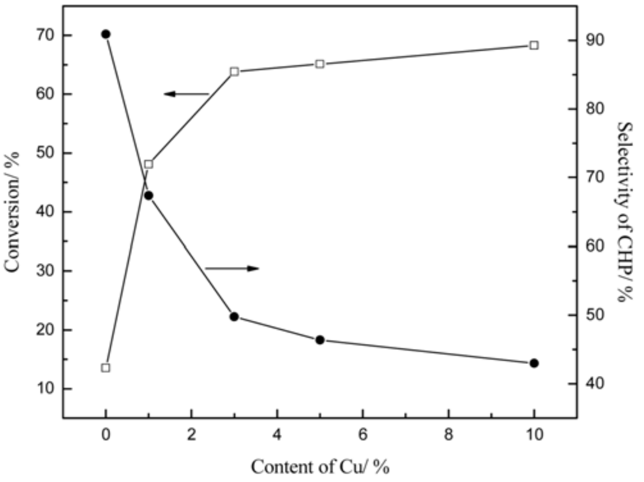


Fig. 4. Effect of the content of the Cu ion in the catalyst. Reaction condition: Cumene, 50 ml; Catalyst, 0.5 g Cu/MgO; Temperature, 90 °C; Air flow, 160 ml/min; Initiator, 1 g CHP.

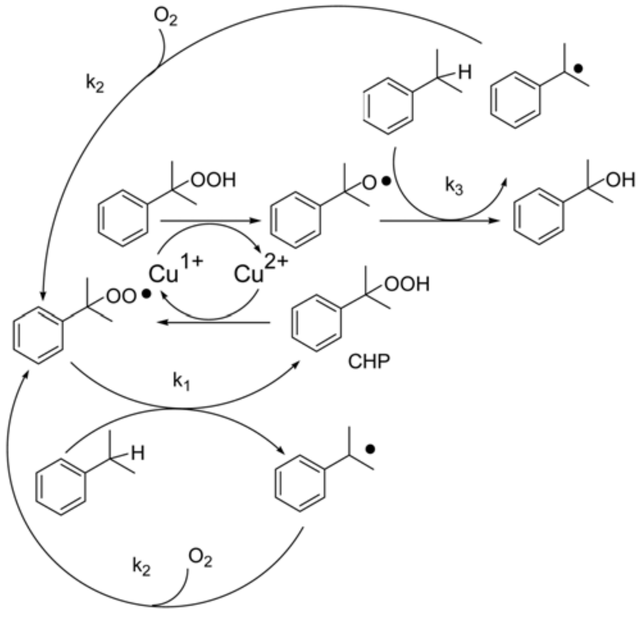
lowing the Cu 2p transition. The profiles corresponding to the catalysts are included in Fig. 3. The bands centered at 933.4 and 953.4 eV represent the Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The results are consistent with the standard spectrum of CuO approximately [21,22]. The existence of the shake-up features for Cu (2p) rules out the possibility of the presence of Cu_2O phase.

2. Catalytic Performance and Mechanism

2-1. Effect of the Content of the Cu in the Catalyst

Cumene is oxidized with O_2 in the liquid-phase according to the widely known free-radical mechanism. The main products of the cumene oxidation are acetophenone, 2-phenyl-2-propanol and CHP. The results with Cu/MgO as catalyst are shown in Fig. 4. It can be seen that the conversion of cumene increased with the copper loading. On the contrary, the selectivity of CHP decreased with the content of copper. The conversion increased significantly with copper loading increasing from 0% to 3%. However, the improvement of the cumene conversion was slight in the copper loading range of from 3% to 10%. When MgO was used as catalyst without copper, the conversion was 13.5% in reaction time of 10 h. The conversion increased to 63.8% with 3%Cu/MgO as catalyst. When the copper loading increased from 3% to 10%, the conversion increased from 63.8% to 68.3%.

The results can be interpreted by the effect of copper ion on the catalytic reaction. The role of the copper ion is presented in Scheme 1. Based on the theory of free radicals, oxidation is mediated by free radical intermediates and is characterized by the elementary process of initiation, propagation and termination. Three kinds of radical species, i.e., cumyl radical (R•), cumylhydroxy radical (RO•) and cumylhydroperoxy radical (ROO•), are mainly involved in the oxidation. The CHP could be decomposed by copper ion to form RO• and •OH. This is consistent with the result of the CHP selectivity in Fig. 4. In the next step, the radical species RO• abstracted the hydrogen atom from cumene to form 2-phenyl-2-propanol (ROH) and R•. Thus, cumene was converted. The reaction of hydrogen atom abstraction from cumene by RO• (k3 in Scheme 1) is much faster than that by ROO• (k1 in Scheme 1). This is confirmed by the fact that there is a great reactivity difference for hydrogen atom abstraction from C-H bonds by t-BuO· (k≈105-106 M^{-1} S^{-1}) and t-BuOO· (k≈10^{-3}-10^{-1} M^{-1} S^{-1}) [1]. So, the conversion was increased under the catalyst of Cu/MgO. The reaction of hydrogen atom abstraction from cumene by ROO• (k1 in Scheme 1) is the rate-determining step. As a result, the conversion increased slightly for high copper loading. The phenomenon was also consistent with the results of H_2-TPR. The area of the high temperature band increased from 3%Cu/MgO to 10%Cu/MgO, indicating that the amount of the larger CuO particles increased.



Scheme 1. The mechanism of the oxidation of cumene over Cu/MgO.

2-2. Effect of MgO

MgO was not only used as supporter but also as catalyst without copper. The results with MgO as catalyst are shown in Fig. 5. Compared with the results without catalyst, the conversion was almost

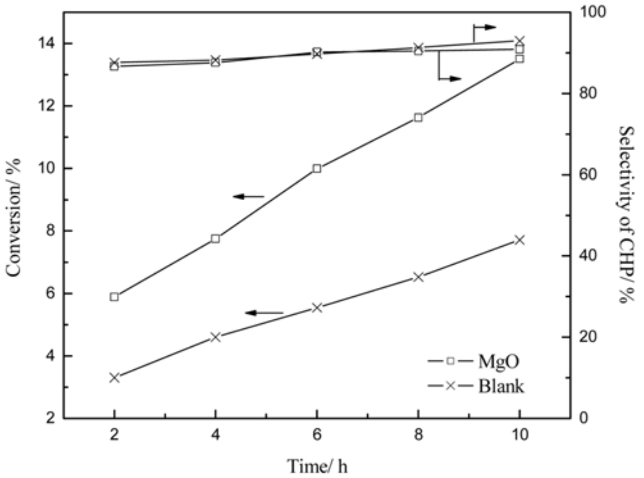


Fig. 5. Effect of MgO catalyst on the conversion and selectivity of CHP. Reaction condition: Cumene, 50 ml; Catalyst, 0.5 g MgO; Temperature, 90 °C; Air flow, 160 ml/min; Initiator, 1 g CHP.

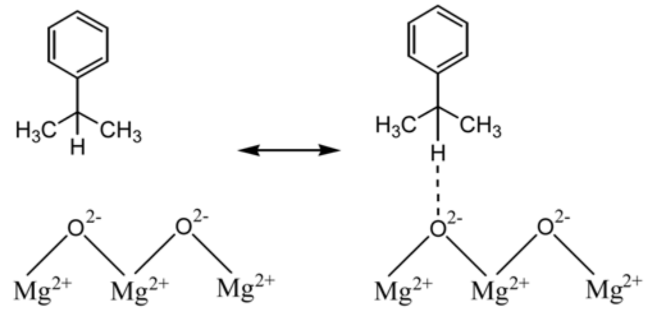


Fig. 6. The adsorption of cumene on MgO.

doubled by the catalyst of MgO without decreasing the selectivity of CHP nearly. The conversion and selectivity without catalyst were 7.7% and 91.5% in reaction time 10 h, respectively. In the presence of MgO, the conversion and selectivity were 13.5% and 90.9%, respectively. As mentioned above, the reaction of hydrogen atom abstraction from cumene by ROO• (k1 in Scheme 1) is the rate-determining step. To improve the conversion, it is a pathway to activate the tertiary C-H bond of cumene. The catalytic role of MgO is presented in Fig. 6. The hydrogen atom at the position of the tertiary C of cumene may be adsorbed on the site of O^{2-} in MgO. Due to the interaction of the hydrogen atom and O^{2-}, the tertiary C-H bond of cumene was weakened. Thus, the reaction progressed at a faster rate.

2-3. Effect of the Amount of Catalyst

In this section, the effect of the amount of 1%Cu/MgO catalyst was investigated. The results are shown in Fig. 7. The selectivity of CHP was 84.5% at 10 h. The selectivity decreased with the amount of the added catalyst, which is consistent with the mechanism discussed above. With increasing the amount of catalyst, the opportunity that the CHP was decomposed by copper ion also increased. The conversion increased due to the activation of C-H bond by the catalyst and the attack of the C-H by much more RO•.

2-4. Influence of Temperature

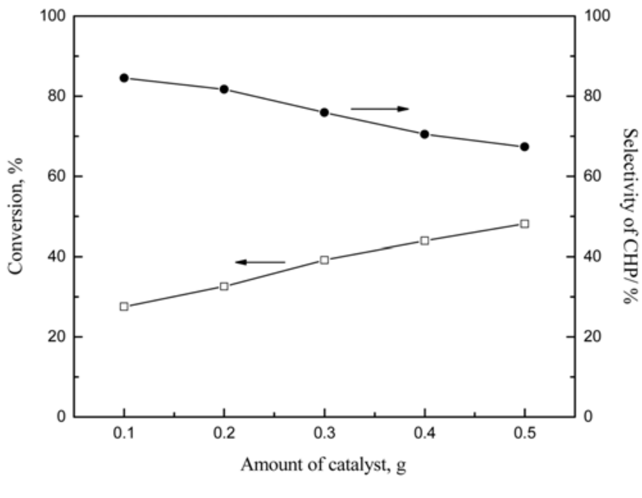


Fig. 7. Effect of the amount of 1%Cu/MgO on the conversion and selectivity of CHP. Reaction condition: Cumene, 50 ml; Catalyst, 1%Cu/MgO; Temperature, 90 °C; Air flow, 160 ml/min; Initiator, 1 g CHP.

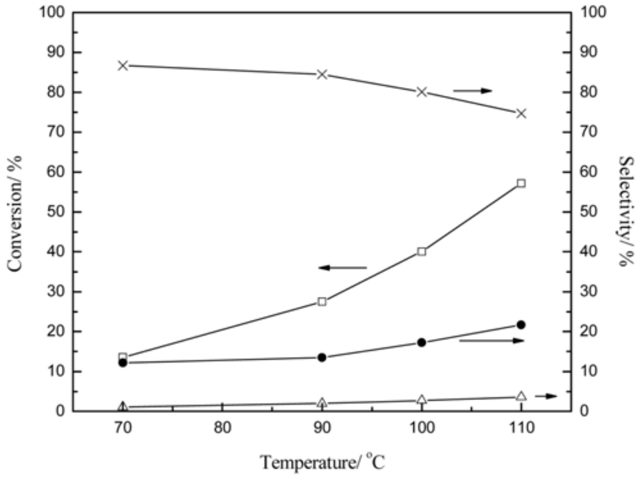


Fig. 8. Effect of temperature on the oxidation. □ cumene; × CHP; ● 2-phenyl-2-propanol; △ acetophenone. Reaction condition: Cumene, 50 ml; Catalyst, 0.1 g 1%Cu/MgO; Air flow, 160 ml/min; Initiator, 1 g CHP.

As shown in Fig. 8, the conversion increased with temperature. A little effect on the selectivity of CHP can be seen with temperature increasing from 70 °C to 90 °C. But the selectivity of CHP decreased largely in the range above 90 °C. At the same time, the yields of the by-products increased. In the range of 70 °C to 90 °C, the reaction temperature had little influence on the decomposition of CHP. However, the C-H bond was activated at the higher temperature. Above 90 °C, much more CHP started to decompose under the catalysis of copper ion. In the meanwhile, thermal decomposition of CHP played an important role due to the instability of CHP at high temperature. High temperature also favors another reaction that yields acetophenone from RO• through β-scission. Considering all of these, 90 °C was a suitable temperature for both the conversion and selectivity of CHP.

2-5. Influence of Air Flow

The results of the influence of air flow on the reaction are summarized in Fig. 9. It can be seen from Fig. 9(a) that the conversion increased slightly from 100 to 160 ml/min, and then significantly for higher air flow. As presented in Fig. 9(b), the selectivity of CHP remained almost at the same level from 100 to 160 ml/min. But the selectivity of CHP decreased to 74.6% for 300 ml/min. The selectivity of ROH in the air flow of 160 ml/min was the less than that of 100 and 300 ml/min (Fig. 9(c)). And the selectivity of acetophenone at 10 h increased with the air flow (Fig. 9(d)). Based on the results, the conversion increased at the cost of decreasing the selectivity of CHP. The reaction of hydrogen atom abstraction from cumene by ROO• (k1 in Scheme 1) is the rate- determining step. The reaction (k2) between O_2 and a RO• was usually much faster than the reaction (k1) between the cumene and the ROO•. So, at low air flow, the conversion increased slightly from 100 to 160 ml/min without decreasing the selectivity of CHP. With increasing the air flow further, the selectivity of CHP at the air flow of 300 ml/min was lower than that of 160 ml/min during all the reaction period from 2 h to 10 h. So higher air flow may not be good for the selectivity of CHP. The selectivity of ROH was much higher for 300 ml/min than that of 160 ml/min. The significant increase of the conversion from 160

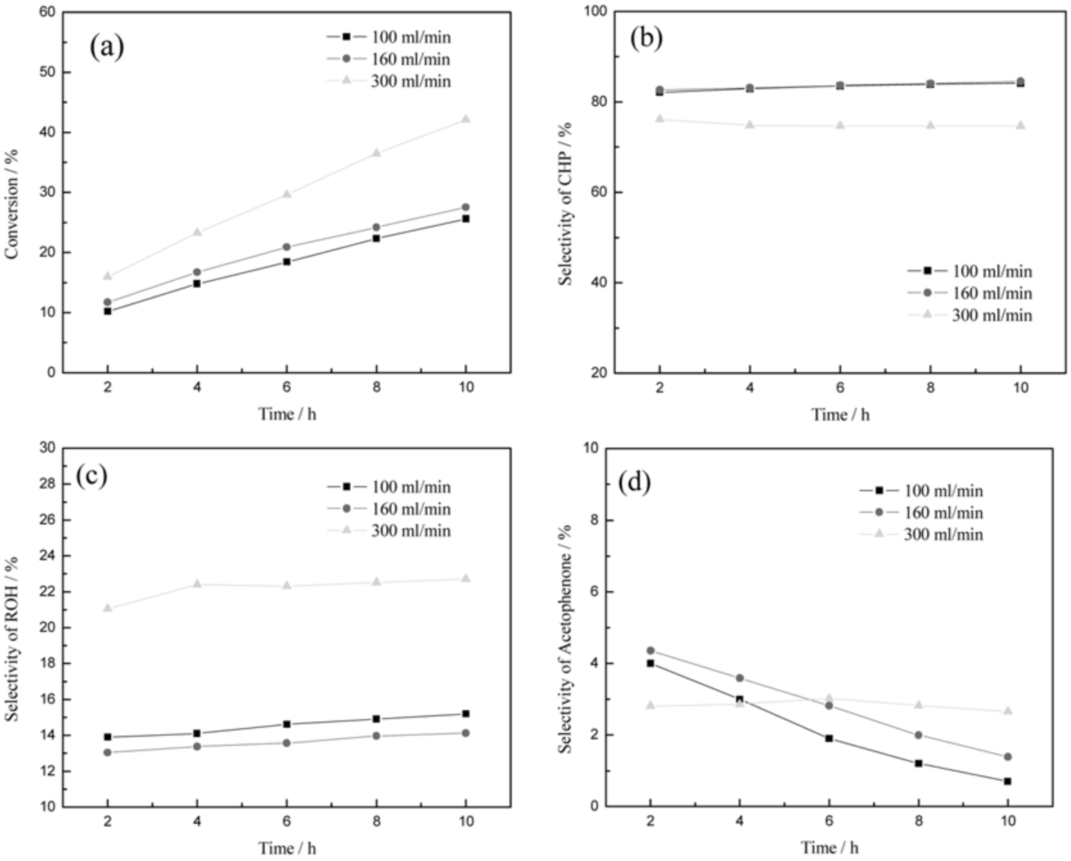


Fig. 9. Influence of air flow on the oxidation of cumene. (a) Influence of air flow on the conversion of cumene. (b) Influence of air flow on the selectivity of CHP. (c) Influence of air flow on the selectivity of ROH. (d) Influence of air flow on the selectivity of acetophenone. Reaction condition: Cumene, 50 ml; Catalyst, 0.1 g 1%Cu/MgO; Temperature, 90 °C; Initiator, 1 g CHP.

to 300 ml/min may be mainly arising from the RO• produced. This is because cumene more easily reacted with RO• than ROO•.

CONCLUSION

It has been found that the tertiary C-H bond of cumene could be activated by MgO because of the adsorption of the hydrogen atom on the O^{2-} site in MgO. From the characterization of XRD, H_2-TPR and XPS, copper ion in catalyst of 1%CuMgO dispersed finely. The conversion and CHP selectivity were in a trade-off relationship because cumene oxidation was subject to the decomposition of CHP. Thus, low content and amount of copper in catalyst were beneficial for CHP production. When the temperature was 90 °C, air flow was 160 ml/min, amount of catalyst was 0.1 g; a 84.5% selectivity of CHP with 27.5% conversion of cumene could be achieved over 1%Cu/MgO.

ACKNOWLEDGMENTS

We acknowledge the financial support from the National Nature Science Foundation of China (Project 20490209 and 20625621).

REFERENCES

1. F. Minisci, F. Recupero, A. Cecchetto, C. Gambarotti, C. Punta and R. Paganelli, *Org. Process Res. Dev.*, **8**, 163 (2004).
2. S. Matsui and T. Fujita, *Catal. Today*, **71**, 145 (2001).
3. G. R. Varma and W. F. Braydon, *J. Catal.*, **28**, 236 (1973).
4. S. Takaç and T. H. Özdamar, *Appl. Catal. A*, **95**, 35 (1993).
5. R. A. Sheldon and I. W. C. E. Arends, *J. Mol. Catal. A*, **251**, 200 (2006).
6. G. B. Shul'pin, *J. Mol. Catal. A*, **189**, 39 (2002).
7. M. Y. Zhang, L. F. Wang, H. B. Ji, B. Wu and X. P. Zeng, *J. Natural Gas Chem.*, **16**, 393 (2007).
8. F. G. Boyaí, S. Takaç and T. H. Özdamar, *Appl. Catal. A*, **179**, 279 (2000).
9. A. K. Suresh, M. M. Sharma and T. Sridhar, *Ind. Eng. Chem. Res.*, **39**, 3958 (2000).
10. F. G. Boyaí, S. Takaç and T. H. Özdamar, *Appl. Catal. A*, **172**, 59 (1998).
11. S. Takaç, F. G. Boyaí and T. H. Özdamar, *Chem. Eng. J.*, **71**, 37 (1998).
12. P. P. Toribio, J. M. Campos-Martin and J. L. G. Fierro, *J. Mol. Catal. A*, **227**, 101 (2005).
13. S. Xie, M. P. Rosynek and J. H. Lunsford, *J. Catal.*, **188**, 24 (1999).
14. H. J. Seo and E. Y. Yu, *Korean J. Chem. Eng.*, **12**, 485 (1995).
15. J. E. Lee, B. S. Jin, S. H. Cho, S. H. Han, O. S. Joo and K. D. Jung, *Korean J. Chem. Eng.*, **22**, 536 (2005).
16. T. Wang, P. Yu, S. K. Gong, Q. Li and Y. B. Luo, *Korean J. Chem. Eng.*, **25**, 998 (2008).

17. E. Promaros, S. Assabumrungrat, N. Laosiripojana, P. Praserthdam, T. Tagawa and S. Goto, *Korean J. Chem. Eng.*, **24**, 44 (2007).
18. S. H. Cho, M. S. Cheong, K. D. Jung, C. S. Kim and S. H. Han, *Appl. Catal. A*, **267**, 241 (2004).
19. F. E. López-Suárez, A. Bueno-López and M. J. Illán-Gómez, *Appl. Catal. B*, **84**, 651 (2008).
20. E. Moretti, M. Lenarda, L. Storaro, A. Talon,T. Montanari, G. Busca, E. Rodríguez-Castellón,A. Jiménez-López, M. Turco, G. Bagnasco and R. Frattini, *Appl. Catal. A*, **335**, 46 (2008).
21. G. Avgouropoulos and T. Ioannides, *Appl. Catal. A*, **244**, 155 (2003).
22. X. M. Liu, W. D. Yin, S. B. Miao and B. M. Ji, *Mater. Chem. Phys.*, **113**, 518 (2009).