

Solid base and their performance in synthesis of propylene glycol methyl ether

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Abstract

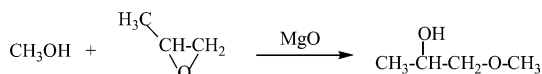
The base strength and basicity of MgO, CaO and Mg–Al oxide were studied for the synthesis of propylene glycol methyl ether from methanol and propylene oxide. The results showed that solid base with moderate strength such as MgO facilitated the formation of propylene glycol methyl ether. FTIR illustrated that methanol dissociated to methoxide species on MgO surface, while no dissociation took place on CaO. The moderate base strength and weak Lewis acid sites on MgO were very important for the methanol dissociation and then the synthesis of propylene glycol methyl ether.

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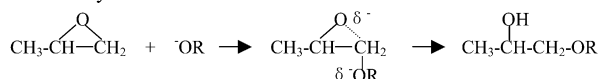
Keywords: Solid base; Propylene glycol methyl ether; Methanol; Propylene oxide

1. Introduction

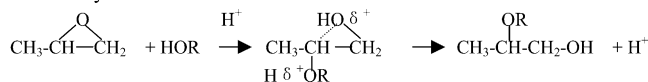
Glycol ether is one kind of fine chemicals widely used as solvent due to its ether bond and hydroxyl group, which is hydrophobic and hydrophilic, respectively. Because of the negligible toxicity of propylene glycol ether, it is expected as a safe substitute for toxic ethylene glycol ether [1]. There are several methods for the synthesis of propylene glycol ether [2–4]. Among them the propylene oxide method is mostly convenient and industrial feasible. Generally, propylene oxide reacts with fatty alcohol via base or acid catalysis, the mechanism of which was considered as followed [5,6]:



base-catalyzed reaction



acid-catalyzed reaction



The epoxies ring of propylene oxide might open at either of the C–O bonds. In basic catalysis, the bond preferentially opened at the least sterically hindered position, leading to most secondary alcohols. But acid catalysts provided a mixture of secondary and primary alcohols; the proportion depended on the acid strength. The addition of methanol to propylene oxide might form primary alcohols (such as 2-methoxy-1-propanol), which revealed the reproduction and developmental toxicity [7]. Therefore, the high selectivity is required for this process.

Although basic homogenous reaction showed high selectivity to secondary alcohols, they had the drawbacks of separation, liquid waste treating and corrosion problems. Thus

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solid bases and acids were developed to synthesize propylene glycol ether. Those heterogeneous catalysts included acid zeolites [8], cation-exchangeable layered clay [9], anionic double hydroxide clays [10] and basic zeolites [11]. Among them basic catalysts has attracted much attention due to high selectivity of secondary alcohols [10–12]. Unfortunately, few studies have reported the effect of base strength and basicity on the synthesis of propylene glycol ether over solid base catalysts. Alkaline earth metal oxides appeared to be active and selective solid base catalysts in a variety of organic reactions involving formation of carbanion intermediates. Particularly, MgO-based catalysts which have acid–base property, have been shown to promote several reactions such as esterification [13], etherification [14], double bond isomerization [15], aldol condensation [16,17], Knoevenagel condensation [18] and alcohol coupling [19]. The present work mainly compares MgO with CaO and Mg–Al oxide to investigate the effect of base strength and basicity on the synthesis of propylene glycol methyl ether from methanol and propylene oxide.

2. Experimental

2.1. Preparation of catalyst

CaO was prepared from CaCO₃ calcined at 1073 K in N₂ atmosphere, and MgO was obtained by thermal decomposition of Mg(OH)₂ at 673, 773, 873, and 973 K, respectively. Mg–Al composite sample with an Mg/Al mole ratio of 3 was prepared by co-precipitation method. The solution A was prepared by 0.12 mol of Mg(NO₃)₂·6H₂O and 0.02 mol of Al₂(NO₃)₃·9H₂O with the total concentration of 0.64 mol/l, and the solution B contained 8.9% ammonia in 180 ml water. Both were then mixed at a rate of 4 ml/min under a vigorous mechanical stirring at 333 K. The suspension was left overnight at 333 K, filtered and washed until pH = 7. The resultant solid was dried overnight at 333 K, and then activated in a dry nitrogen flow at 773 K for 4 h.

2.2. X-ray diffraction

XRD of the catalysts were measured in Rigaku D/max-γA using Cu target with Ni filter. Diffraction patterns were obtained with X-ray gun operated at 50 kV and 30 mA, using a scan speed rate 0.2°/min (2θ).

2.3. BET measurement

BET surface areas of the samples were determined with the BET method using a Micromeritics ASAP-2000 apparatus.

2.4. CO₂ temperature programmed desorption (CO₂-TPD)

Catalyst (0.1 g, 40–60 mesh) was placed in the quartz reactor bed. Pretreatment for TPD procedure consisted of

1 h treatment in flowing argon at assigned temperature, and then the sample was cooled to room temperature. CO₂ was pulsed to the reactor using six-way valve till reaching saturation. Once the physically absorbed CO₂ was purged off, TPD experiment was started with heating rate of 10 K/min under Ar flow (50 ml/min), and the effluent was detected by a BALZAQ-mass spectrometer.

2.5. Methanol TPSR

The catalyst pretreatment procedure was the same as the CO₂-TPD. Methanol was injected to reactor using 1 μl syringe at room temperature, once the physical absorbed methanol was purged off, the temperature program was started with the heating rate of 10 K/min under Ar flow (50 ml/min), and the effluent was detected by a BALZAQ-mass spectrometer.

2.6. FTIR spectroscopy of adsorbed methanol

FTIR spectra were recorded on a Nicolet Magna 550II Fourier-transform infrared spectrometer in the region 4000–1000 cm⁻¹. 128 scans with a resolution of 4 cm⁻¹ were collected. Magnesium oxide or calcium oxide wafer pressed at 2.4 × 10⁸ Nm⁻² and weighing 15–20 mg, was thermally pretreated by heating at 673 K in vacuo. The build-up of methanol species on the surface was studied by adding methanol vapor, which had been degassed by freezing and pumping several times, to the cell for 15 min. After removing the gas phase with evacuation, IR spectra of surface species were obtained.

2.7. Catalytic performance

The catalytic performance was evaluated in a 75 ml batch reactor with mole ratio of methanol and propylene oxide being 5:1. After running at 393 K for 5 h under magnetic stirring, the reactor was cooled down to room temperature. The products were analyzed by a gas chromatograph with a flame ionization detector after centrifugal separation from the catalyst.

3. Results

3.1. Structures

MgO and CaO treated at elevated temperature were typical solid bases [20,21]. The XRD pattern of MgO and CaO illustrated that cubic MgO and CaO could be prepared via the dissociation of magnesium hydrate and calcium carbonate, respectively (see Fig. 1), and Mg–Al oxide only showed the character of MgO. BET surface area is listed in Table 1. It can be seen that the surface area of MgO is much higher than that of CaO.

Table 1
BET surface area and CO₂ uptake

Catalyst	BET surface area (m ² /g)	CO ₂ uptake (mmol/m ²)			
		373 K	513 K	573 K	923 K
CaO	12.30	–	–	–	2.1×10^{-2}
MgO ^a	198.00	3.13×10^{-6}	6.06×10^{-5}	6.97×10^{-5}	–
Mg–Al oxide	130.00	3.23×10^{-5}	–	–	–

^a Calcined at 673 K.

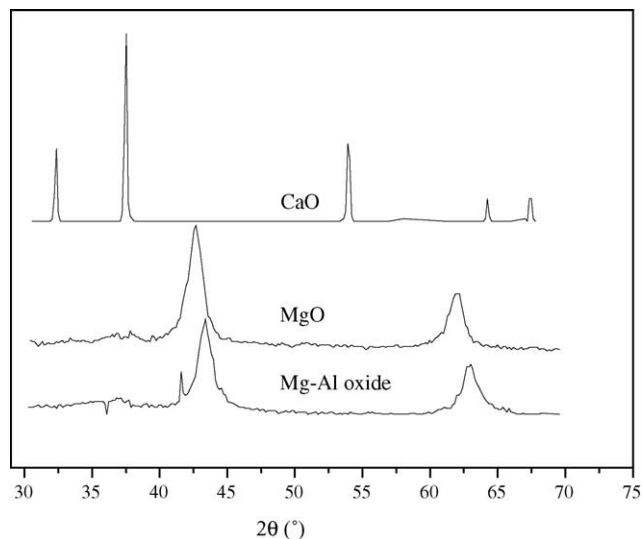


Fig. 1. XRD patterns of CaO, MgO and Mg–Al oxide.

3.2. Base strength and basicity of MgO, CaO and Mg–Al oxide

CO₂-TPD revealed the presence of three kinds of base sites on the surface of MgO calcined at 673 K with CO₂ desorption peaks at 373, 513 and 573 K, respectively (see Fig. 2). This demonstrated that MgO had weak and moderate strength base sites on the surface. However, CaO mainly exhibited a

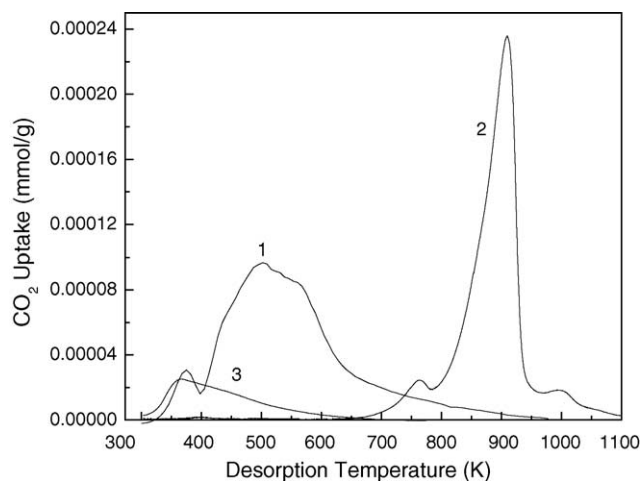


Fig. 2. CO₂-TPD of CaO, MgO and Mg–Al oxide: (1, MgO; 2, CaO; 3, Mg–Al oxide).

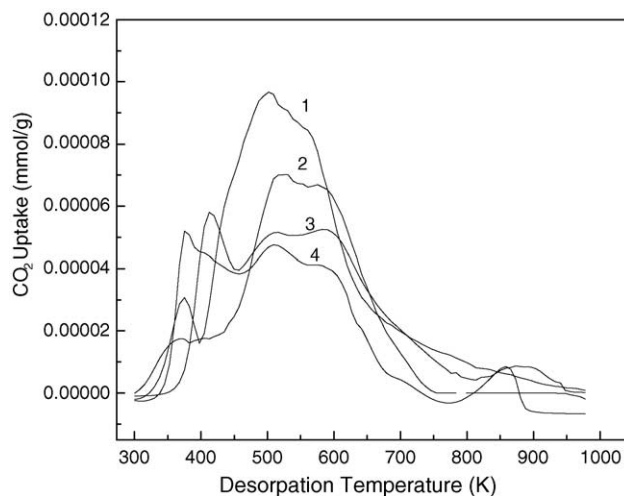


Fig. 3. CO₂-TPD of MgO calcined at various temperatures: (1, 673 K; 2, 773 K; 3, 873 K; 4, 973 K).

major desorption at 923 K, indicating the strong basic sites on its surface. Mg–Al oxide only had weak base sites with CO₂ desorption peak at 373 K. CO₂ uptake of CaO, MgO and Mg–Al oxide, which reflected the basicity, are listed in Table 1. Although MgO had the higher BET surface area, CaO showed the highest basicity.

Fig. 3 illustrated the effect of calcinations temperature on the MgO base strength and basicity, it can be seen that there exist three kinds of base site on the surface as mentioned above when the calcinations temperature was lower than the 773 K. As the calcinations temperature reached 873 K, strong strength base sites appeared as evidenced by the CO₂ desorption peak around 873 K. At the same time, CO₂-TPD in Fig. 3 also indicated that the CO₂ uptake desorbed from moderate strength base sites decreased gradually with the increase of calcinations temperature. The BET surface area and CO₂ uptake that desorbed from weak, moderate and strong basic sites are listed in Table 2. We can see that CO₂ uptakes varied drastically with the rise of calcinations temperature, however, the basicity of MgO on moderate base sites changed a little if CO₂ uptakes were referred to sample surface area.

3.3. FTIR spectroscopy of absorbed methanol and methanol TPSR

IR spectra of methanol adsorbed on MgO at various temperatures are shown in Fig. 4. The bands observed around 2915–2800 and 1200–1000 cm⁻¹ were assigned, respec-

Table 2
BET surface area and CO₂ uptake of MgO calcined at various temperatures

Calcinations temperature (K)	BET surface area (m ² /g)	CO ₂ uptake (mmol/m ²)		
		373 K	513 and 573 K	873 K
673	198.00	3.13×10^{-6}	1.30×10^{-4}	–
773	150.49	5.52×10^{-6}	1.26×10^{-4}	–
873	105.92	1.54×10^{-5}	1.17×10^{-4}	5.91×10^{-6}
973	96.92	2.18×10^{-5}	1.22×10^{-4}	7.21×10^{-6}

tively, to the C–H and C–O stretching vibrations due to the methoxide species [22]. Upon increasing temperature from 298 to 423 K, the intensities of the band at 2800 and 1097 cm⁻¹ increased, while the band at 1055 cm⁻¹ decreased. Junko Kondo et al. [23] reported similar results, which were attributed to two kinds of methoxide species. The new OH group formed from the dissociative adsorption gave rise to broad bands near 3500 cm⁻¹. When the adsorption temperature reaches 393 K, new bands appeared at 1599 and 1394 cm⁻¹, which could be ascribed to the transformation of methoxide species into formate ions [24,25]. Fig. 5 illustrates the TPSR of methanol over MgO. It is found that methanol desorbs molecularly with maximum at 432 K, however it decomposes at high temperatures as evidenced by CO₂ and CO desorption peaks. Thus, methanol adsorbed onto MgO in both undissociated and dissociated forms. The undissociated one was coordinated to the catalyst surface in a weakly absorbed molecular state, correspondingly to the methanol desorption at low temperature. The dissociated one produced methoxide species and desorbed into CO₂ and CO at high temperature in the TPSR patterns.

FTIR spectra of methanol adsorbed on CaO at various temperatures were shown in Fig. 6. Here, the bands around 2800 and 1200–1000 cm⁻¹ were not clearly observed, and only trace adsorption took place. At the same time, the broad bands due to hydroxyl group were hardly observed near 3500 cm⁻¹. Although CaO had the strong basic strength and high basicity, methanol could not be dissociated to form methoxide species

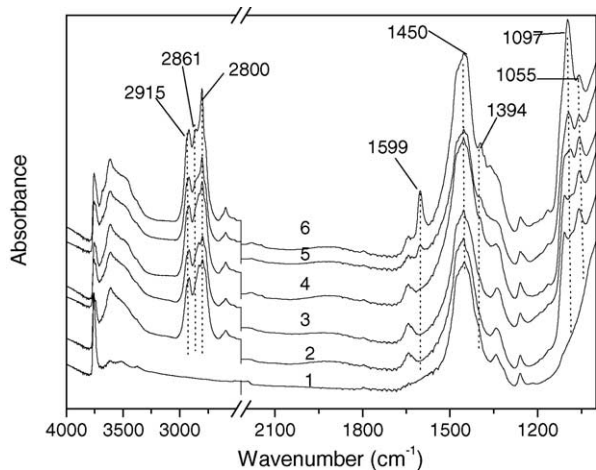


Fig. 4. IR spectra of methanol adsorbed on MgO at various temperatures: (1, MgO; 2, RT; 3, 323 K; 4, 363 K; 5, 393 K; 6, 423 K).

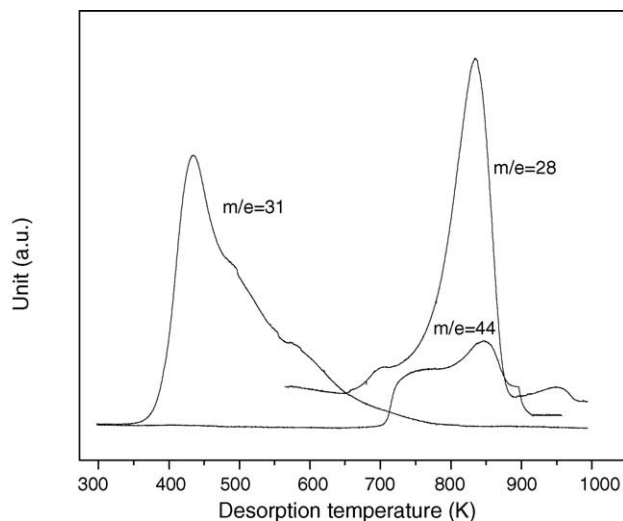


Fig. 5. TPSR of methanol on MgO: (*m/e* = 31, 28, 44 corresponding to the strongest mass spectra signal of methanol, CO and CO₂, respectively).

on its surface (trace dissociation might be possible). Only methanol desorption was observed with the maxima in TPSR at 609 K (see Fig. 7). Because of the strong basic strength of oxygen anion, molecular methanol would be coordinated to the CaO surface in a stronger manner than that of MgO, resulting the higher desorption temperature.

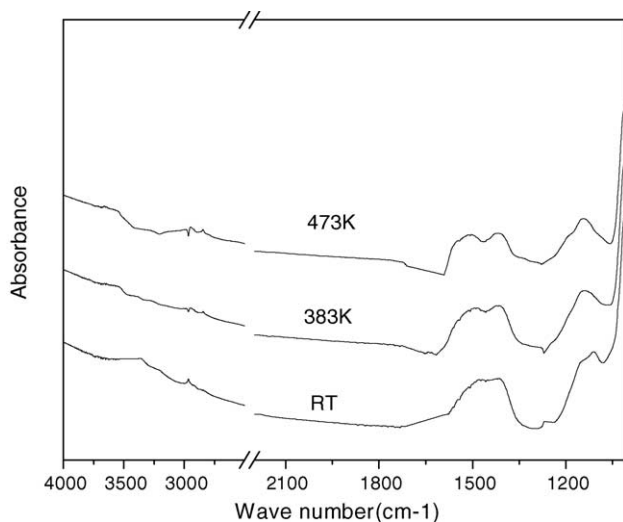


Fig. 6. IR spectra of methanol adsorbed on CaO at various temperatures.

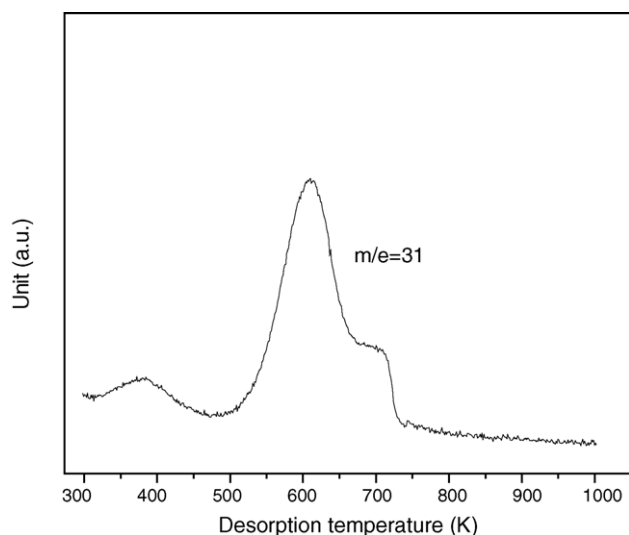


Fig. 7. TPSR of methanol on CaO: ($m/e = 31$ corresponding to the strongest mass spectra signal of methanol).

Table 3
The catalytic properties of CaO, MgO and Mg–Al oxide

Catalyst	PO conversion (%)	Isomer selectivity (%)
CaO	37.3	85.1
MgO ^a	71.1	89.2
Mg–Al oxide	31.4	74.1
None	27.3	72.3

^a Calcined at 673 K.

3.4. Catalytic performance

Data in Table 3 illustrate the catalytic performance of CaO, MgO and Mg–Al oxide in synthesis of propylene glycol methyl ether from propylene oxide and methanol. MgO showed the highest PO conversion and isomer selectivity (the ratio of 1-methoxy-2-propanol/total propylene glycol methyl ether). Although CaO had strong base and high basicity, its performance was lower than MgO. Mg–Al oxide with only weak base also showed low activity and isomer selectivity,

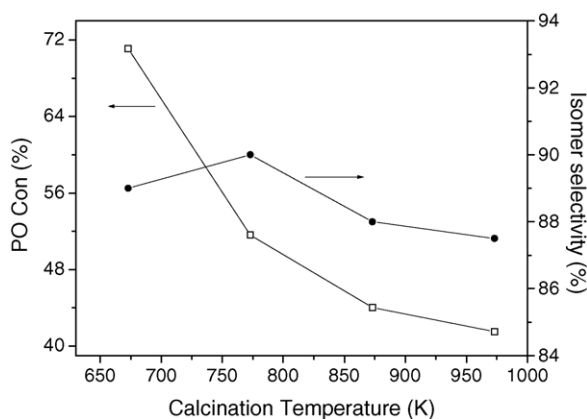


Fig. 8. The effect of calcinations temperature on MgO catalytic activity.

which might be due to the acidity of Al_2O_3 [26]; therein the reaction underwent the mechanism that was different from the basic catalysis. In addition, PO conversion and isomer selectivity are 27.3, 72.3%, respectively when no catalyst was loaded (see Table 3).

Fig. 8 indicates that PO conversion of MgO decreased monotonically with the rise of calcinations temperature from 673 to 973 K, and isomer selectivity changed a little.

4. Discussion

Compared with CaO and Mg–Al oxide, MgO with the highest moderate basicity showed the best PO conversion and isomer selectivity (see Table 3). This indicated that synthesis of propylene glycol methyl ether should be closely related to the moderate basic site. In order to further understand the effect of base strength on the catalytic performance, MgO obtained from magnesium hydrate calcined at various temperatures, which lead to the different amount of moderate base sites, showed interesting relationship between basicity and catalytic performance (see Fig. 8), i.e. both the PO conversion and the amount of moderate basic sites decreased with the rise of calcinations temperature. As a result, the catalytic activity (PO conversion) could be linearly correlated with the amount of moderate base sites (see Fig. 9). The line would cross the Y-axis at about 25%, which agrees with the data listed in Table 3, i.e. the reaction could take place without the presence of catalyst. Thus, the formation of propylene glycol methyl ether over solid base occurs on the base site with moderate strength.

As mentioned above, FTIR illustrated that methanol adsorbed on MgO could generate undissociated methanol, and then dissociated species. The latter produced methoxide species, which desorbs as CO_2 and CO at high temperature, as shown in TPSR. These species could react with propylene oxide to form propylene glycol methyl ether. As far as CaO was

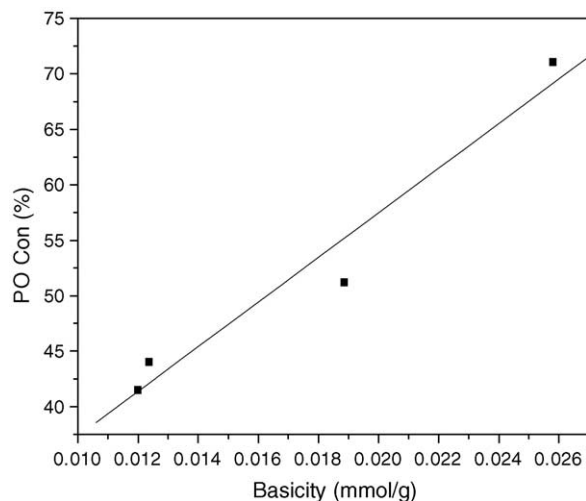
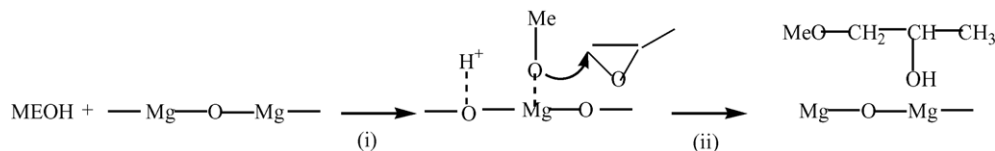


Fig. 9. The relationship between activity and MgO basicity.



Scheme 1. Plausible mechanism of 1-methoxy-2-propanol formation.

concerned, no methoxide species were formed on its surface due to the acid strength of Ca cation is too weak to stabilize the methoxide species and then CaO showed low catalytic activity. Thus, the formation of methoxide species was very important for the synthesis of propylene glycol methyl ether. Mg–Al oxide had no enough strong basic sites to activate methanol, but its acidity could cause the reaction in an acid catalyzed route, being indicative of the isomer products.

The plausible mechanism of 1-methoxy-2-propanol formation on MgO is illustrated in Scheme 1. A proton was abstracted from the hydroxyl group of methanol and a methoxide ion was generated in path (i). The methoxide ion and proton were absorbed on acidic and basic sites on the MgO surface, respectively. In path (ii), because of the sterically hindered CH_3 of propylene oxide, the methoxide ion attacked the C (1) position and C (1)–O bond cracked, followed by pick up of the proton to form 1-methoxy-2-propanol.

It seems reasonable to consider that the highest activity of MgO was due to the ability for a proton and a methoxide ion generation from methanol. CaO with strong basic sites seems unfavorable for the present reaction because of strong adsorption of methanol and could not generate methoxide ion and proton. Thus, moderate basic sites are effective for the present reaction.

5. Conclusion

The results presented above led to the following conclusions: (1) because of its moderate basic strength, MgO promotes the formation of 1-methoxy-2-propanol from methanol and propylene oxide, but CaO and Mg–Al oxide with the strong and weak basic strength, respectively, appears not to favor the formation of 1-methoxy-2-propanol, (2) methanol absorbed on MgO surface could dissociate into proton and methoxide ion due to the existence of basic sites with moderate strength and weak Lewis acid sites, (3) because of strong adsorption of methanol on CaO surface, it was very difficult

to generate methoxide ion and then resulted in a low activity. Thus, the generation of methoxide ion was very important to the reaction.

References

- [1] European Chemical Industry Ecology and Toxicological Center Report, No. 4, 1982.
- [2] H.C. Chitwood, *J. Am. Chem. Soc.* 68 (1946) 680.
- [3] J.F. Knifton, US Patent 4,390,734 (1983).
- [4] U. Junko, F. Keizo, JP Patent 63,316,749 (1988).
- [5] G. Woods, *The ICI Polyurethanes Book*, 2nd ed., Wiley, 1990.
- [6] R.E. Parker, N.S. Isaacs, *Chem. Rev.* 59 (1959) 737.
- [7] ECETOC Technical Report No. 64, 1995.
- [8] W.Y. Dong, T.N. Gao, CN Patent 1,033,742C (1993).
- [9] Gregory, D.J. Westlake, US Patent 4,440,958 (1984).
- [10] P.A. Martin, T. William, C. Malama, US Patent 5,110,992 (1992).
- [11] W.J. Smith, F.C. Malherbe, US Patent 6,291,720B1 (2001).
- [12] Z.S. Jin, X.M. Jiang, L. Zhang, CN Patent 1,087,651C (1998).
- [13] A. Coma, S. Iborra, S. Miquel, J. Primo, *J. Catal.* 173 (1998) 315.
- [14] T. Yamakawa, M. Takizawa, T. Ohnishi, H. Koyama, S. Shinoda, *Catal. Commun.* 2 (2001) 191.
- [15] H. Hattori, *Proceedings of the Third International Symposium on Heterogeneous Catalysis and Fine Chemicals*, Poitiers, 1993, p. 19.
- [16] G. Zhang, H. Hattori, K. Tanabe, *Appl. Catal.* 36 (1988) 98.
- [17] J.I. Di Cosimo, V.K. Díez, C.R. Apesteguía, *Appl. Catal.* 137 (1996) 149.
- [18] A. Coma, S. Iborra, J. Primoo, F. Rey, *Appl. Catal.* 114 (1994) 215.
- [19] M. Xu, M.J.L. Ginés, A.-M. Hilmen, B.L. Stephens, E. Iglesia, *J. Catal.* 171 (1997) 130.
- [20] N.E. Fouad, Ph. Thomasson, H. Knozinger, *Appl. Catal. A: Gen.* 194–195 (2000) 213.
- [21] S. Coluccia, F. Bocuzzi, G. Ghiotti, C. Morterra, *J. Chem. Soc. Faraday Trans. 1* (78) (1982) 2111.
- [22] A.J. Tench, D. Giles, J.F.J. Kibblewhite, *Trans. Faraday Soc.* 67 (1971) 854.
- [23] J. Kondo, Y. Sakata, K. Maruya, K. Tamaru, T. Onishi, *Appl. Surf. Sci.* 28 (1987) 457.
- [24] R.O. Kagel, R.G. Greenler, *J. Chem. Phys.* 49 (1968) 1638.
- [25] Q. Zaihu, G. Canxiong, N. Shuichi, T. Kenzi, *Chem. J. Chin. Universities (Gao deng Xue Xiao Hua Xue Xue Bao)* 13 (1992) 246.
- [26] H. Knozinger, P. Ratnasamy, *Catal. Rev.: Sci. Eng.* 1 (17) (1978) 31.