

# Effect of the Brønsted acidity on the behavior of CO<sub>2</sub> methanol reaction

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## Abstract

The CO<sub>2</sub> methanol reforming reaction in liquid phase over Keggin type heteropoly compounds catalysts was investigated. The prepared catalysts, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and its copper salt Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> were characterized by means of IR, and TG. Catalysts tests were carried out at 0.12 MPa and at different temperatures. The effects of temperature and the catalyst amount were investigated. When the protons of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> were replaced with copper cations, the activity decreased while the selectivity of dimethyl carbonate (DMC) increased slightly. Brønsted acid sites reduce the formation of DMC in favor of dimethyl ether (DME). When raising the reaction temperature, it was found that a lower temperature is favorable for DMC formation, and a maxima in the DMC formation was observed at 328 K.

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## 1. Introduction

Conversion of methanol is still a subject of numerous investigations in fundamental research for modeling the mechanism of the catalytic reaction, as well as in practical research in order to optimize all the parameters (conversion, selectivity, reaction conditions, etc.) required for specific reactions of economic importance. It is well known that the methanol reaction can lead to various products depending on the catalyst used, the reaction conditions and the reactants (O<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>, CO<sub>2</sub>, etc.). Recently the conversion of methanol in presence of carbon dioxide has gained considerable attention. The reason of this attention is due to the abundance, the cheapness, the non-toxicity and the non-flammability of the carbon dioxide, compared to currently used phosgene and carbon monoxide [1–7]. Moreover, the reaction can lead to the formation of the dimethyl carbonate (DMC), which is considered as an important chemical product that can have several uses and applications. For example, it can be used as an environmentally friendly intermediate and starting material for organic synthesis via carbonylation and methylation substituting poisonous phosgene and dimethyl sulfate [8]. In addition, it is also a promising octane enhancer for replacing

methyl *tert*-butyl ether (MBTE) in gasoline [9]. Several studies reported in the literature have demonstrated that the DMC can be obtained by the reaction of methanol with carbon dioxide (2CH<sub>3</sub>OH + CO<sub>2</sub> → (CH<sub>3</sub>O)<sub>2</sub>CO + H<sub>2</sub>O) [10–16]. Unfortunately few industrial processes involve carbon dioxide as a reactant, hence still now the DMC synthesis is mainly via oxidative carbonylation of methanol [17–19]. The major difficulty is due to the poor reactivity of CO<sub>2</sub> molecule, thermodynamically stable. Nevertheless, the inertness of carbon dioxide constitutes a serious drawback for further applications, the main problem being to find an efficient catalyst, as well as optimal operating conditions. Therefore, the direct synthesis of DMC from methanol and carbon dioxide is still at the laboratory scale stage.

In our present investigation, we report the study of methanol conversion in presence of CO<sub>2</sub> in liquid phase using Keggin-type heteropoly compounds as catalysts. It is well known that these kinds of materials provide suitable model structure for mechanistic studies, since they have a well-characterized structure and a flexibility of both the acid–base and redox properties needed for bifunctional catalyzed reactions. Their redox and acid–base properties can be adjusted by varying the counter-cation, the addenda atoms. Thus, this attractive bifunctional catalysts (oxidative and acidic), have been successfully applied in a large variety of acid and redox catalyzed reactions in homogenous and heterogenous phases [20–22]. Among them, the methanol reaction has been extensively investigated

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[23–27]. In order to investigate the influence of Brønsted acid sites and redox sites on the behavior of the methanol transformation in presence of carbon dioxide, we have catalyzed the reaction under the same conditions by the heteropolyacid  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ , then by the copper salt  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ , where the protons were replaced with copper cations.

## 2. Experimental

### 2.1. Preparation of the catalysts

The heteropolyacid  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  was prepared according to the methods of Rocchiccioli-Deltcheff et al. [28]. The copper salt form  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ , was obtained from the heteropolyacid  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  as precipitate by adding slowly the required amount of  $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$  (to neutralize the three proton) to the aqueous solution of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , then the required amount of  $\text{CuSO}_4\cdot 6\text{H}_2\text{O}$  was added. After eliminating the formed  $\text{BaSO}_4$  precipitate, the obtained solution was allowed to stand few days at  $4^\circ\text{C}$ . The  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$  salt was recovered from the solution by filtration.

### 2.2. Physicochemical techniques

The purity and the Keggin structure of 12-molybdophosphoric acid  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , and its copper salt were checked by means of infrared (IR) and thermogravimetry (TGA).

IR spectra were recorded with an infrared spectrometer GENESIS II-FTIR ( $4000\text{--}400\text{ cm}^{-1}$ ) as KBr pellets. TGA was performed in flow of argon in a thermogravimeter (PERKIN-ELMER, TGA/DSC), 10 mg of 12-molybdophosphoric was heated at  $5^\circ\text{C}/\text{min}$  up to  $520^\circ\text{C}$ .

### 2.3. Catalytic measurements

Catalytic tests were carried out in a 200 ml pyrex flask. The standard procedure is as follow: 20 ml of  $\text{CH}_3\text{OH}$  and 0.25 g of heteropolyanions were charged into the flask and it was heated to the desired temperature then pressurized to 0.12 MPa. After the required time, the liquid phase was cooled, sampled, and analyzed with a gas phase chromatography (PYE UNICAM PU 4500) using flame ionization and catharometer. The products were separated by SE-30 packed column of 1.5 m of length.

## 3. Results and discussion

### 3.1. Characterization of catalysts

#### 3.1.1. Infrared spectra

The spectra of the catalysts used are shown in Fig. 1. They have been assigned according to Refs. [28,29]. The main characteristic features of the Keggin structure are observed for both catalysts. The relevant frequencies ( $\text{cm}^{-1}$ ) and assignments observed, respectively, for  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$  were 1060, 1064 ( $\nu_{\text{as}}\text{P-O}_a$ ), 979, 961 ( $\nu_{\text{as}}\text{Mo-O}_d$ ), 895, 873 ( $\nu_a\text{Mo-O}_d\text{-Mo}$ ), and 798, 785 ( $\nu_{\text{as}}\text{Mo-O}_c\text{-Mo}$ ).

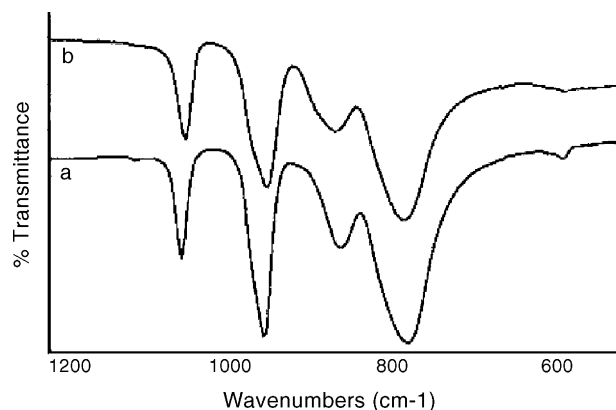


Fig. 1. IR spectra of samples at ambient conditions: (a)  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and (b)  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ .

### 3.1.2. Thermogravimetric analysis

The number of hydrogen atoms and water molecules in heteropolyanions were determined by thermogravimetric analysis through the loss of weight as soon as temperature is increased. For the heteropolyacid, it was found that there are two steps of mass loss. The first was observed between  $140$  and  $270^\circ\text{C}$  and it corresponds to loss of hydration water (13-hydrates). The second observed at  $350\text{--}450^\circ\text{C}$ , is the loss of structural water ( $1.5\text{H}_2\text{O}$ ). As for the copper salt, it was found one step of mass loss corresponding of 13-hydrates.

### 3.2. Catalytic reactivity

#### 3.2.1. Effect of time reaction

Fig. 2 shows the effect of the reaction time on the total activities. It is known from the figure that the total activities were rapidly stabilized (about 1 h) for the both catalysts,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , and  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ . During all the time of the catalytic test, the total activity of the heteropolyacid remained higher than that obtained with the copper salt. This result indicating that Brønsted acid sites seem to be favorable for  $\text{CH}_3\text{OH}$  activation is in agreement with that of Jiang et al. [30]. As for the

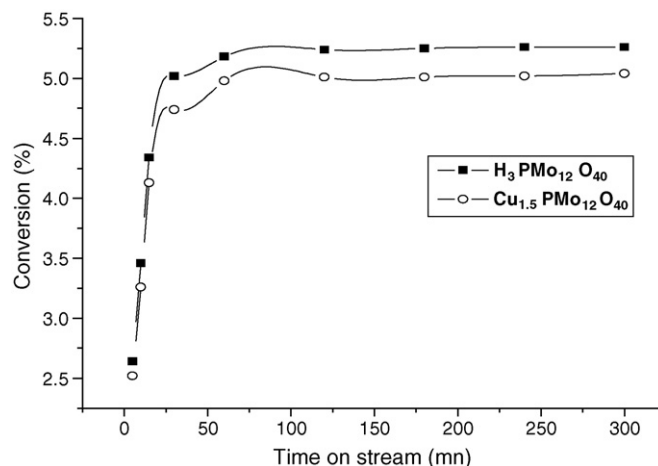


Fig. 2. Total activities vs. time reaction over  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$  (test conducted at  $40^\circ\text{C}$  with a sample weight of 0.25 g).

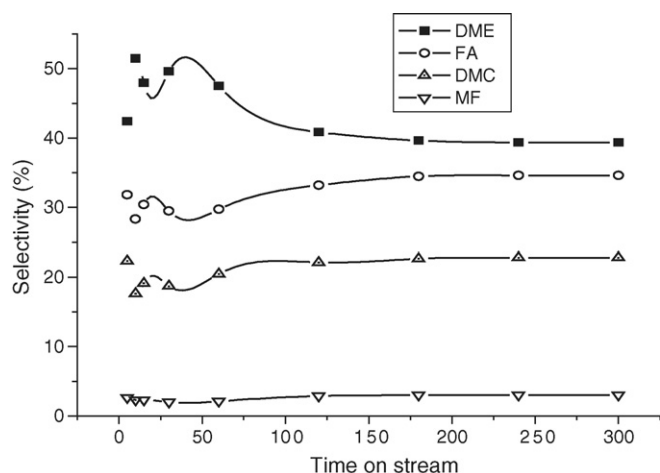


Fig. 3. Selectivities of the reaction products vs. time reaction over  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (test conducted at  $40^\circ\text{C}$  with a sample weight of 0.25 g).

selectivities (Figs. 3 and 4), and as expected, it was found that the DME was obtained with the high selectivity (39.6%) over  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ . The selectivity of formaldehyde (FA), dimethyl carbonate (DMC) and methyl formate (MF) obtained was 34.6, 22.8 and 3.0%, respectively. When the protons have been replaced by copper cations, the selectivities of FA and DMC increased to 52.8 and 28%, respectively, to the detriment of that of DME, which decreased to 16.3%. On the other hand, the selectivity of MF remained almost unchanged.

### 3.2.2. Effect of the catalyst amount

Fig. 5 shows that the total activities obtained for both catalysts have remarkably the same tendency; however, the acidic form of the heteropoly compound presents a slight higher conversion than its copper salt form.

The effect of the amount of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  on the selectivities of the products is shown in Fig. 6. It was found that when increasing the weight of the catalyst beyond 0.25 g, the selectivity of FA increased to the expense of DME and DMC due to further conversion of DME to FA as reported in the literature [31]. The selectivity of MF remained con-

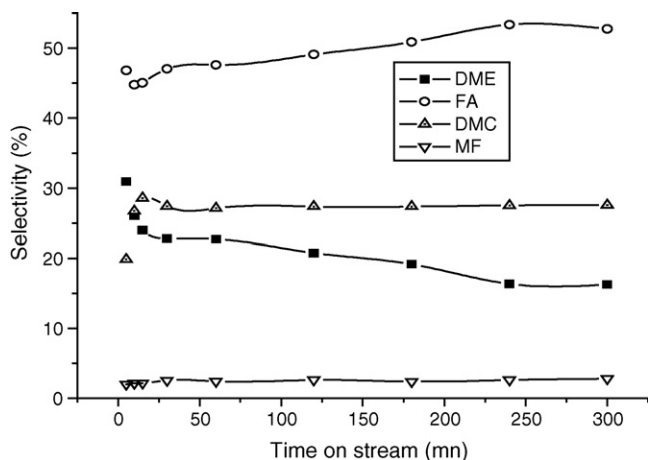


Fig. 4. Selectivities of the reaction products vs. time reaction over  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$  (test conducted at  $40^\circ\text{C}$  with a sample weight of 0.25 g).

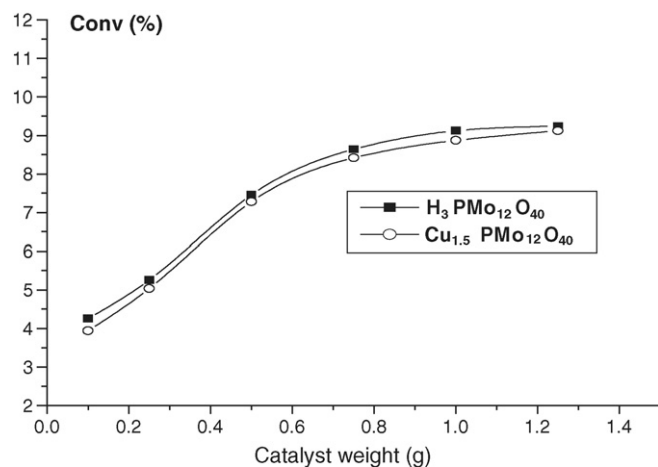


Fig. 5. Dependence of total activities on catalyst weight for  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$  (test conducted at  $40^\circ\text{C}$ ).

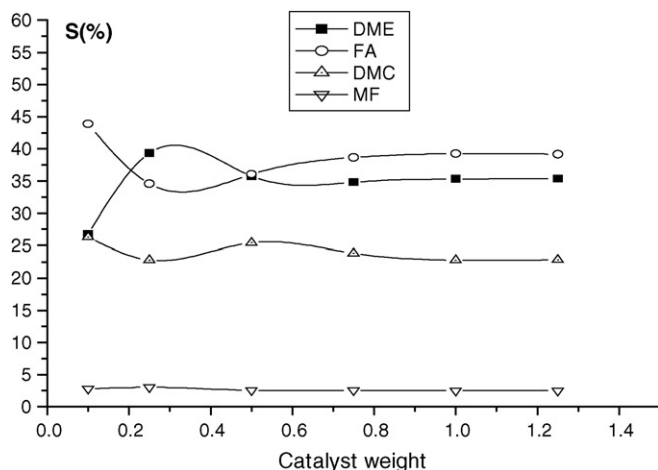


Fig. 6. Dependence of catalyst weight on the reaction product selectivities over  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  at  $40^\circ\text{C}$ .

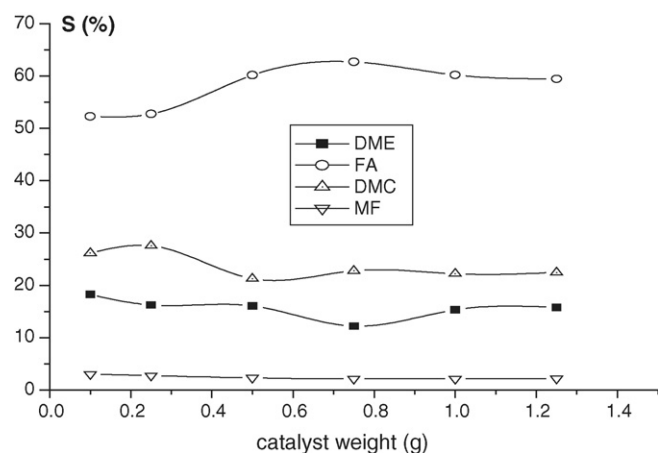


Fig. 7. Dependence of catalyst weight on the reaction product selectivities for  $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$  at  $40^\circ\text{C}$ .

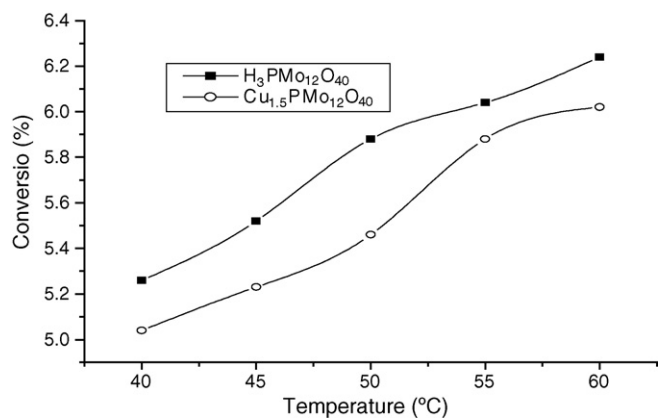


Fig. 8. Dependence of total activities on reaction temperature over H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> (catalyst weight of 0.25 g).

stant. As for Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> (Fig. 7), it was found that when the amount was increased beyond 0.25 g, the selectivity of FA increased (then remained stable) at the expense of DMC. The selectivity of MF remained also constant for this catalyst.

### 3.2.3. Effect of the reaction temperature

The effect of temperature on the total activities and selectivities were checked on 0.25 g weight samples for both catalysts. Fig. 8 shows that the total activity obtained with H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> remained higher than that obtained with Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> in all the range of temperature. As for selectivities (Figs. 9 and 10) it was observed that DMC selectivity decreases with temperature in favor of FA. In the case of Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> (Fig. 11), it was found that a lower reaction temperature is more favorable for DMC formation, and a maxima in the DMC formation was observed at 328 K. This result is in agreement with those reported in literature and with the thermodynamic calculation [30,32].

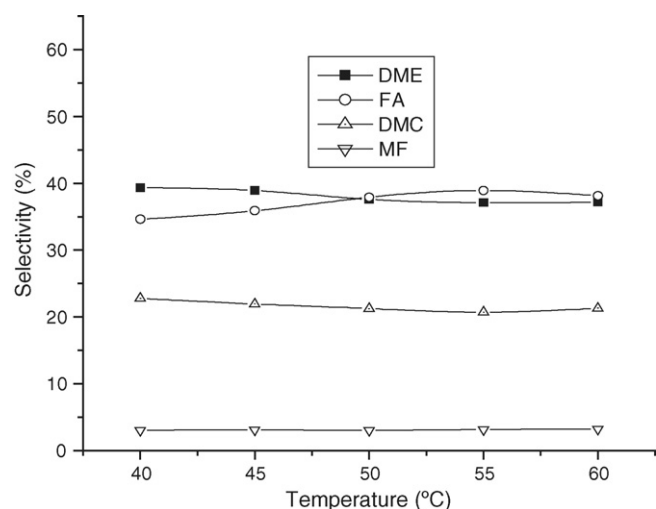


Fig. 9. Dependence of product selectivities on reaction temperature over H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (sample weight of 0.25 g).

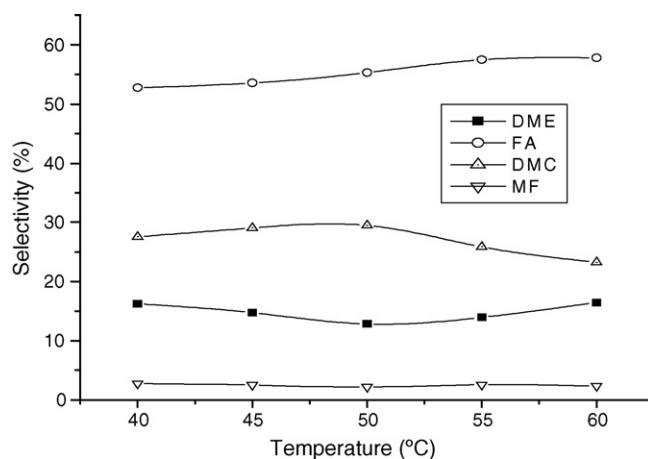


Fig. 10. Dependence of product selectivities on reaction temperature over Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> (sample weight of 0.25 g).

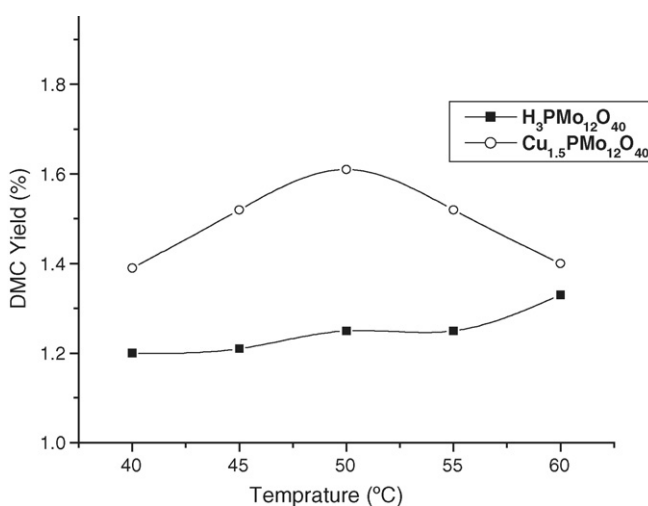


Fig. 11. Dependence of DMC yield on reaction temperature over H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> (sample weight of 0.25 g).

## 4. Conclusion

In the present study the effect of the Brønsted acid sites on the behavior of the conversion of the methanol in presence of CO<sub>2</sub> was investigated. The reactivity of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> was compared to that of Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>. The effects of the amount of the catalysts and temperature were examined.

When the protons of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> were replaced with the copper cations, the total activity decreased while the selectivities of FA and DMC increased to the detriment of that of DME. This result seems to indicate that Brønsted acid sites were more favorable for the CH<sub>3</sub>OH activation but unfavorable for the DMC formation. When the amount of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>, were increased beyond 0.5 g, the selectivity of FA increased in detriment of DME and DMC. The selectivity of MF remained constant for the both catalysts.

The influence of temperature on both catalysts indicates that H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> was slightly more active than Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> in all the range of temperatures but less selective in DMC. In the case of Cu<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>, it was found that a lower reaction tem-

perature is more favorable for DMC formation, and a maxima in the DMC formation was observed at 55 °C.

## References

- [1] S. Inoue, H. Koinuma, *Rev. Inorg. Chem.* 6 (1984) 291.
- [2] P. Braunstein, D. Matt, D. Nobel, *Chem. Rev.* 27 (1988) 747.
- [3] P.G. Jessop, T. Ikariya, R. Noyori, *Science* 269 (1995) 1065.
- [4] P.G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* 99 (1999) 475.
- [5] W. Leitner, *Coord. Chem. Rev.* 155 (1996) 257.
- [6] W. Leitner, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 2207.
- [7] D.J. Darensbourg, M.W. Holtcamp, G.E. Struck, M.S. Zimmer, S.A. Niezgodna, P. Rainey, J.B. Robertson, J.D. Drapper, J.H. Reibenspies, *J. Am. Chem. Soc.* 121 (1999) 107.
- [8] Y. Ono, *Appl. Catal. A* 155 (1997) 133.
- [9] A.A. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [10] S. Sakai, T. Fujinami, S. Furusawa, *Nippon Kagaku Kaishi* (1975) 1789.
- [11] J. Kizlink, I. Pastucha, *Collect. Czech. Chem. Commun.* 58 (1995) 225.
- [12] K. Tomishige, T. Furusawa, Y. Ikeda, M. Asadullah, K. Fujimoto, *Catal. Lett.* 76 (2001) 71.
- [13] J. Kizlink, I. Pastucha, *Collect. Czech. Chem. Commun.* 59 (1994) 2116.
- [14] T. Zhao, Y. Sun, *Fuel Process. Technol.* 62 (2000).
- [15] K. Tomishige, T. Sakai, Y. Ikeda, K. Fujimoto, *J. Catal.* 192 (2000) 355.
- [16] C.F. Li, S.H. Zhong, *Catal. Today* 82 (2003) 83–90.
- [17] U. Romano, R. Tesei, M.M. Mauri, P. Rebora, *Ind. Eng. Chem. Prod. Res. Dev.* 19 (1980) 386.
- [18] S.T. King, *J. Catal.* 161 (1996) 530.
- [19] M.Y. Lee, D.C. Park, *Stud. Sci. Catal.* 66 (1991) 631.
- [20] (a) M. Misono, in: H.F. Barry, P.C.H. Mitchell (Eds.), *Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum*, Climax Molybdenum Company, Ann Arbor, Michigan, 1982, p. 289;  
(b) M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269;  
(c) J.B. McMonagle, J.B. Moffat, *J. Catal.* 91 (1985) 132;  
(d) I.V. Kozhevnikov, *Russ. Chem. Rev.* 56 (1987) 811;  
(e) M. Misono, *Appl. Catal.* 64 (1990) 1.
- [21] C.L. Hill, C.M. Posser-McCarthy, *Coord. Chem. Rev.* 143 (1995) 407.
- [22] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 198.
- [23] H. Liu, E. Iglesia, *J. Catal.* 223 (2004) 161–169.
- [24] J.M. Tatibouet, *Appl. Catal.* 148 (1997) 213.
- [25] C.M. Sorensen, R.S. Weber, *J. Catal.* 142 (1993) 1.
- [26] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1994) 113.
- [27] C. Rocchiccioli-Deltcheff, A. Aouissi, M.M. Bettahar, S. Launay, M. Fournier, *J. Catal.* 164 (1996) 16.
- [28] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* 22 (1983) 207.
- [29] C. Rocchiccioli-Deltcheff, M. Fournier, *J. Chem. Soc. Faraday Trans.* 87 (24) (1991) 3919.
- [30] C. Jiang, Y. Guo, C. Wang, C. Hu, Y. Wu, E. Wang, *Appl. Catal.* 256 (2003) 203.
- [31] H. Liu, E. Iglesia, *J. Phys. Chem. B* 107 (2003) 10840.
- [32] T. Zhao, Y. Han, Y. Sun, *Fuel Process. Technol.* 62 (2000) 187.