Catalysis Letters Vol. 99, Nos. 3–4, February 2005 (© 2005)
DOI: 10.1007/s10562-005-2117-5

Comparative preparation of MoO_3/SiO_2 catalysts using conventional and slurry impregnation method and activity in transesterification of dimethy oxalate with phenol

Jinlong Gong, Xinbin Ma*, Xia Yang, Shengping Wang, Ning Gao and Dali Wang
[1]*Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China*

Received 23 March 2004; accepted 15 September 2004

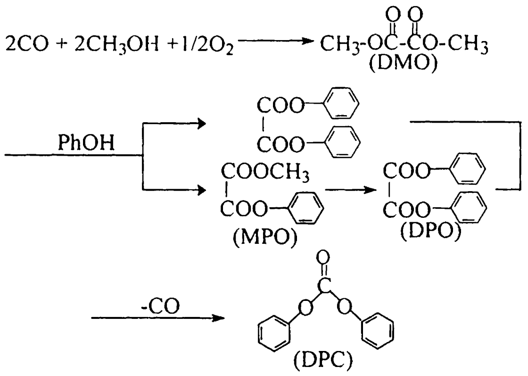
Silica-supported MoO_3 catalyst prepared by slurry impregnation method exhibits higher activity and dispersion capacity compared to the MoO_3/SiO_2 prepared conventionally. Slurry MoO_3/water is used instead of the solution ammonium heptamolybdate. Highly dispersed amorphous Mo catalysts are obtained, which is closely related the catalytic activities, without calcination, waste solutions, and calcining nitrogenous gases. The dependence of catalytic activity on Mo loading for the slurry prepared catalysts was similar to the samples prepared by the conventional impregnation method, indicating the slurry method is a simple and clean alternative to the conventional one.

KEY WORDS: diphenyl carbonate; diphenyl oxalate; methyl phenyl oxalate; transesterification; dimethyl oxalate; MoO_3/SiO_2 catalysts; slurry impregnation.

1. Introduction

In the current demand for the sustainable and environmentally benign processes, phosgene-free processes for preparing diphenyl carbonate (DPC), an important intermediate for polycarbonates synthesis, have been proposed to replace the conventional phosgene method [1,2]. Among these processes [3–13], transesterification of dimethyl oxalate (DMO) with phenol is an alternative that avoids the use of phosgene via a three-step synthesis of DPC (Scheme 1). Since raw materials such as carbon monoxide, phenol and oxygen are used as starting reactants [14], in the atom-economical [15] and environmental points of view, transesterification of DMO with phenol is a promising and possible route for DPC synthesis. A pilot plant test in DMO production has been completed by Ube Industries and the technology for large-scale commercial production has been established. And one of the possible applications of this process is to supply DMO for the production of DPC [16].

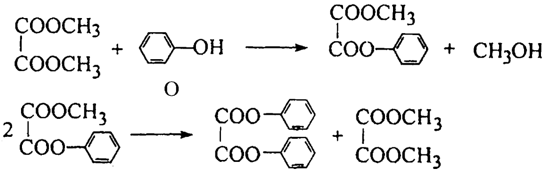
This method is effective because co-products of methanol and CO can be separated easily leading to breaking of reaction equilibrium, which can also be reusable in the DMO production via oxidative carbonylation of methanol, also as shown in Scheme 1.



(1)

Scheme 1.

For the synthesis of DPC from the transesterification of DMO with phenol, the decarbonylation of diphenyl oxalate (DPO) to produce DPC could be carried out easily over PPh_4Cl catalyst, and the yield of DPC may be up to 99.5% [17,18]. Furthermore, the synthesis of DPO from the transesterification of phenol with DMO follows 2-step reaction module consisting of the transesterification of phenol with phenol into methyl phenyl oxalate (MPO), and then the production of DPO via the disproportionation of MPO, as shown in the following reaction.



(2)

(3)

Reaction (2), (3).

The thermodynamic equilibrium constants of reaction (2) and (3) at 453 K are only 0.23 and 2.09×10^{-7}, respectively [19], as determined from thermodynamic calculations made with functional group contribution

---

*To whom correspondence should be addressed.
E-mail: xbma@tju.edu.cn

1011-372X/05/0200–0187/0 © 2005 Springer Science+Business Media, Inc.

method on liquid components. This indicates that the transesterification between DMO and phenol, especially for the disproportionation of MPO, is not favorable thermodynamically, which leads to the limitation in DPO yield.

Although recently promising results were published in literatures for the transesterification of DMO with phenol in homogenous conditions [20–22], the separation and recovery of the catalysts remains a critical item when applied to the industrial process. In addition, the catalytic efficiency, especially for selectivity to target product, is still far from the commercially feasible level. Thanks to these reasons, the development of active solid catalysts with excellent catalytic performance is highly desirable in view of regeneration and separation. However, to our best knowledge, few reports were known about the development of active heterogeneous catalysts for the reaction.

Recently, we, for the first time, reported that impregnation prepared MoO_3/SiO_2 was an effective heterogeneous catalyst for the transesterification of DMO with phenol [23]. The Mo species highly dispersion in the form of amorphism is more responsible than that of crystalline MoO_3 for the synthesis of MPO and DPO [24]. Therefore, it is crucial to promote the dispersion capacity of Mo species in order to improve catalytic activities. In the present work, the silica-supported molybdenum oxide catalysts were prepared by conventional impregnation (CI) and a new slurry impregnation (SI), respectively. In addition, their dispersion capacity and catalytic activity in transesterification of DMO with phenol were examined.

2. Experimental

2.1. Preparation of the catalysts

Commercial silica was used as the supported material. Prior to impregnation it was dried at 393 K for 2 h with the aim of being dehydrated. This treatment results in silica with a surface area of 231 m^2/g and average pore size of 80 Å, as measured with nitrogen adsorption.

2.1.1. Conventional impregnation

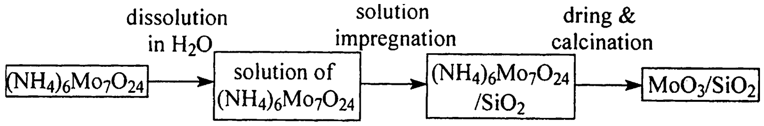
The silica-supported molybdenum oxide catalysts were prepared by impregnation with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ in excess of solution. For this purpose, 20 g of the silica support were impregnated with 50 mL of the salt solution, and water was removed in a rotary evaporator at 353 K until dryness. The impregnation sample was dried in an oven at 393 K overnight and then calcined in a muffle furnace at 823 K for 5 h. Molybdenum loadings were 4, 8 and 16 wt%, respectively. (The composition of molybdenum are expressed in weight percent and based on Mo content throughout the paper.). This catalyst will be named Mo/SiO_2 (CI) (Scheme 2(a)).

2.1.2. Slurry impregnation

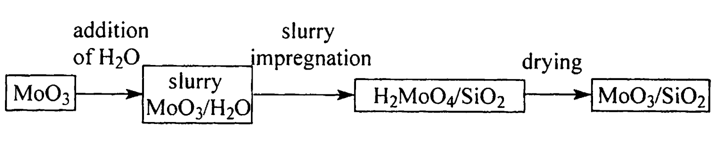
MoO_3 (+99.5%) was ground in an agate mortar before use. The mixture of the appropriate amount of MoO_3, water (the level of the liquid was about 5 mm above the layer of the support), and 20 g SiO_2 were prepared in a set of rotary flasks. For instant, the flask of 8 wt% Mo/SiO_2 sample content 2.73 MoO_3, 20 g of silica and 80 mL water. The mixture was heated under a rotary condenser to 368 K for 12 h (it was left standing at room temperature overnight). After impregnation, the whole mixture was dried in a muffle furnace at 433 K for 6 h and calcination was not necessary. This catalyst was classified as Mo/SiO_2 (SI) (Scheme 2(b)).

2.2. Characterization

The specific surface areas (S_{BET}, m^2 g^{-1}) of samples were determined on a constant volume adsorption apparatus (CHEMBET-3000) by the N_2 BET method at the liquid nitrogen temperature. X-ray powder diffraction (XRD) analysis were carried out on a Rigaku C/max-2500 diffractometer using graphite filtered Cu–Ka radiation ($\lambda = 1.5405$ Å) at 40 kV and 100 mA with a scanning rate of 8° min^{-1} from $2\theta = 5°$ to $2\theta = 80°$.



(a) Conventional solution impregnation



(b) Slurry impregnation

Scheme 2. Processes for catalyst preparation by slurry and conventional impregnation.

The XRD phases present in the samples were identified with the help of JCPDS Powder Data Files.

2.3. Catalytic test

The reaction was conducted in a 250 mL glass flask equipped with a thermometer, a distillation apparatus, and a stirrer under refluxing condition at atmosphere pressure. Especially, the top of distillation column was kept at 353 K by following through recycled water in order to remove methanol from the reaction system. By this means, the reaction equilibrium limitation in reaction (2) was broken and the reaction was accelerated to develop towards the desired direction. The reaction mixture contained 0.1 mol DMO, 0.5 mol phenol and catalyst. After the raw materials and catalyst were placed into the batch reactor, nitrogen gas was flowed at 30 SCCM to purge the air from the reaction system. After 10 min, nitrogen was stopped and the flask was heated at a rate of 8 K min^{-1}. The reaction was conducted at 453 K at an atmospheric pressure. Qualitative and quantitative analysis of reaction products and distillates were carried out on a HP 5890-HP5971MSD and a HP 5890 gas chromatograph equipped with a flame ionization detector (FID). An OV-101packed column was used to separate products for GC analysis. The products were mainly DPO, MPO, anisole (AN), and together with trace amounts of isomer products of anisole. The conversions were reported on the basis of the limiting reagent, DMO, and defined as the ratio of the moles of converted DMO to the moles of DMO fed initially to the reactor. The selectivity to MPO and DPO was defined as the moles of MPO and DPO produced per 100 mol of consumed DMO, and the yields of MPO and DPO were obtained from multiplication of DMO conversion by the selectivity to MPO and DPO.

3. Results and discussion

Usually, the supported MoO_3 catalyst was fabricated by conventional solution impregnation using ammonium heptamolybdate, AHM [$(NH_4)_6Mo_7O_{24}$], as a precursor. In this case, ammonia in AHM serves as a helping ion that is firstly added to the system and then removed from it by calcination. However, it was found that the use of the ammonia ion is not necessary and MoO_3 alone can be used as the impregnation compound to form highly dispersed amorphous Mo catalyst [25]. Slurry impregnation is a special case of equilibrium adsorption impregnation method (for review of the equilibrium adsorption method, see Refs. [26–28]). So, although the solubility of MoO_3 is low (0.1 g MoO_3 per 100 mL of water at room temperature), it is sufficient for gradual transport of molybdena species to the surface in pores. The dissolved species is adsorbed and another solid MoO_3 is dissolved. The mixture was heated under a rotary condenser to 95°C for 12 h and left standing at room temperature overnight. At the end of impregnation all molybdena is deposited; the original solid MoO_3 disappeared and the amount of molybdena present in dissolved form is negligible. The catalyst is dried at 160 °C and it is not necessary to calcinate.

The BET surface areas of MoO_3/SiO_2 catalysts prepared by the conventional impregnation and slurry impregnation methods are listed in table 1. Generally, the slurry MoO_3/SiO_2 catalysts exhibited larger S_{BET} than conventional ones, which could be rationalized by

Table 1

The BET surface area of MoO_3/SiO_2 catalysts prepared by the conventional impregnation and slurry impregnation methods.

Entry	Mo. Loading (wt%)	Preparation Method	BET Surface (m^2/g)
1	4	c.i.[a]	134
2	4	s.i.[b]	141
3	8	c.i.	129
4	8	s.i.	128
5	16	c.i.	59
6	16	s.i.	65

[a] c.i.: conventional impregnation.

[b] s.i.: slurry impregnation.

Table 2

Comparison of the activity of MoO_3/SiO_2 catalysts prepared by the conventional solution impregnation and new slurry impregnation method in transesterification of DMO and phenol[a]

Entry	Mo loading (wt%)	Preparation method	Conversion[b] (%)	Selectivity (%)			Yield (%)	
				An	MPO	DPO	MPO	DPO
1	4	c.i.[c]	44.4	0.8	84.3	14.9	37.4	6.6
2	4	s.i.[d]	46.1	0.2	82.7	14.8	38.1	6.8
3	8	c.i.	54.4	0.8	81.7	17.5	44.4	9.5
4	8	s.i.	57.8	0.4	81.8	17.8	47.3	10.3
5	14	c.i.	51.8	1.0	83.4	15.6	43.2	8.1
6	16	s.i.	54.6	0.7	84.2	15.1	46.0	8.2

[a] Reaction conditions:catalyst 1.8 g, phenol 0.5 mol, n(PhOH)/n(DMO) = 5.0, reaction time 2 h, reaction temperature 453 K.

[b] Based on DMO charged.

[c] c.i.: conventional impregnation.

[d] s.i.: slurry impregnation.MPO: methyl phenyl oxalate, DPO: dipheny oxalate, AN: anisole.

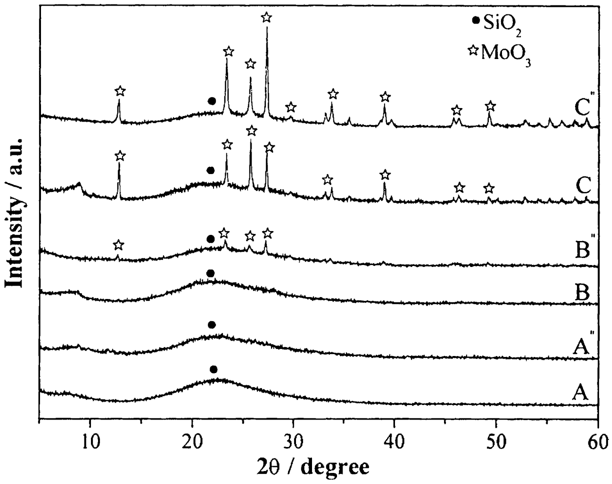


Figure 1. Comparison of the XRD patterns of MoO_3/SiO_2 catalysts with different Mo loading prepared by the slurry impregnation (SI) and conventional impregnation (CI) method. (A) 4%Mo/SiO_2 (SI); (B) 8%Mo/SiO_2(SI); (C) 16%Mo/SiO_2 (SI); (A'') 4%Mo/SiO_2(CI); (B'') 8%Mo/SiO_2(CI); (C'') 16%Mo/SiO_2(CI).

assuming that the high calcination temperature damaged the frame structure of SiO_2. It was observed that there were no apparent changes in the surface area of MoO_3/SiO_2 when Mo loading was below 8 wt%. The samples with the higher molybdenum content exhibited a lower surface area, may be, due to an increasing of the size of supported molybdenum particles or a plugging of the pores of the supports with molybdenum-oxide species.

The XRD patterns for silica-supported molybdenum oxide with a range of Mo loadings from 4, 8, to 16 wt%, prepared by slurry and conventional impregnation, respectively, are shown in figure 1. For MoO_3/SiO_2 catalyst prepared by slurry method, when Mo loading below 16 wt%, only diffraction peaks associated with the amorphous SiO_2 support are apparent and no characteristic peaks of MoO_3 formed. At higher loadings, the XRD patterns display a number of diffraction peaks observed for the corresponding bulk MoO_3 phase. However, for the samples prepared by the impregnation method, the characteristic peaks of crystalline MoO_3 appeared at 8 wt% Mo loading.

Why is the Mo species of slurry-prepared MoO_3/SiO_2 dispersed more highly on support surface than conventional impregnation one? We think the drying and calcination temperature is of great importance on catalyst's surface structure. High temperature calcination, e.g., 550 °C, for MoO_3/SiO_2 catalyst may lead to sintering or overlayer of the Mo species, as can be assumed from the fact that slurry impregnation without calcination can effectively increase dispersion capacity on silica support.

Comparisons of the activity of MoO_3/SiO_2 catalysts prepared by the conventional and slurry impregnation method were investigated and the results were summarized in table 1. Generally, although the selectivity to DPO was not very high, the intermediate, MPO, could be effectively converted to DPO by disproportionation reaction using suitable catalysts. Therefore, it was deemed that the target products were not only DPO but also MPO [22]. From the comparisons of the data in table 1, it was observed that the MPO and DPO yields and DMO conversion for slurry MoO_3/SiO_2 were higher than those for conventional one. Moreover, all MoO_3/SiO_2 catalysts can effectively catalyzed the transesterification of DMO with phenol with good total selectivities to MPO and DPO (above 99%) and only a trace amount of byproduct, anisole (below 1%), was detected. More interestingly, the activities of the MoO_3/SiO_2 catalysts prepared by conventional and slurry methods showed a homologous volcano profile with the highest catalytic performance at 8 wt% Mo loading, giving maximum DMO conversion of 54.4, 57.8%, respectively. Thereafter, the decreases of catalyst performance were observed with the appearance of MoO_3 crystalline phase. Detailed characterization for MoO_3/SiO_2 catalyst is conducting for better understanding of slurry-enhanced activity.

4. Conclusions

In the present work, we report the benefits brought by slurry impregnation methodology via comparing the catalytic performance of catalysts prepared by conventional impregnation. SiO_2-supported MoO_3 catalysts with different Mo content were tested in transesterification of DMO and phenol. Not only is slurry impregnation MoO_3/SiO_2 catalysts' performance for transesterification of DMO with phenol better conventional impregnation ones, but also calcination is not necessary and no waste. Solutions and calcining nitrogenous gases are formed and highly dispersed (Mo species) catalysts are obtained. Thus, the slurry impregnation method for preparation of MoO_3/SiO_2 catalysts is an environmentally friendly process and a simple, clean alternative to the conventional preparation using Solutions of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$. The present investigation will lead to a significant improvement in the catalyst preparation for the transesterification reaction.

Acknowledgments

The authors are grateful to National Natural Science Foundation of China (NSF) and Tianjin Science and Technology Committee (TSTC) of China for the financial support under projects 20276050 and 033103511.

References

[1] A.G. Shaikh and S. Sivaram, Chem. Rev. 96 (1996) 951.
[2] Y. Ono, Pure Appl. Chem. 68 (1996) 367.

[3] R. Kuwano, Y. Kondo and Y. Matsuyama, J. Am. Chem. Soc. 125 (2003) 12104.
[4] K.J.L. Linsen, J. Libens and P.A. Jacobs, Chem. Commun. (2002) 2728.
[5] W.B. Kim and J.S. Lee, J. Catal. 185 (1999) 307.
[6] A. Kawada, S. Mitamura and S. Kobayashi, J. Chem. Soc. Chem. Commun. 14 (1993) 1157.
[7] G. Barcelo, D. Grenouillat, J.P. Senet and G. Sennyey, Tetrahedron 46 (1990) 353.
[8] J.E. Hallgren and R.O. Mathews, J. Organomet. chem. 175 (1979) 135.
[9] Z.H. Fu and Y. Ono, J. Mol. Catal. A: Chem. 118 (1997) 293.
[10] H. Ishii, M. Goyal, M. Ueda, K. Takeuchi and M. Asai, Appl. Catal. A: Gen. 201 (2000) 101.
[11] H. Musso, Angew. Chem. Int. Ed. 2 (1963) 7.
[12] J.L. Gong, X.B. Ma and X. Yang, Catal. Commun. 5 (2004) 179.
[13] X.B. Ma, H.L. Guo and S.P. Wang, Fuel Process Technol. 83 (2003) 275.
[14] T. Matsuzaki and A. Nakamura, Catal. Surv. Jpn. 1 (1997) 77.
[15] B.M. Trost, Science 254 (1991) 1471.
[16] S. Vchtumi, K. Ataka and T. Matsuzaki, J. Organomet. Chem. 576 (1999) 279.
[17] H. Katsumasa, S. Ryoji and K. Kashiwagi, US Patent 5892089, (1998).
[18] S.P. Wang, X.B. Ma, Z.H. Li and G.H. Xu, Natural Gas Chem. Eng. (China) 27 (2002) 1.
[19] S.P. Wang, X.B. Ma, G.H. Li and J.L. Gong, J. Mol. Catal. A: Chem. In press.
[20] N. Keigo, T. Shuji, H. Katsumasa and S. Ryoji, US Patent 5834615, (1997).
[21] N. Keigo, T. Shuji and N. Yuki, US Patent 5811573, (1998).
[22] N. Keigo, T. Shuji, H. Katsumasa, S. Ryoji, S. Akinori and W. Katsutoshi, US Patent 5922827, (1999).
[23] J.L. Gong, X.B. Ma and S.P. Wang, J. Mol. Catal. A: Chem. 207 (2004) 215.
[24] X.B. Ma, J.L. Gong and S.P. Wang, Catal. Commun. 5 (2004) 101.
[25] M. Zdrail, Catal. Today 65 (2001) 301.
[26] Y.C. Xie and Y.Q. Tang, Adv. Catal. 37 (1990) 1.
[27] A. Lycourghiotis, Stud. Surf. Sci. Catal. 91 (1995) 95.
[28] E. Hillerov, H. Morishige, K. Inamura and M. Zdražil, Appl. Catal. A: Gen. 156 (1997) 1.