The Effect of Catalyst Preparation on the Activity of MoO₃–SiO₂ Catalyst in Transesterification of Diethyl Oxalate¹

L. Bian^{*a*, *b*}, S. P. Wang^{*a*, *}, and X. B. Ma^{*a*}

^aKey Lab for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University; Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072 P.R. China

^bCollege of Science, Hebei University of Engineeing, Handan, 056038 P.R. China

**e-mail: spwang@tju.edu.cn* Received December 10, 2013

Abstract—Transesterification of diethyl oxalate (DEO) with phenol over MoO_3 -SiO₂ catalysts prepared by the sol-gel technique (MoO₃-SiO₂ (SG)) and the impregnation method (MoO₃-SiO₂ (I)) was conducted to produce diphenyl oxalate (DPO), which can be used as a precursor for manufacturing diphenyl carbonate (DPC). The sample MoO_3 -SiO₂ (SG) containing 12 wt % of MoO_3 showed the best performance with 71.0% conversion of DEO and 32.0% selectivity to DPO. Compared to MoO₃-SiO₂ (I), improvements in the DEO conversion and DPO selectivity with MoO₃-SiO₂ (SG) were 16.1 and 7%, respectively. Crystal structure and phase composition of MoO_3 -SiO₂ (I) and MoO_3 -SiO₂ (SG) catalysts with varying MoO₃ contents were investigated. The sample MoO_3 -SiO₂ (SG) with a similar chemical composition to MoO_3 -SiO₂ (I) has a larger specific surface area, indicating that the active component is well dispersed on the surface of the MoO₃-SiO₂ (SG) catalysts. Results of XRD and XPS measurements suggest a high degree of dispersion of MoO₃-SiO₂ (SG) catalysts that can account for an increase in DEO conversion and DPO selectivity. Coordinately unsaturated MoO₃ species play a significant role in the catalytic performance of MoO₃-SiO₂ (SG) catalysts in transesterification of DEO with phenol. In addition, IR measurements of pyridine adsorption and NH_3 -TPD data indicate that the amount of acid sites on the surface of MoO₃-SiO₂ (SG) exceeds that found for the surface of MoO_3 -SiO₂ (I). An enhanced concentration of surface MoO_3 species in tetrahedral coordination coupled with the presence of weak Lewis acid sites appear to be the main reason why MoO_3-SiO_2 (SG) catalysts are superior to the MoO_3 -SiO₂ (I) system.

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Polycarbonates (PCs) are important engineering thermoplastics with excellent mechanical, optical as well as electrical and heat resistant properties. Therefore, they have been used in many fields as the substitutes of glass and metals. A conventional method for PCs synthesis is the interfacial polycondensation of bisphenol-A (BPA) with the highly toxic phosgene in the presence of bases [1]. To meet increasing demand for safe and environmentally friendly processes for PCs synthesis an alternative route was recently proposed. A process involves the synthesis of diphenyl carbonate (DPC) followed by the transesterification between DPC and bisphenol–A [2]. In this scheme, no toxic solvents are used and the by-product phenol could be recycled.

However, DPC is prepared commercially by the reaction of phenol and phosgene in the presence of bases such as sodium hydroxide [3]. Again, the obvious drawback of this traditional process for DPC is the use of phosgene. Therefore, in order to produce PCs without social consequences of pollution, the key

technology is the synthesis of DPC via a green process. Phosgene-free processes for DPC synthesis have been proposed to replace the conventional phosgene process [4-11].

A promising approach is the transesterification of dimethyl oxalate (**DMO**) with phenol to prepare diphenyl oxalate (**DPO**), followed by the decarbonylation of DPO to DPC [12, 13]. There are many reports about the ester exchange between DMO and phenol to produce DPO [10, 11, 14–19], followed by the decarbonylation of DPO to produce DPC. However, there are few reports [20] describing the preparation of DPO by the transesterification of diethyl oxalate (**DEO**) with phenol followed by the decarbonylation of DPO.

Due to low equilibrium constants a two-step production of DPO was proposed for the transesterification of DEO with phenol [21]. The first step is the formation of ethyl phenyl oxalate (**EPO**) and the second step is the production of DPO *via* disproportionation of EPO:

¹ The article is published in the original.

$$\begin{array}{c} \text{COOCH}_2\text{CH}_3 + \swarrow - \text{OH} \rightleftharpoons \stackrel{\text{COOCH}_2\text{CH}_3}{\leftarrow} + \text{CH}_3\text{CH}_2\text{OH} \end{array} (I) \\ \text{COOCH}_2\text{CH}_3 + \swarrow \stackrel{\text{COO}}{\leftarrow} \stackrel{\text{COOC}}{\leftarrow} + \stackrel{\text{COOCH}_2\text{CH}_3}{\leftarrow} \\ \begin{array}{c} \text{COOCH}_2\text{CH}_3 \\ \text{COO} - \swarrow \stackrel{\text{COO}}{\leftarrow} \stackrel{\text{COO}}{\leftarrow} + \stackrel{\text{COOCH}_2\text{CH}_3}{\leftarrow} \\ \begin{array}{c} \text{COOCH}_2\text{CH}_3 \\ \text{COOCH}_2\text{CH}_3 \end{array} (II) \end{array}$$

Safe operation and low corrosion effects on the equipment are the main factors in determining the compatibility of this process with the requirements of the green chemistry. Moreover, because DEO is a liquid at room temperature it can be easy feed-in and in addition it is cheaper than DMO.

Generally, the transesterification to DPO is carried out in the liquid phase using homogeneous catalysts such as Lewis acids or soluble organic Pb, Sn, or Ti compounds [12, 13]. However, in these homogeneous transesterification systems, the separation of the catalysts from the products is complicated under industrial conditions. Therefore, to make the regeneration and separation easier, the development of active solid catalysts is highly desirable. Molybdenum oxide has found a wide application in the industrial processes such as dehydration, dehydrogenation, and isomerization [22-25]. Earlier the reactivities of supported MoO₃ catalysts in the transesterification of dimethyl oxalate with phenol were described [18]. In this work, we present results of the investigation on the synthesis of DPO from the transesterification of DEO with phenol over MoO_3 -SiO₂ catalysts prepared by different methods. By comparing the catalytic performance of the catalyst prepared by the sol-gel method (MoO₃- SiO_2 (SG)) with the catalysts prepared by the impregnation method (MoO_3 -SiO₂ (I)) an attempt is made to illustrate advantages of using the sol-gel technique.

EXPERIMENTAL

Catalyst Preparation

The sol-gel method. The sol-gel method was used to prepare a series of MoO_3 -SiO₂ (SG) catalysts with the composition ranging from 1 to 24 wt % MoO_3 . Ethyl silicate (**TEOS**) and ammonium molybdate (**AHM**) were used as precursors of SiO₂ and MoO_3 respectively. The calculated amounts of AHM and TEOS were dissolved in 30 mL of distilled water and 60 mL of ethanol respectively. AHM solution was then added drop-wise into the TEOS ethanol solution with stirring. The sol color turned from slight green to dark green, and a dark green gel was formed consequently. The gel was dried under atmosphere of nitrogen for 24 h, and then ground. The catalysts were prepared by drying the pellets in oven at 393 K for 4 h and calcining dry pellets at 823 K for 5 h in a muffle furnace.

The impregnation method. A series of MoO_3 -SiO₂ (I) catalysts with the composition ranging from 1 to 24 wt % of MoO₃ was prepared by the impregnation

method. As a typical procedure, the dried SiO_2 support was contacted with an aqueous solution of ammonium molybdate of appropriate concentration with stirring. The support immersed in a solution was then stored at ambient temperature in nitrogen for 48 h to ensure that molybdenum compound is incorporated and can diffuse through the surface of SiO₂. The pretreated catalysts were dried in an oven for 4 h at 393 K and calcined in a muffle furnace at 823 K for 5 h.

Transesterification of Diethyl Oxalate with Phenol

Transesterification of DEO with phenol was carried out in a three-necked flask (250 mL) equipped with a distillation column and a thermometer to monitor and control the reaction temperature. Particularly, the temperature in the top of distillation column was kept at 363 K by recycling hot water in order to remove ethanol from the reaction system. Using this method the reaction equilibrium limitation for reaction (I) was avoided and the reaction was accelerated to proceed towards the desired direction. The reaction mixture contained 0.1 mole of DEO, 0.3 mole of phenol and 1.8 g of the catalyst. After raw materials and catalyst were placed into a batch reactor, the reactor system was purged in 30 SCCM nitrogen to displace air. The feed of nitrogen was stopped after 10 min and the three-necked flask was heated at a rate of 10 K/min. The reaction was conducted at 453 K and normal pressure.

Qualitative analysis of the reaction products and the distillates were conducted on a GC–MS (Agilent HP5890–HP5971MSD) equipped with an HP-5 30 m capillary column. Quantitative analysis of the reaction mixture was carried out using an HP 4890 (with a capillary column HP-INNOWAX, 30 m length, 0.32 mm i.d. and 0.25 μ m film thickness) with a flame ionization detector. The products were composed of ethyl phenyl oxalate and diphenyl oxalate and alcohol emerged as distillate.

Catalyst Characterization

The BET surface area was determined using a volumetric adsorption unit (CHEMBET-3000) by low temperature adsorption of nitrogen.

X-ray diffraction (**XRD**) was performed on a Rigaku C/max-2500 diffractometer provided with graphite monochromator employing nickel-filtered Cu K_{α} radiation ($\lambda = 1.5405$ Å) at 40 kV and 100 mA.

The samples were scanned at a rate of $8^{\circ}/\text{min}$ over the $5^{\circ} \le 2\theta < 80^{\circ}$ range. The diffractograms were compared with JCPDS–ICDD references for identification purposes.

Surface composition and structure of catalysts were studied by X-ray photoelectron spectroscopy (**XPS**). The measurements were performed using a Perkin-Elmer PHI 1600 ESCA spectrometer with Mg K_{α} radiation (1253.6 eV) as incident beam. The samples were mounted in a specimen holder via double-sided adhesive tape. Spectra were recorded in steps of 0.15 eV. The C1s (284.5 eV) was used as an internal standard to calibrate the binding energies. An estimated error of ± 0.1 eV can be assumed for all the measurements. The scanning of the spectra was done at pressures less than 10^{-8} Torr.

IR measurements of adsorbed pyridine were carried out on a Bruker Vector 22 FT-IR spectrometer. The scanning range was from 4000 to 500 cm^{-1} and the resolution was 4 cm⁻¹. The sample powder was pressed into a self-supporting wafer. Prior to each experiment, the catalysts were evacuated (1 Pa) at 693 K for 1.5 h. After the samples were cooled to 333 K, large portions of pyridine were admitted to saturate the catalysts. Subsequently, the samples were out-gassed for 0.5 h at 333 K and the spectra were recorded.

 NH_3 -TPD spectra were recorded using a Micromeritics Co. model 2910 chemical adsorption instrument. The catalysts were heated to 393 K in flowing Ar for 1 h, and then cooled to room temperature. Adsorption of NH_3 was carried out at 323 K for the time period needed to saturate catalysts. After saturation was achieved, the reactor was switched from NH_3 to Ar and the catalysts were heated to 873 K at a rate of 10 K/min.

RESULTS AND DISCUSSION

Performances of Catalysts

The results of DEO conversions, selectivities and yields of DPO over MoO₃-SiO₂ (SG) and MoO₃- SiO_2 (I) are demonstrated in Tables 1 and 2, respectively. For the MoO_3 -SiO₂ (SG) catalysts, the conversion of DEO, selectivity and yield of DPO were improved steadily from 37.8, 15.4, and 5.8% to 71.0, 32.0, and 22.7% with MoO₃ contents increasing from 1 to 12 wt %, respectively. Thereafter, all parameters characterizing the reactivity deteriorated, indicating that MoO_3 -SiO₂ (SG) with 12 wt % MoO₃ showed the best catalytic performance for the transesterification of DEO with phenol. At the same time, the behavior of MoO₃-SiO₂ (I) was tested and it was found that trends pertinent to catalytic properties of MoO_3 -SiO₂ (I) were similar to that of MoO_3 -SiO₂ (SG). The highest DEO conversion, DPO selectivity and yield (54.9, 25.0 and 13.7% respectively) were found with 6 wt % MoO_3 -SiO₂ (I) catalysts. It seems that reactivity of MoO₃-SiO₂ (SG) catalysts was

Table 1. Catalytic activities of MoO ₃ –SiO ₂ (SG) catalys	sts
with different content of MoO ₃ prepared by the sol-g	gel
method in the transesterification of DEO with phenol	

MoO ₃ contents (wt %)	Conver- sion (%)	Selectivity (%)		Yield (%)	
	DEO	DPO	EPO	DPO	EPO
1	37.8	15.4	84.6	5.8	32.0
3	55.2	26.8	73.2	14.8	40.4
6	61.6	26.5	73.5	16.3	45.3
12	71.0	32.0	68.0	22.7	48.3
24	70.8	19.4	80.6	13.7	57.1

Reaction conditions: phenol 0.3 mol, DEO 0.1 mol, catalyst 1.8 g, reflux temperature 363 K, reaction temperature 453 K, reaction time 3 h.

Table 2. Catalytic activities of MoO_3 -SiO₂ (I) catalysts with different content of MoO_3 prepared by the impregnation method in the transesterification of DEO with phenol

MoO ₃ DEO		Selectiv	vity (%)	Yield (%)		
(wt %)	sion (%)	DPO	EPO	DPO	EPO	
1	32.6	18.8	81.2	6.1	26.5	
3	53.2	24.2	75.8	12.9	40.3	
6	54.9	25.0	75.0	13.7	41.2	
12	54.8	18.1	81.9	9.9	44.9	
24	44.5	13.7	86.3	6.1	38.4	

Reaction conditions: phenol 0.3 mol, DEO 0.1 mol, catalyst 1.8 g, reflux temperature 363 K, reaction temperature 453 K, reaction time 3 h.

Table 3. Specific surface area of MoO_3 -SiO₂ catalysts prepared by sol-gel and impregnation methods

MoO ₃ contents (wt %)	1	3	6	12	24
MoO_3 -SiO ₂ (SG) (m ² /g)	223.9	191.8	157.1	131.1	95.3
MoO_3 -SiO ₂ (I) (m ² /g)	155.1	148.0	134.3	99.0	59.1

greatly improved compared with that of MoO_3 -SiO₂ (I). It can be thus inferred that in terms of activity in transesterification MoO_3 -SiO₂ (SG) was superior to MoO_3 -SiO₂ (I).

Specific Surface Area Measurements

The specific surface area of molybdenum oxide catalysts prepared by sol–gel and the impregnation methods is shown in Table 3. The specific surface area of MoO_3 –SiO₂ (SG) catalysts decreased gradually from 223.9 to 95.3 m²/g as the content of MoO_3 increased from 1 to 24 wt %. The similar trend was observed for MoO_3 –SiO₂ (I) catalysts prepared by the impregnation method. However, for the catalysts with comparable MoO_3 content, the specific surface area of





Fig. 1. XRD patterns of MoO_3 -SiO₂ (SG) catalysts with different content of MoO_3 prepared by the sol-gel method: 1 (*a*), 3 (*b*), 6 (*c*), 12 (*d*), 24 wt % (*e*).

 MoO_3 -SiO₂ (SG) was much larger than that of MoO_3 -SiO₂ (I), suggesting that the active component in the MoO_3 -SiO₂ (SG) catalysts has a higher degree of dispersion than that in the MoO_3 -SiO₂ (I) catalysts.

XRD Measurements

Structure and chemical state of Mo species in MoO_3 -SiO₂ (SG) and MoO_3 -SiO₂ (I) with various MoO₃ content were investigated by XRD (Figs. 1, 2). The MoO₃ phase could be detected by XRD only in MoO₃-SiO₂ (SG) samples with a MoO₃ content above 12 wt %, indicating that in the samples with a lower MoO₃ molybdenum oxide occurs as a finely dispersed species. Strong diffraction peaks could be detected at a loading of 24 wt %, indicating the formation of crystalline MoO₃. However, as shown in Fig. 2, the diffraction peaks corresponding to MoO₃ were observed in the 12 wt % MoO₃-SiO₂ (I) catalysts prepared by the impregnation method. These observations provide further evidence that the extent of dispersion of the active components in MoO₃-SiO₂ (SG) catalysts is higher than that in MoO_3 -SiO₂ (I). Zhao et al. proposed [26] that there are two kinds of surface MoO₃ species on SiO₂ support. The hexavalent Mo cation can occur in oxygen coordinations 4 or 6. In the amorphous MoO₃ predominant coordination is tetrahedral whereas in the crystalline MoO₃ molybdenum oxide adopts octahedral coordination. The surface MoO₃ species in tetrahedral surrounding has lower oxygen coordination than the "coordinately unsaturated" bulk MoO₃ in octahedral coordination. The coordination sphere of a surface atom can be completed by adsorbed molecules, which can also be acti-



Fig. 2. XRD patterns of MoO_3 -SiO₂ (I) catalyses with different content of MoO_3 prepared by the impregnation method: 1 (*a*), 3 (*b*), 6 (*c*), 12 (*d*), 24 wt % (*e*).

vated for catalytic transformations [27, 28]. Accordingly, the surface MoO_3 in tetrahedral coordination had a higher catalytic performance than the MoO_3 in octahedral coordination. The improvement in catalytic performance observed when MoO_3 content increased from 1 to 12 wt % for MoO_3 –SiO₂ (SG) and from 1 to 6 wt % for MoO_3 –SiO₂ (I), respectively, may be caused by the increasing fraction of amorphous MoO_3 . By contrast, the appearance of crystalline MoO_3 on the catalyst surface brings about deterioration effects on DEO conversion and DPO selectivity. The reason may lie in the reduction of the surface species in tetrahedral coordination. Therefore, the coordinately unsaturated MoO_3 plays a significant role in the catalytic transesterification of DEO with phenol.

X-Ray Photoelectron Spectroscopy

In order to obtain more detailed information regarding the structure of the surface and dispersion of the Mo species of the catalysts for both preparation methods, MoO₃-SiO₂ (SG) and MoO₃-SiO₂ (I) catalysts (12 wt %) were characterized by XPS. The O1s spectra of MoO₃-SiO₂ (SG) and MoO₃-SiO₂ (I) catalysts (12 wt %) are shown in Fig. 3. It can be noticed that the O1s XPS spectrum of MoO_3 -SiO₂ (I) catalyst was deconvolved to three binding energy profiles of 530.5, 528.9, and 532.8 eV, which can be ascribed to Mo-O-Si, Mo-O and Si-O-Si, respectively [29]. On the other hand, the deconvolution procedure of the O1s XPS spectrum of the MoO₃-SiO₂ (SG) catalyst yielded only two binding energy profiles, corresponding to MoO-Si and Si-O-Si. In other words, no binding energy profile of 528.9 eV attributable to Mo-O was observed. This result suggests that ammo-



Fig. 3. O1s XPS spectra of MoO_3 -SiO₂ (SG) and MoO_3 -SiO₂ (I) catalysts (12 wt % of MoO_3).

nia molybdate as molybdenum source and ethyl silicate as silica source were adequately dispersed during the process of the catalyst preparation by sol–gel. It can be concluded that molybdenum ions on the surface of $12\%MoO_3$ –SiO₂ (SG) catalyst occur in Mo– O–Si rather than in Mo–O species. Combined with the results of XRD shown in Fig. 1 these data suggest that MoO₃ particles can not be found in the 12 wt % MoO₃–SiO₂ (SG) catalyst, indicating that the high degree of dispersion of MoO₃ in MoO₃–SiO₂ (SG) catalysts. On the other hand, XRD patterns and the O1s XPS spectra of MoO₃–SiO₂ (I) provide evidence



Fig. 4. IR spectra of pyridine absorbed on MoO_3 -SiO₂ (SG) catalysts with different content of MoO_3 : 1 (*a*), 3 (*b*), 6 (*c*), 12 (*d*), 24 wt % (*e*).

of the formation of crystalline MoO_3 in the 12 wt % MoO_3 -SiO₂ (I). It seems that a higher extent of dispersion of the active components in the 12 wt % MoO_3 -SiO₂ (SG) compared to that found for the 12 wt % MoO_3 -SiO₂ (I), results in improved DEO conversion and DPO selectivity.

IR Measurements of Adsorbed Pyridine

IR measurements of adsorbed pyridine were performed to determine the nature of acidic sites (Lewis and Brönsted) on the surface of the MoO₂-SiO₂ catalysts. Figures 4 and 5 show IR spectra of pyridine adsorbed on MoO₃-SiO₂ (SG) and MoO₃-SiO₂ (I) catalysts, respectively. For all samples three absorption bands at 1490, 1445 and 1600 cm⁻¹ were detected. MoO_3 -SiO₂ (SG) catalysts exhibited also the band at 1540 cm⁻¹. Absorption frequencies of 1445 and 1600 cm⁻¹ correspond to pyridine chemisorbed on the Lewis acid sites, while the absorption band at 1540 cm⁻¹ is indicative of Brönsted acidity. The band at 1490 cm⁻¹ can be attributed to the presence of Lewis and Brönsted acid sites. The spectra in Figs. 4 and 5 suggest that the absorption bands detected on the surface of MoO₃-SiO₂ (SG) and MoO₃-SiO₂ (I) were predominantly caused by the interaction of pyridine with Lewis acid sites. It can be therefore inferred that the Lewis acid sites were responsible for the formation of DPO in the transesterification of DEO and phenol. Using IR measurements of adsorbed pyridine, the amounts of acid sites in the MoO₃-SiO₂ (SG) and the MoO₃-SiO₂ (I) catalysts with different content of MoO₃ were calculated (Tables 4 and 5 respectively). It can be readily seen that the amount of acid sites decreases with the increasing MoO₃ content on both

Absorbance, arb. units



Fig. 5. IR spectra of pyridine absorbed on MoO_3 -SiO₂ (I) catalysts with different content of MoO_3 : 1 (*a*), 3 (*b*), 6 (*c*), 12 (*d*), 24 wt % (*e*).

 MoO_3 -SiO₂ (SG) and MoO_3 -SiO₂ (I) samples. Notably, a marked reduction of the amount of acid sites can be observed for the samples with an enhanced concentration of MoO_3 , resulting in a poorer catalytic performance of the catalysts. Comparing the samples with similar chemical compositions the conclusion can be made the amount of acid sites in MoO_3 -SiO₂ (SG) exceeds that of MoO_3 -SiO₂ (I). Accordingly, the catalytic performance of MoO_3 -SiO₂ (SG) is superior to MoO_3 -SiO₂ (I).

NH₃-TPD Measurements

 NH_3 -TPD characterizations of MoO_3 -SiO₂ (SG) and MoO_3 -SiO₂ (I) catalysts with different contents of MoO_3 were conducted. The results showed that the ammonia is desorbed at low temperatures, implying that only weak acid sites exist on the surface of all catalysts. Therefore, weak Lewis acidity is the source of the active sites in the transesterification between DEO and phenol. However, amounts of NH_3 desorbed from MoO_3 -SiO₂ (SG) and MoO_3 -SiO₂ (I) catalysts with varying MoO_3 contents are different, as illustrated in Figs. 6 and 7, respectively. Amounts of NH_3 desorbed

Table 4. Acidity of MoO_3 -SiO₂ (SG) catalysts with different MoO_3 contents

MoO ₃ -SiO ₂ contents (wt %)	1	3	6	12	24
Number of acid sites*	1096.7	1009.8	909.7	891.3	500.4

* Calculated from the ratio of the integrated area of IR absorption peak to sample mass.

Amount of desorbed NH₃ (mmol NH₃/g catalyst)



Fig. 6. Amount of NH_3 desorbed from MoO_3 -SiO₂ (SG) catalysts with different content of MoO_3 .

from MoO_3 -SiO₂ (SG) samples are higher than those removed from MoO_3 -SiO₂ (I) catalysts. As a result, MoO_3 -SiO₂ (SG) samples were more active as catalysts than MoO_3 -SiO₂ (I).

Comparing the data collected in Tables 4 and 5, it can be readily recognized that the number of acid sites is not consistent with amounts of NH_3 desorbed. As a possible reason a large size of pyridine molecule can be evoked that prevents diffusion of the adsorbate inside the pores. Correspondingly, using pyridine as probe molecule only acid sites on the outer surface of catalysts could be detected. On the other hand, smaller NH_3 molecules could move freely inside the catalysts and the amount of acid sites on the surface and in internal pores of catalysts could be measured. It is therefore conceivably that the amounts of NH_3 and pyridine desorbed are different.

Amount of desorbed NH₃ (mmol NH₃/g catalyst)



Fig. 7. Amount of NH_3 desorbed from MoO_3 -SiO₂ (I) catalysts with different content of MoO_3 .

KINETICS AND CATALYSIS Vol. 55 No. 6 2014

Table 5. Acidity of MoO_3 -SiO₂ (I) catalysts with different MoO₃ contents

MoO ₃ -SiO ₂ (I) (wt %)	1	3	6	12	24
Number of acid sites*	627.6	528.4	456.2	413.3	361.1

* Calculated from the ratio of the integrated area of IR absorption peak to sample mass.

CONCLUSIONS

Catalytic activities of MoO₃–SiO₂ (SG) catalysts in the transesterification of DEO with phenol are higher than those found for MoO_3 -SiO₂ (I). The MoO₃-SiO₂ (SG) catalyst containing 12 wt % of MoO_3 showed the best performance with 71.0% conversion of DEO and 32.0% selectivity to DPO. Specific surface area measurements demonstrated that MoO₃-SiO₂ (SG) exhibited the largest specific surface area. XRD characterization showed that MoO₃ occurred in a finely dispersed state in the MoO₃-SiO₂ (SG) samples with MoO_3 content lower than 12 wt %. In the samples with the concentration of molybdenum oxide exceeding 12 wt % bulk crystalline MoO₃ was found. By contrast, MoO₃ crystals were found on MoO_3 -SiO₂ (I) with 12 wt % of MoO₃. In good agreement with the results of XRD analysis, XPS results indicated that no binding energy profile attributable to Mo–O was observed at 12 wt % MoO₃–SiO₂ (SG). MoO₃-SiO₂ (SG) catalysts containing an enhanced concentration of surface MoO₃ species in tetrahedral coordination had a better catalytic performance than MoO₃-SiO₂ (I) samples. IR analysis of absorbed pyridine and NH₃-TPD verified that MoO₃-SiO₂ (SG) catalysts have significantly higher total concentration of acid sites than MoO₃-SiO₂ (I) samples. Therefore, the coordinately unsaturated MoO₃ species played a key role in the transesterification of DEO with phenol. The MoO_3 -SiO₂ (SG) catalysts are much more active than the MoO_3 -SiO₂ (I) samples and the reason for the different catalytic behavior may be sought in increased concentrations of surface MoO₃ species in tetrahedral surrounding and weak Lewis acid sites in catalysts prepared by the sol-gel method. It is the interaction of surface MoO₃ species with Lewis acid sites that provides the improved performance of the MoO_3 -SiO₂ (SG) catalysts.

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