Article

Comparative Study on the Catalytic Properties of Amino-Functionalized Silica Materials for the Transesterification of Dimethyl Oxalate with Phenol

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Uma série de materiais híbridos mesoporos MCM-41, contendo diferentes grupos amino (como 3-aminopropila (AP-), (2-aminoetilamino)propila (AAP-), ou [2-(2-aminoetilamino) etilamino]propila (AEP-)) foi preparada pelo método de pós-enxertia e caracterizada por difração de raio X de pó (XRD), adsorção de N_2, espectroscopia de infravermelho com transformada de Fourier (FT-IR) e dessorção de CO_2 com temperatura controlada (CO_2-TPD). As propriedades catalíticas destes materiais híbridos para a reação de transesterificação de dimetil oxalato com fenol foram investigadas. Verificou-se que todos são ativos, particularmente o AEP-MCM-41, que apresentou a maior atividade dentre eles. Apenas um pequeno decréscimo na atividade foi observado após vários ensaios catalíticos sucessivos utilizando o mesmo catalisador, indicando uma boa reciclabilidade do mesmo. Notavelmente, a atividade do catalisador pode ser regenerado por simples tratamento com base, sob condições brandas. Além disso, os efeitos da densidade e da força básica dos grupos amino sobre as propriedades catalíticas foram exploradas na proposição do mecanismo de reação, incluindo a provável rota que leva à formação do subproduto anisol.

A series of hybrid mesoporous MCM-41 materials containing different amino groups (such as 3-aminopropyl (AP-), (2-aminoethylamino)propyl (AAP-), or [2-(2-aminoethylamino)ethylamino] propyl (AEP-) group) were prepared by a post-grafting method, and characterized by means of X-ray powder diffraction (XRD), N_2 adsorption, Fourier transform-infrared spectroscopy (FT-IR) and temperature-programmed desorption of CO_2 (CO_2-TPD). The catalytic properties of these hybrid materials were investigated for the transesterification of dimethyl oxalate with phenol. All the samples were active for the transesterification. Among them, the sample AEP-MCM-41 exhibited the highest activity under test conditions. And only a slight decrease in activity could be observed after few runs, indicating the good recyclability of this catalyst. Notably, the activity of the used catalyst could be regenerated by simple treatment with diluted basic agents under mild conditions. Moreover, effects of the density and the basic strength of the amino groups on the catalytic properties were taken into consideration for understanding the reaction mechanism and the possible formation route of the by-product anisole.

Keywords: amino-functionalized, MCM-41, dimethyl oxalate, transesterification, recyclability

Introduction

Diphenyl carbonate (DPC) is an industrially important intermediate for the production of several organic chemicals, especially as the precursor for the synthesis of polycarbonates (PCs), which have been used in many fields due to excellent mechanical, optical, electrical and heat-resistance properties.[1,2] So far, various approaches for DPC synthesis have been reported, including phosgene route, oxidative carbonylation of phenol and transesterification reaction.[1,3-19] Among them, transesterification of dimethyl oxalate (DMO) with phenol to diphenyl oxalate (DPO), following a decarbonylation reaction, is an attractive and environmentally friendly route for the synthesis of DPC.[13-19]

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It was reported that some homogeneous Lewis acid catalysts and soluble organic metal compounds were active for the transesterification of DMO with phenol.[13,14] However, from an industrial point of view, the difficulty of separating catalysts from products in a homogeneous system and the potential environmental impact must be considered. Based on these concerns, heterogeneous catalysis is receiving more attention, and it was reported that a variety of metal oxides bearing weak acidity were effective for the transesterification of DMO with phenol, including Ti-containing phosphate catalysts, $MoO_3/TiO_2\text{-}SiO_2$, TiO_2/SiO_2 and metal modified zeolites.[15-19]

Recently, the heterogenization of organic bases has become an interesting subject owing to a variety of basic compounds showing unusual performance for different catalytic reactions.[20-37] For example, amino-functionalized mesoporous materials have attracted much attention for their wide applications in Knoevenagel condensation, aldol reaction, nitroaldol reaction, Michael additions, and epoxide ring-opening reactions.[27-33] Notably, it was reported that some amino-functionalized materials were efficient catalysts for the transesterification reactions of esters (*i.e.*, ethylene carbonate, diethylmalonate and β-ketoester) with alcohols.[34-37]

During the past few years, our group has also carried out some work on developing novel heterogeneous catalysts for the transesterification of phenol with DMO,[15,18,38] and we just reported recently that cyclopentadienyl-functionalized mesoporous MCM-41 materials bearing weak basic sites were active catalysts for this reaction.[38] In the continuation of this work, several hybrid mesoporous MCM-41 materials containing different amino groups (such as 3-aminopropyl (AP-), (2-aminoethylamino) propyl (AAP-), or [2-(2-aminoethylamino)ethylamino] propyl (AEP-) group) were prepared by a post-grafting method, and their catalytic properties were investigated for the transesterification of DMO with phenol in the present work. Previously, Suzuki *et al.*[31] reported that hybrid mesoporous silica spheres containing the above amino groups, prepared by co-condensation method, showed excellent catalytic activities in the nitroaldol condensation reactions. Here, we found that the grafted MCM-41 materials containing these amino groups were active and recyclable catalysts for the transesterification of DMO with phenol, and the activity of the used catalyst could be easily recovered by simple treatment with diluted basic agents under a mild condition. Moreover, effects of the density and the basic strength of the amino groups on the catalytic properties were discussed, and a possible route for the formation of anisole as by-product was also proposed.

Experimental

Preparation of amino-functionalized materials

The amino-functionalized mesoporous MCM-41 materials were prepared by a post-grafting method.[38] Three types of organosilanes containing different number of amino groups were used: 3-aminopropyltriethoxysilane (APTES), which contains just one amino group in each molecule, [3-(2-aminoethylamino)propyl] trimethoxysilane, (AAPTMS), which contains two amino groups, 3-[2-(2-aminoethylamino)ethylamino] propyltrimethoxysilane (AEPTMS), which contains three amino groups. Typically, the support of MCM-41 (1.0 g), prepared following a literature procedure,[39] was pre-activated by heating to 423 K under vacuum for 3 h. After cooling and release of the vacuum, dry toluene (30 mL) and a certain amount of organosilane was added under N_2 atmosphere, and the mixture was refluxed for 12 h. Finally, the resulting solid was filtered, washed, Soxhlet-extracted with dichloromethane for 24 h, and dried under vacuum at 333 K. The obtained materials were denoted as AP-MCM-41, AAP-MCM-41 and AEP-MCM-41, respectively. In general, the loading of amino group on the three hybrid materials is 0.75 mmol g^{-1} (the corresponding amount of organosilane is as follows: APTES 0.83 mmol, AAPTMS 0.85 mmol, AEPTMS 0.89 mmol). The AEP-MCM-41 samples with different loading of AEP group are denoted as xAEP-MCM-41 (x is the loading of AEP, which is 0.50, 0.75 or 1.02 mmol g^{-1}, and the corresponding amount of AEPTMS is 0.56, 0.89 or 1.25 mmol, respectively.).

Catalyst characterization

Powder XRD patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA) using Ni-filtered CuKα radiation (λ = 0.15418 nm). N_2 adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 423 K for 8 h before measurements. Specific surface areas were calculated using the BET model. The N content was estimated by Perkin-Elmer 2400 CHN analyzer.

FT-IR spectra were obtained using a Nicolet Impact 410 spectrometer. All materials have been dehydrated at 423 K for 5 h prior to spectrum collection. The spectra were recorded using KBr wafers containing 2% of the dried sample at ambient conditions with a resolution of 4 cm^{-1} and 32 scans in the region from 400 to 4000 cm^{-1}.

TPD experiments were carried out using CO_2 as probe molecules. Typically, 50 mg of fresh samples were

pretreated at 423 K under Ar stream for 1 h, then cooled to 303 K. CO_2 was injected into the stream until saturation was reached, and the system was maintained at 303 K for 1 h. After purging the system with flowing Ar for 1 h at 303 K, the samples were heated at the rate of 10 K min^{-1}, and the amount of desorbed CO_2 monitored using an online thermal conductivity detector (TCD).

Catalytic reaction

The catalytic reaction was carried out in a 250 mL three-neck flask equipped with a thermometer, a distillation apparatus, and a stirrer under refluxing condition at atmospheric pressure.[15,38] The reaction temperature was kept at 453 K. The reactants and products were analyzed by gas chromatograph (Shimadzu GC-8A equipped with a HP-5 capillary column) using ethyl benzoate as internal standard. DPO, MPO and the by-product anisole from the transerterification reaction were quantified by comparing the peak areas with their corresponding standards. In all tests, carbon balances were within 100 ± 5%.

Reusability tests were conducted with a used catalyst from a typical experiment after recovery of the solid by filtration, washing with acetone and drying under vacuum at 343 K. In addition, the regeneration of the used catalyst was carried out by treating the catalyst with 0.2 mol L^{-1} methanol solution of tetramethylamonium hydroxide (TMAOH) and thoroughly washing with methanol in a Soxhlet apparatus in order to remove the trace amount of TMAOH adsorbed on the surface of the catalyst.[40]

Results and Discussion

Catalyst characterization

According to the XRD characterization results, it was known that all the amino-functionalized materials display the hexagonally ordered MCM-41-type structure, indicating that the inorganic wall structure of the MCM-41 silica remains intact after functionalization. For the hybrid materials, the reduction in diffraction intensity might be mainly due to contrast matching between the silicate framework and organic groups which are located inside the pore channels of the mesoporous materials.[41,42]

The successful introduction of organic groups into the mesoporous support could be further confirmed by the FT-IR characterization. Typical bands associated with the formation of a condensed silica network are present in all cases (Si–O–Si bands around 1222, 1080, 804 and 460 cm^{-1}). The broad band between 3300 and 3600 cm^{-1} corresponds to the stretching mode of N–H, which are cross-linked with surface silanol (Si–OH) groups.[43] The peak around 1636 cm^{-1} mainly arises from N–H bending mode, which is overlapped with the bending vibrational modes of adsorbed H_2O.[32,40,43] The bands in the region from 2800 to 3000 cm^{-1} can be ascribed to the stretching vibrational mode of –CH_2 groups in aminosilanes.[32,40,44]

N_2 adsorption-desorption isotherms show that all the samples satisfy the type IV hysteresis loop in accordance with IUPAC classification,[45] which is characteristic of mesoporous materials possessing pore sizes between 2 and 50 nm. And the uniformity of the curves shows that the integrity of the mesoporous structure of MCM-41 is preserved after the introduction of organic groups. Compared with the original support, obvious decrease in surface area, pore volume, and pore size was observed for the amino-functionalized MCM-41 materials (as shown in Table 1), which can be assigned to the introduction of amino groups.[41]
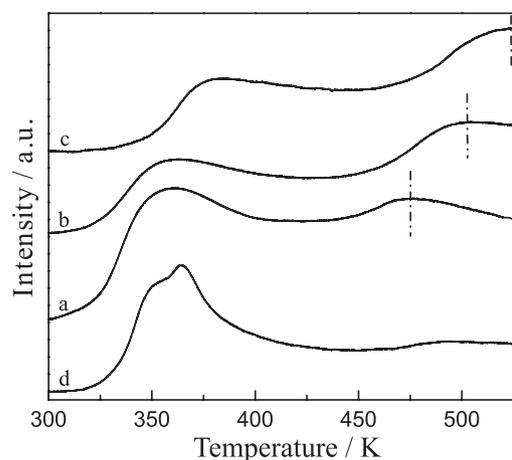
Figure 1. CO_2-TPD profiles of (a) 0.75AP-MCM-41, (b) 0.75AAP-MCM-41, (c) 0.75AEP-MCM-41 and (d) parent MCM-41.

Table 1. The structure parameters of several amino-functionalized silica materials

Samples	BET surface area / (m² g⁻¹)	Pore vol. / (cm³ g⁻¹)	Pore size^a / nm
MCM-41	1429	1.44	3.21
0.75AP-MCM-41	962	0.90	2.91
0.75AAP-MCM-41	952	0.87	2.76
0.75AEP-MCM-41	953	0.94	2.96

^{a}Calculated by using the BJH model on the adsorption branch of the isotherms.

The basicity of amino-functionalized MCM-41 materials was determined on the basis of the CO_2-TPD profiles (as shown in Figure 1). MCM-41 support showed two peaks in the range from 325 to 400 K which can be mainly attributed to the desorption of physisorbed CO_2.[46] For AP-MCM-41, an additional desorption peak appeared at 475 K, which should be due to the chemisorbed CO_2 on the moderate basic sites (*i.e.*, amino group).[47] With the increase of the length of alkyl chain and the number of amino groups, the desorption peak of chemisorbed CO_2 shifted to higher temperature, indicating that the basic strength of different amino-functionalized materials increases in the order: AP-MCM-41 < AAP-MCM-41 < AEP-MCM-41.

Catalytic properties in transesterification of DMO with phenol

The catalytic properties of the amino-functionalized materials are shown in Table 2. Very low conversion of DMO could be observed in the blank reaction (no catalyst). Under such reaction conditions, the activity of parent MCM-41 silica was low, and it showed 18.6% conversion of DMO and very low yield of DPO (1.0%) after 10 h of reaction. The homogeneous catalyst (AEPTMS) was active for the reaction, and it gave 55.5% conversion of DMO and 5.0% yield of DPO after 10 h (entry 6). Comparatively, various amino-functionalized materials exhibited relatively high catalytic activity and DPO yield. In the case of AP-MCM-41, which possesses just one amino group in each organosilane, it gave 55.0% conversion of DMO, with 7.4% yield of DPO after 10 h. Under the same reaction conditions, AAP-MCM-41, which has two amino groups, gave 71.0% conversion of DMO and 13.2% yield of DPO. As for the sample of AEP-MCM-41, which contains three amino groups, it exhibited the highest activity (80.9% conversion of DMO and 21.5% yield of DPO), among the analogous homogeneous catalysts as well as the hybrid materials.

These results suggest that the anchored amino groups are the main active sites of these functionalized catalysts, and the mesoporous support may also play a role in improving the catalytic activity of the hybrid materials.

According to the CO_2-TPD results, it was known that AEP-MCM-41 bears a stronger basicity than either AP-MCM-41 or AAP-MCM-41. Moreover, it was also known that the basicity of the primary amine ($-NH_2$) is higher, and the steric hindrance of this primary amine is smaller than of other amino groups ($-NH-$) present in the same organosilane molecule. Hence, we propose that the primary amine should be the main active sites of AEP-MCM-41 material, and the relatively high activity of AEP-MCM-41 may be assigned to its relatively strong basicity. Besides, the chemical and structural features of the support may also affect the catalytic properties. We suppose that the solid support can improve the degree of site-isolation of organosilane groups and thus enhancing the catalytic activity and selectivity to the main products.

In addition, the reusability of the amino-functionalized mesoporous silica was examined over AEP-MCM-41 catalyst (Table 3). It was found that the activity decreased slightly in the second run, and the conversion of DMO remained constant in the subsequent runs (entries 1-4). Here, the difference in activity between the fresh catalyst and the used one might be partially attributed to the adsorption of a certain amount of DMO to the catalyst. Furthermore, the TMAOH treated catalyst showed a 79.8% conversion of DMO with 31.0% selectivity of DPO (see Table 3, entry 5), indicating that most of the active sites could be regenerated by such simple basic treatment. Previously, by investigating the catalytic properties of aminopropyl-functionalized material for the nitroaldol reaction of aldehyde with nitroalkane, Zhang *et al.*[40] and Sartori *et al.* [48] reported that the deactivated catalyst could be regenerated by the treatment with propylamine (10% v/v ethanol solution) or TMAOH (0.2 mol L^{-1} methanol solution). They suggested that the deactivation

Table 2. The catalytic properties of amino-functionalized silica catalysts for transesterification of phenol with DMO[a]

Entry	Catalysts	Conversion of DMO / (%)	Selectivity / (%)			Yield / (%)	
			MPO	DPO	anisole	MPO	DPO
1	no catalyst	6.4	91.0	2.7	1.9	5.8	0.2
2	MCM-41	18.6	88.1	5.4	3.0	16.4	1.0
3	0.75AP-MCM-41	55.0	84.4	13.4	2.2	46.4	7.4
4	0.75AAP-MCM-41	71.0	67.4	18.6	14.1	47.9	13.2
5	0.75AEP-MCM-41	80.9	59.6	26.6	13.7	48.2	21.5
6	AEPTMS	55.5	75.8	9.0	15.2	42.1	5.0

[a]Reaction conditions: catalyst 1.8 g (or 1.35 mmol AEPTMS), phenol 0.5 mol, phenol/DMO = 5.0, reaction time 10 h , reaction temperature 453 K. MPO: methyl phenyl oxalate.

Table 3. The stability of 0.75AEP-MCM-41 for transesterification of phenol with DMO[a]

Entry	Run	Conversion of DMO / (%)	Selectivity / (%)			Yield / (%)	
			MPO	DPO	anisole	MPO	DPO
1	1	80.9	59.6	26.6	13.7	48.2	21.5
2	2	62.4	74.5	14.2	11.1	46.5	8.9
3	3	65.4	78.8	15.5	5.7	51.5	10.1
4	4	62.4	77.1	17.6	5.3	48.2	11.0
5[b]	5	79.8	66.9	31.0	2.1	53.4	24.7

[a]Reaction conditions: catalyst 1.8 g, phenol 0.5 mol, phenol/DMO = 5.0, reaction time 10 h, reaction temperature 453 K. MPO: methyl phenyl oxalate. [b]Before the 5th running, the used catalyst was treated with 0.2 mol L^{-1} methanol solution of TMAOH, Soxhlet-extracted with methanol and dried under vacuum.
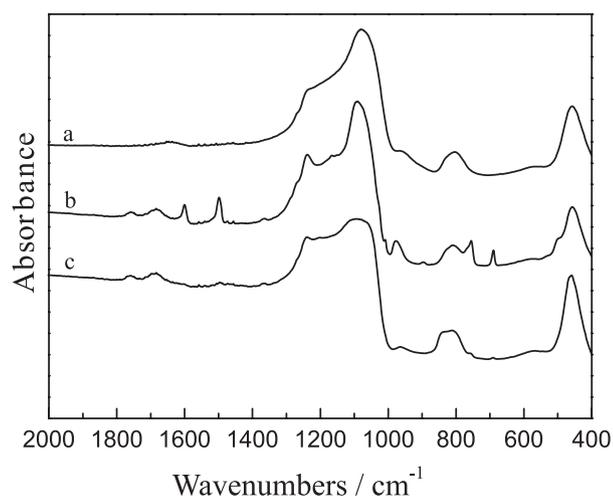
Figure 2. FT-IR spectra of the 0.75AEP-MCM-41 catalyst in different stages: (a) fresh catalyst, (b) used catalyst, which was filtrated, washed with acetone and dried under vacuum at 343 K after the fourth run, and (c) TMAOH treated catalyst, *i.e.* the used catalyst was treated with 0.2 mol L^{-1} methanol solution of TMAOH for 30 min at room temperature, then filtrated, Soxhlet-extracted with methanol for 48 h and dried under vacuum.

of the catalyst might be caused by the reaction of the supported propylamine with CO_2 present in air, or with some benzoic acid present in the benzaldehyde or produced by *in-situ* oxidation.

Figure 2 shows the FT-IR spectra of the fresh, used and TMAOH treated 0.75AEP-MCM-41 catalysts. Compared with the fresh catalyst (Figure 2a), it could be seen that some additional bands (at around 690, 758, 1237, 1365, 1498, 1601 and 1757 cm^{-1}) are observed in the spectrum of the used AEP-MCM-41 (Figure 2b). Herein, two bands at 690 and 758 cm^{-1} might be attributed to the C–H bending mode of phenol. The band at 1237 cm^{-1} was ascribed to the C–O stretching vibrational mode of phenol and anisole. The intense adsorption bands at 1498 and 1601 cm^{-1} were ascribed to the C=C stretching mode of aromatic ring, while the peak around 1757 cm^{-1} mainly arose from the C=O stretching mode of DMO (or methyl phenyl oxalate (MPO), DPO).[49] Moreover, it was found that the color

of the catalyst turned from white to yellow after the first run, and a possible explanation could be the adsorption of organic molecules on the active sites during the reaction. Thus, we speculate here that the main reason for the decrease of the catalytic activity could be assigned to the adsorption of reactants and products on the surface of the hybrid catalysts. Notably, the intensity of those additional bands, which are assigned to the adsorption of organic molecules, decreased considerably after the used catalyst was treated with 0.2 mol L^{-1} methanol solution of TMAOH (see Figure 2c), which means that most of the adsorbed organic molecules on the active sites was removed via such treatment, thus recovering the catalytic activity. It is worthy to mention here that the catalyst was found to be much more selective for MPO and DPO than the fresh catalyst, after reactivation with TMAOH. This may suggest that the used catalyst could not be fully recovered by the treatment with TMAOH, and a trace amount of reactant and product is still present on the surface of catalyst, influencing the surface properties (basicity and/or polarity), and thus changing the catalytic performance.

It is known that the transesterification of DMO with phenol is an equilibrium reaction.[17] The control of the reaction parameters has an important impact on the catalytic properties. Because of the prominent catalytic features of AEP-MCM-41, it was chosen for further study and its catalytic properties were investigated in more detail.

The effect of the amino group loading on the performance of AEP-MCM-41 catalyst was investigated (Table 4). An increase in the loadings of AEP group increased the conversion of DMO. The catalyst 1.02AEP-MCM-41 gave 95.8% conversion of DMO with a high anisole selectivity of 61.1% after 10 h of reaction (Table 4, entry 4). Additionally, the density of AEP groups also can affect their catalytic properties (Table 4, entries 2 and 3). When the conversion of DMO was kept approximately at 80% for the 0.75AEP-MCM-41 and 1.02AEP-MCM-41, the selectivity to anisole reached 29.5% for the sample with 1.0 mmol g^{-1} of AEP groups, which was higher than for the

Table 4. The catalytic properties of AEP-MCM-41 with different loadings of amino group[a]

Entry	time / h	Loading / (mmol g^{-1})[b]	Conversion of DMO / (%)	Selectivity / (%)			Yield / (%)	
				MPO	DPO	anisole	MPO	DPO
1	10	0.55	59.0	81.8	10.7	7.5	48.3	6.3
2	10	0.75	80.9	59.6	26.6	13.7	48.2	21.5
3	6	1.02	79.9	45.7	24.8	29.5	36.5	19.8
4	10	1.02	95.8	15.1	23.8	61.1	14.4	22.8

[a]Reaction conditions: catalyst 1.8 g, phenol 0.5 mol, phenol/DMO = 5.0, reaction temperature 453 K. MPO: methyl phenyl oxalate. [b]Based on CHN elemental analysis.

Table 5. The catalytic properties of 1.02AEP-MCM-41 for transesterification of phenol with DMO[a]

Entry	time / h	Conversion of DMO / (%)	Selectivity / (%)			Yield / (%)		
			MPO	DPO	anisole	MPO	DPO	anisole
1	2	21.0	99.0	0	1.0	20.8	0	0.2
2	6	79.9	45.7	24.8	29.5	36.5	19.8	23.6
3	8	91.5	30.8	25.6	43.5	28.2	23.4	39.8
4	10	95.8	15.1	23.8	61.1	14.4	22.8	58.5

[a]Reaction conditions: catalyst 1.8 g, phenol 0.5 mol, phenol/DMO = 5.0, reaction temperature 453 K. MPO: methyl phenyl oxalate.

catalyst with lower loading of AEP group. These results suggest that there is an optimum loading such that higher loadings of amino groups may result in higher selectivity for the by-product anisole.

Based on the reaction data above, it can be found that these amino-functionalized MCM-41 materials are active and recyclable for the transesterification of DMO with phenol. Both the basic strength and density of amino groups have considerable effects on the catalytic properties of the hybrid materials. Previously, the mechanism of the transesterification of DMO with phenol to MPO on catalysts containing Lewis or Brönsted acid sites has been proposed by Ma and co-workers.[17,50] Here, on the basis of some related references,[51,52] a plausible mechanism for the transesterification of phenol with DMO catalyzed by amino-functionalized materials was proposed. In short, the amino group acts as Lewis base to assist hydrogen transfer from phenol to the carbonyl oxygen of DMO forming a hexahedral intermediate, which then decomposes to form the main product and methanol.

Notably, anisole is an important by-product in our case, and it would be significant to understand its formation mechanism. For this purpose, additional catalytic reactions were carried out using AEPTMS as homogeneous catalyst. The reaction of phenol and CH$_3$OH performed (phenol: 0.13 mol, CH$_3$OH: 0.067 mol, AEPTMS catalyst: 0.9 mmol) at 453 K, gave no detectable amount of anisole after 10 h. But the reaction of DPO and CH$_3$OH carried out (DPO: 0.025 mol, CH$_3$OH: 0.1 mol, AEPTMS: 0.675 mmol) at 453 K lead to the formation of anisole

under the test conditions. Moreover, the reaction of DPO and DMO using AEPTMS as catalyst (DPO: 0.0125 mol, DMO: 0.0125 mol, AEPTMS: 0.675 mmol), also lead to the formation of anisole.

The selectivity to anisole was rather low when the conversion of DMO was kept at relatively low level (*e.g.*, 40%), thus the formation of anisole by direct reaction of DMO with phenol should be negligible. Besides, considering that the methanol produced in the reaction was removed from the system by distillation in order to accelerate the desired reaction, the formation of anisole from the reaction of methanol with phenol should also be negligible. The reaction of DPO with DMO to produce anisole should be also unfavorable due to steric effects of the two large substituents. Thus, we suppose that the formation of anisole should be mainly due to the reaction of MPO with phenol. In order to clarify this point, the catalytic performance of 1.02AEP-MCM-41 in the reaction time range between 2 and 10 h was monitored (Table 5). When the conversion of DMO was very low (*i.e.*, 21%), the selectivity to anisole was quite low (1.0%). As the reaction proceeded, the conversion of DMO increased considerably (above 79% after 6 h), while the selectivity to DPO was almost unchanged. However, the selectivity to MPO decreased significantly along with the rapid increase of the selectivity to anisole (Table 5, entries 2-4). Notably, the total selectivity to MPO and anisole remained almost steady at about 75% after 6 h of reaction, implying that there might be a correlation between MPO and anisole.

Conclusions

In summary, amino-functionalized mesoporous materials are active and promising heterogeneous catalysts for the transesterification of DMO with phenol. The main products MPO and DPO were successfully obtained via a Lewis base-catalyzed route, in which the amino groups located on the surface of mesoporous support are the main active sites. Both the density and basic strength of amino groups have considerable effects on the catalytic properties of the hybrid materials. The formation of the by-product anisole might be attributed to the reaction between MPO and phenol.

Acknowledgments

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