



Cyclopentadienyl-functionalized mesoporous MCM-41 catalysts for the transesterification of dimethyl oxalate with phenol

Yan Liu, Guoming Zhao, Gang Liu, Shujie Wu, Guohua Chen, Wenxiang Zhang*, Huiyan Sun, Mingjun Jia*

Key laboratory of Surface and Interface Chemistry of Jilin Province, College of Chemistry, Jilin University, Changchun 130012, China

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ABSTRACT

Two kinds of hybrid inorganic–organic catalysts (denoted as Cp′-MCM-41 and Cp″-MCM-41) are prepared by grafting methylcyclopentadienyl (Cp′) or pentamethylcyclopentadienyl (Cp″) group onto the surface of mesoporous MCM-41. Such cyclopentadienyl-functionalized materials are active for the transesterification of dimethyl oxalate (DMO) with phenol. Under test conditions, Cp″-MCM-41 gives higher conversion of DMO and selectivity of diphenyl oxalate (DPO) than Cp′-MCM-41, and this might be assigned to the relatively strong Lewis basicity of Cp″ group.

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1. Introduction

Diphenyl carbonate (DPC) is widely used for the synthesis of many organic intermediate and polymer materials, e.g., polycarbonates (PCs) [1–4]. Traditionally, DPC is synthesized by phosgene approaches, based on the reaction between phenol and phosgene [3]. However, with the development of chemical industry, there has been an increasing demand for searching safer and more environmentally friendly processes for the synthesis of DPC [4,5]. Transesterification of dimethyl oxalate (DMO) with phenol to diphenyl oxalate (DPO), following a decarbonylation reaction, is an appropriate and attractive route for the synthesis of DPC [6–11]. Previously, it was found that some homogeneous Lewis acid catalysts and soluble organic metal compounds were active for the transesterification of DMO with phenol [6,7]. However, the separation of the homogeneous catalysts from the reactive system is difficult. Hence, interest on developing efficient heterogeneous catalysts is growing. Recently, several relatively effective heterogeneous catalysts have been reported for the transesterification of DMO with phenol, including TiO₂/SiO₂, Ti-containing phosphate catalysts, MoO₃/TiO₂-SiO₂, and metal modified zeolites [8–11].

Currently, immobilizing organic groups onto the surface of inorganic supports is becoming a popular way to synthesize heterogeneous catalysts, the so-called hybrid inorganic–organic materials. By using this strategy, various efficient and recyclable hybrid catalysts for different catalytic reactions have been reported [12–15]. As the important organic groups or ligands, cyclopentadiene and

its derivatives, have played important role in curative, synthetic and catalytic chemistry, owing to its special coordination ability. Pakkanen and co-workers [16–18] have reported that cyclopentadienyl group could be grafted onto the surface of SiO₂ support by a saturated gas–solid reaction, then heterogeneous olefin polymerization catalysts could be obtained by immobilization of transition metal compounds (e.g., CpTiCl₃, CpZrCl₃, etc.) onto the surface of hybrid silica materials.

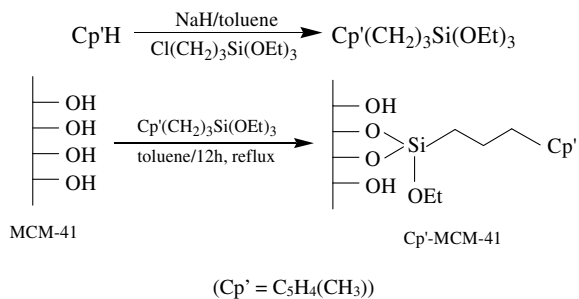
In this work, we synthesize two kinds of hybrid inorganic–organic catalysts by grafting cyclopentadienyl groups onto the surface of mesoporous MCM-41 material, and their catalytic properties for the transesterification of DMO with phenol are investigated. We find these metal-free hybrid materials show good activity for the transesterification of DMO with phenol, and can be recycled at least for a few times under test conditions.

2. Experimental

2.1. Preparation of the catalyst

Preparation of (methylcyclopentadienyl)propyltriethoxysilane (Cp′(CH₂)₃Si(OEt)₃) and (pentamethylcyclopentadienyl)propyltriethoxysilane (Cp″(CH₂)₃Si(OEt)₃) (Scheme 1): These compounds were prepared according to a literature procedure [19]. Typically, 0.02 mol of methylcyclopentadiene (Cp′H) was added to a suspension of 0.02 mol sodium hydride in 20 ml of dry toluene. The mixture was stirred for 3 h at room temperature and then cooled to 253 K when 0.02 mol of 3-chloropropyltriethoxysilane (in 5 ml of toluene) was added slowly. After standing overnight at room temperature, the solid of NaCl was filtered off and the product

* Corresponding authors. Tel.: +86 431 85155390; fax: +86 431 88499140.
E-mail addresses: zhwenx@jlu.edu.cn (W. Zhang), jiamej@jlu.edu.cn (M. Jia).



Scheme 1. Synthesis of cyclopentadienyl-functionalized MCM-41 material.

Cp'(CH₂)₃Si(OEt)₃ was obtained by distillation. Similarly, Cp''(CH₂)₃Si(OEt)₃ was also prepared using the same route.

Preparation of hybrid materials Cp'-MCM-41 and Cp''-MCM-41 (Scheme 1): The support of mesoporous MCM-41 (1.0 g), prepared following a literature procedure [20], was pre-activated by heating to 423 K under vacuum for 3 h. After cooling and release of the vacuum, Cp'(CH₂)₃Si(OEt)₃ (3.8 mmol in 30 ml of toluene) was added under N₂ atmosphere, and the mixture was then refluxed for 12 h. Finally, the resulting solid of Cp'-MCM-41 was filtered, washed, Soxhlet-extracted with chloroform for 24 h, and dried in a vacuum at 343 K. And pentamethylcyclopentadienyl functionalized MCM-41 (Cp''-MCM-41) was synthesized by the same method. The loading amount of cyclopentadienyl group (Cp' or Cp'') on the hybrid material (Cp'-MCM-41 or Cp''-MCM-41) is approximately 0.5 mmol/g, which is calculated according to the content of carbon (CHN elemental analysis).

2.2. Catalytic reaction

The catalytic reaction was carried out in a 250 ml three-neck flask equipped with a thermometer, a distillation apparatus, and a heater with magnetic stirring under refluxing condition at an atmospheric pressure [9]. 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).

After carrying out the reaction, the catalyst was filtered, washed with acetone, dried under vacuum at 343 K and reused directly without further purification.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns for the support MCM-41 material and the hybrid materials Cp'-MCM-41 and Cp''-MCM-41. It is found that all samples show similar XRD patterns, indicating that the hybrid materials still keep the long-range ordering of the mesoporous structure and the inorganic wall structure of the MCM-41 silica remains intact after the grafting process. For the hybrid materials, the intensity reduction of diffraction peaks may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41 [12,13].

The N₂ adsorption-desorption isotherms and pore size distribution profiles of Cp'-MCM-41, Cp''-MCM-41 and MCM-41 support are shown in Fig. 2. All the samples display type IV isotherm (IUPAC by classified) [21], which is characteristic of mesoporous material. And the uniformity of the curves shows that the integrity of the mesoporous structure of the MCM-41 silica is remained after the introduction of organic moieties. The relevant structure parameters of the hybrid materials and MCM-41 support are given in Table 1. Compared with the MCM-41 support, two hybrid MCM-

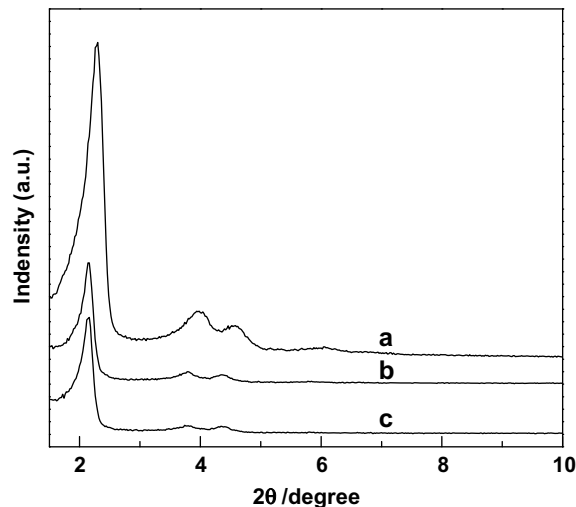


Fig. 1. Powder XRD patterns of (a) MCM-41, (b) Cp'-MCM-41 and (c) Cp''-MCM-41.

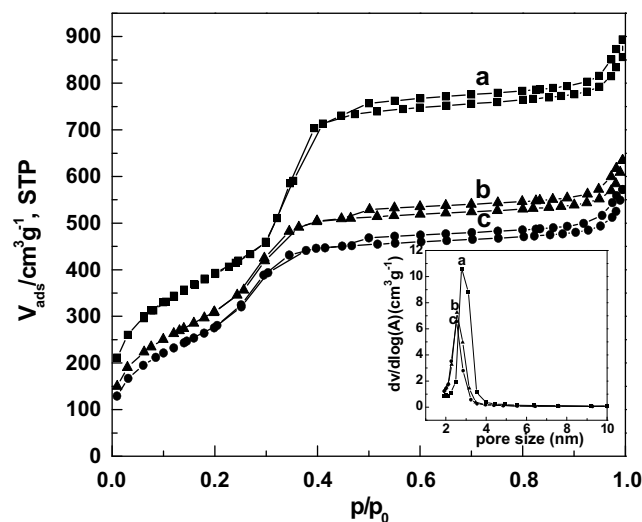


Fig. 2. N₂ adsorption-desorption isotherms at 77 K and pore size distribution profiles (inset) of (a) MCM-41, (b) Cp'-MCM-41 and (c) Cp''-MCM-41.

Table 1

The structure parameters of several materials

Samples	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size ^a (nm)
MCM-41	1429	1.44	3.21
Cp'-MCM-41	1147	1.10	3.08
Cp''-MCM-41	1032	0.99	3.05

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

41 materials show lower specific surface area, smaller pore volume and mean pore size, which can be assigned to the introduction of organic moieties [12]. According to the related literatures [12,14,15], it can be concluded that the cyclopentadienyl groups (Cp' or Cp'') should have been grafted onto the surface of MCM-41 by covalent Si-O-Si coupling, since it is well known that the condensation reaction to form Si-O-Si bonds between organosilane moieties and the surface Si-OH groups of MCM-41 is easily occurred under our experimental conditions.

3.2. Catalytic properties in transesterification of DMO with phenol

The catalytic properties of various catalysts in the transesterification of DMO with phenol are shown in Table 2. Very low conversion of DMO can be observed in the blank reaction (no catalyst). Support of MCM-41 gives 15.5% conversion and very low selectivity of DPO (5.2%) under the given reaction conditions. The catalytic activities of homogeneous methylcyclopentadiene (Cp'H) and pentamethylcyclopentadiene (Cp''H) are also low, and just give 10.3% and 18.7% DMO conversion, respectively. The hybrid materials of Cp'-MCM-41 and Cp''-MCM-41 are more active than the corresponding homogeneous catalysts, and give 49.9% and 76.5% conversion of DMO, with 12.6% and 30.1% selectivity of DPO, respectively. Moreover, the recyclability of these two hybrid catalysts is also investigated (Table 3). It is found that Cp'-MCM-41 shows relatively high stability since the catalytic activity of the recycled sample does not change considerably. However, the catalytic activity of Cp''-MCM-41 decreases gradually with the increase of recycle time, which might be mainly because the adsorption of organic molecules on the active sites easily occurs on this material.

Previously, it was known that some organic metal compounds bearing weak Lewis acidity were active and selective catalysts for the transesterification of DMO with phenol [6–11]. Moreover, it was reported that cyclopentadienyl transition metal compounds, like titanocene complexes, were efficient homogeneous catalysts for the transesterification of dimethyl carbonate (DMC) with phenol [22,23]. However, to our knowledge, there was no report about a metal-free organic compound catalyst for the application in transesterification of DMO with phenol. Currently, it is still unclear for why these cyclopentadienyl-functionalized materials are active for the title reaction. We suppose that it might be assigned to the special nucleophilic ability or Lewis basicity of cyclopentadienyl groups [24,25], since it is known that some basic catalysts are active for other kind of transesterification reactions [14,15,26]. The

relatively high activity of Cp''-MCM-41 might be due to the fact that the Lewis basicity of pentamethylcyclopentadienyl (Cp'') group is stronger than that of methylcyclopentadienyl (Cp') group [24,25]. Besides, we should point out here that the selectivity of DPO is not very high on the two hybrid Cp'-MCM-41 and Cp''-MCM-41 catalysts. This might be mainly assigned to the thermodynamic limitation, since it is known that the transesterification of methyl phenyl oxalate (MPO) with phenol to DPO are not favorable in the thermodynamics compared with the transesterification of DMO with phenol to MPO [8]. Moreover, the size constraint of the MCM-41 support may also be unfavorable to the transesterification of MPO with phenol to DPO.

As for why the catalytic activities of cyclopentadienyl-functionalized materials are higher than those of the corresponding homogeneous catalysts and the support, in our opinion, there are at least two possible explanations: first, the strength of Lewis basicity of cyclopentadienyl group may be changed after introducing it onto the surface of mesoporous MCM-41. Second, a cooperative effect between the organic groups and the support might be existed since the support of MCM-41 is also active for the transesterification reaction.

It is worthy to mention here that Ti species could also be introduced to the hybrid materials of Cp'-MCM-41 or Cp''-MCM-41 by using the coordination ability of cyclopentadienyl groups. The fresh Ti-containing catalysts show much higher activities than the metal-free materials of Cp'-MCM-41 and Cp''-MCM-41 for the transesterification of DMO with phenol. However, serious Ti-leaching could be observed, thus resulting in considerable decrease of catalytic activity when the catalysts were reused. In fact, leaching of metal species is prevalent in other various liquid-phase reactions, including an example of the transesterification reaction of methyl-methacrylate with 1-butanol [27]. Hence, it would be desirable if an efficient metal-free catalyst could be obtained for the transesterification of DMO with phenol.

4. Conclusions

In conclusion, active hybrid inorganic–organic catalysts for the transesterification of DMO with phenol can be obtained by grafting cyclopentadienyl groups onto the surface of mesoporous MCM-41 material. Currently, the synthesis and characterization of other kinds of hybrid materials containing different derivatives of cyclopentadiene or organic functional groups are underway in order to obtain more efficient and stable catalysts for the title reaction.

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Table 2

The catalytic properties of different catalysts for transesterification of phenol with DMO^a

Entry	Catalysts	Conversion of DMO (%)	Selectivity (%)			Yield (%)	
			MPO	DPO	AN ^b	MPO	DPO
1	No catalyst	4.9	89.6	2.9	4.0	4.4	0.1
2	MCM-41	15.5	88.0	5.2	3.2	13.7	0.8
3	Cp'H	10.3	96.6	0	3.4	10.0	0
4	Cp''H	18.7	88.4	2.9	2.0	16.6	0.5
5	Cp'-MCM-41	49.9	86.2	12.6	1.2	43.1	6.3
6	Cp''-MCM-41	76.5	65.4	30.1	4.2	50.1	23.0

^a Reaction conditions: catalyst, 1.8 g (or 0.01 mol Cp'H and Cp''H); phenol, 0.5 mol; phenol/DMO, 5.0; reaction time, 8 h; reaction temperature, 453 K.

^b Anisole.

Table 3

The stability of hybrid materials for transesterification of phenol with DMO^a

Catalysts	Run	Conversion of DMO (%)	Selectivity (%)			Yield (%)	
			MPO	DPO	AN ^b	MPO	DPO
Cp'-MCM-41	1	49.9	86.2	12.6	1.2	43.1	6.3
	2	42.1	88.8	9.8	1.4	37.4	4.1
	3	54.8	88.1	11.9	0	48.3	6.5
Cp''-MCM-41	1	76.5	65.4	30.1	4.2	50.1	23.0
	2	56.4	82.9	16.1	1.1	46.8	9.1
	3	23.1	94.5	6.2	2.3	21.8	0.7
	4	23.1	90.7	5.2	2.7	20.9	1.2

^a Reaction conditions: catalyst, 1.8 g; phenol, 0.5 mol; phenol/DMO, 5.0; reaction time, 8 h; reaction temperature, 453 K.

^b Anisole.

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