

Synthesis of dimethyl carbonate from methyl carbamate and methanol using MCM-41 functionalized with sulfonic acid groups as catalyst

Xianye Qin, Wenbo Zhao[†], Bing Han, Biao Liu, Peichao Lian, and Shuisheng Wu

Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650500, P. R. China

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Abstract—The catalytic synthesis of dimethyl carbonate from methyl carbamate and methanol was investigated in a batch reactor. All of the homogeneous Brønsted acid catalysts show favorable catalytic activity. As homogeneous Brønsted acid catalyst is difficult to separate after reaction, it is converted to heterogeneous catalyst by grafting sulfonic acid groups to MCM-41 with three different methods. Their catalytic activity investigation indicated that sulfonic acid groups grafted by sulfonating with chlorosulfonic acid directly showed activity near to that of homogeneous sulfuric acid catalyst. It was further selected as a model catalyst to investigate the effect of acid amount on its catalytic activity. The results indicated that its activity was positively correlated with its acid amount.

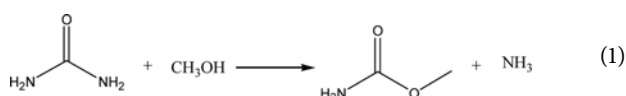
Keywords: Dimethyl Carbonate, Methyl Carbamate, Methanol, Sulfonic Acid Groups, MCM-41

INTRODUCTION

As a green raw material, dimethyl carbonate (DMC) has attracted more and more attention in recent years. It contains several basic groups and its reaction activity is excellent. It can replace hyper-toxic phosgene as benign carbonylation reagent or take the place of dimethyl sulfate as methylation reagent [1]. It is also considered as a potential reactant to produce biodiesel and a promising electrolytic solution for lithium batteries [2,3]. DMC can also be used as a fuel oil additive instead of methyl tertiary-butyl due to its high oxygen content [4]. At the same time, DMC has been widely used in many other fields, such as medicine, pesticide, composite material and dyestuff [5].

DMC can be synthesized by several methods, such as phosgenation of methanol [6], oxidative carbonylation of methanol [7] and transesterification of cyclic carbonate with methanol [8]. All have either commercial or environmental disadvantages. Phosgenation of methanol has been obsoleted gradually because phosgene is extremely toxic. Oxidative carbonylation of methanol suffers from toxicity of carbon monoxide and potential danger of explosion. High energy consumption and investment are the major disadvantages of transesterification [9]. Recently, a green process of DMC synthesis using carbonate dioxide and methanol as raw materials was developed. However, this reaction is limited by thermodynamics and the catalyst is easily deactivated by water [10].

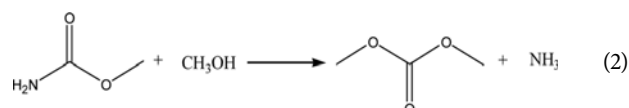
Another process of DMC synthesis developed recently is methanolysis of urea. In this process, DMC is synthesized by a two-step reaction from urea and methanol via methyl carbamate (MC) intermediate. The reaction equations are as follows:



[†]To whom correspondence should be addressed.

E-mail: wenshuixing@126.com

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The first step easy even without a catalyst, but the second step as the rate-control step is more difficult. Hence, the key to this process is to find a catalyst that can effectively promote the second reaction. The disadvantage is that the generated ammonia will restrict the further generation of DMC [11]. However, this process has a great advantage of avoiding a methanol-water-DMC ternary azeotrope system. Since the ammonia formed during the reaction can be used to produce urea again by reacting with carbon dioxide, this method is considered as a process of indirect synthesis of DMC from CO₂ and methanol. Up to now, the catalysts used to methanolysis of urea or MC to DMC mainly include ionic liquids [12], Zn/Fe mixed oxide [13,14], Zn compounds [11], rare earth metal compounds [15], solid base [16], polyphosphoric acid [17], Cerium-based catalysts [18,19] and support material Fe₂O₃/HMCM-49 [9]. Among them, ionic liquids and support material Fe₂O₃/HMCM-49 show high DMC selectivity. Rare earth metal compounds, Cerium-based catalysts and polyphosphoric acid exhibit high yield of DMC especially for polyphosphoric acid with DMC yield of 67.4%. Polyphosphoric acid as a Brønsted acid shows excellent catalytic activity by absorbing the ammonia generated in the reaction to promote the formation of DMC. Thus, we can considerable infer that other Brønsted acids such as sulfuric acid, pyrophosphoric acid and sodium hydrogen sulfate can also enormously promote the generation of DMC by absorbing the generated ammonia. Though homogeneous Brønsted acid catalysts may show favorable activity, they are difficult to separate after reaction. To simplify the separation process of catalyst, we anchor sulfonic acid groups to mesoporous material MCM-41 to realize heterogenization of homogeneous Brønsted acid catalyst.

MCM-41 possesses hexagon-ordered channels, high surface area, hydrophobic nature, and its pore size can adjust continuously in

the range of 1.6–10 nm [20]. Its high surface area and mesoporous channel make it possible to adjust the acidity of MCM-41 by grafting sulfonic acid groups to it. Generally, immobilizing sulfonic acid groups to MCM-41 can be achieved by one-step synthesis route or by post synthesis route. Grafting sulfonic acid groups to MCM-41 by post synthesis can be realized by grafting 3-(mercaptopropyl)triethoxysilane followed by oxidation [21], anchoring of benzyl alcohol followed by sulfonating with ClSO_3H [22] or sulfonating with ClSO_3H directly [23]. The acidity of the modified MCM-41 can be adjusted by controlling the ratio of sulfonating agent volume to MCM-41 mass. As a solid acid catalyst, sulfonic acid group functionalized MCM-41 (SO_3H -MCM-41) has been used as an excellent catalyst in many reactions, such as esterification [24], Fischer indole synthesis [22], Claisen-Schmidt condensation [25] and Friedel-Crafts alkylation [26].

In this work, our purpose was to realize heterogenization of homogeneous Brönsted acid catalyst by grafting sulfonic acid groups to MCM-41 and illustrate the relation of catalytic activity and acid amount of SO_3H -MCM-41.

EXPERIMENT SECTIONS

1. Materials

All the chemicals used were of analytical grade and used without any further purification. MCM-41 zeolite was purchased from Dongguan Jun Yi Chemical Technology Co., Ltd. of China. Before use, MCM-41 was calcined at 560°C for 6 h with a heating rate of about $1^\circ\text{C}/\text{min}$ from 80°C to remove organic template.

2. Catalyst Preparation and Characterization

Method A HSO_3 -MCM-41(A) was prepared according to the procedure involving 3-(mercaptopropyl)triethoxysilane (MPTS) [21]. Typically, 1 g MCM-41, 4 mL MPTS and 50 mL toluene were added to a three-neck flask and refluxed at 140°C for 12 h with stirring under N_2 atmosphere. The solid was separated by filtration, washed with toluene and dried at 40°C under vacuum for 12 h. The recovered solid was oxidized to HSO_3 -MCM-41 by stirring in the solution of 15 mL H_2O_2 and 50 mL methanol for 24 h. After oxidation, the solid particles were filtered off and washed with water and ethanol followed by dispersing in 0.05 mol L^{-1} H_2SO_4 solution for 4 h with stirring. The solid sample was recovered by filtration, washed with water and ethanol and dried at 40°C under vacuum for 15 h.

Method B HSO_3 -MCM-41(B) was prepared by a grafting process [22]. 1.0 g MCM-41, 5 mL benzyl alcohol and 20 mL toluene were refluxed in a three-neck flask at 150°C for 12 h with stirring. The solid was filtered off, washed with CH_2Cl_2 and dried at 60°C for 12 h and then sulfonated in the solution of 0.8 mL ClSO_3H and 20 mL CHCl_3 by refluxing at 60°C for 2 h. After sulfonation, the solid was recovered by filtration, washed with CH_2Cl_2 and dried at 80°C for 5 h.

Method C HSO_3 -MCM-41(C) was prepared as previously described [23]. 2 mL ClSO_3H (or other volume of ClSO_3H) was slowly added to a three-neck flask which contained 1 g MCM-41 and 10 mL CH_2Cl_2 through constant pressure funnel under stirring at 25°C . The HCl generated during the process of sulfonation was absorbed by sodium hydrate solution. From the addition of ClSO_3H on, the mixture was stirred for 1 h. After sulfonation, the solid sample was

filtered off, washed with CH_2Cl_2 and dried at 60°C for 1 h followed by activating at 100°C over night. The sample was marked as HSO_3 -MCM-41(C-x), where x indicates the ratio of ClSO_3H volume to MCM-41 mass (mL/g).

The XRD patterns of HSO_3 -MCM-41 samples were performed on a Rigaku D/max-3B X-ray diffractometer. The FT-IR spectra were recorded on a Biorad FTS-40 infrared spectrometer with KBr method. The acid amount of HSO_3 -MCM-41 was determined by acid-base back titration. Typically, HSO_3 -MCM-41 was reacted with an aqueous solution of sodium hydrate (0.12 mol L^{-1}) for 3 h under vibrating. Then the reaction liquid was titrated by 0.02 mol L^{-1} HCl aqueous solution using phenolphthalein as indicator. The corresponding sulfur content of the sample was determined by ICP-AES.

3. Catalytic Activity Evaluations

The catalytic activity of homogenous Brönsted acids was evaluated in an autoclave of 50 mL with magnetic stirring. Typically, 15.00 mmol MC, 300.00 mmol methanol and homogeneous Brönsted acid catalyst were added into the autoclave and reacted at 160°C for 6 h in oil bath. To ensure the acid amount of all the homogeneous Brönsted acid was equal, the catalyst dose of different homogeneous Brönsted acid was $n_{\text{NaHSO}_4} = 2n_{\text{H}_2\text{SO}_4} = 4n_{\text{H}_4\text{P}_2\text{O}_7} = 6.20 \text{ mmol}$. The catalytic reactions catalyzed by HSO_3 -MCM-41 were carried out in an autoclave of 10 mL with magnetic stirring. In a typical procedure, 3.75 mmol MC, 75.00 mmol methanol and 0.25 g catalyst were charged into the autoclave and reacted at 160°C for 6 h in oil bath. After reaction, the autoclave was cooled to room temperature naturally and the insoluble components were separated by centrifugation. The liquid phase was analyzed by GC equipped with an FID detector and SE-54 capillary column using internal standard method.

RESULTS AND DISCUSSION

At the process of DMC synthesis from MC and methanol, DMC was produced by substituting the amino of MC with the methoxy group derived from methanol. Moreover, DMC could further react with MC to produce N-methyl methyl carbamate. It also could decompose into dimethyl ether and carbon dioxide [27]. Since we

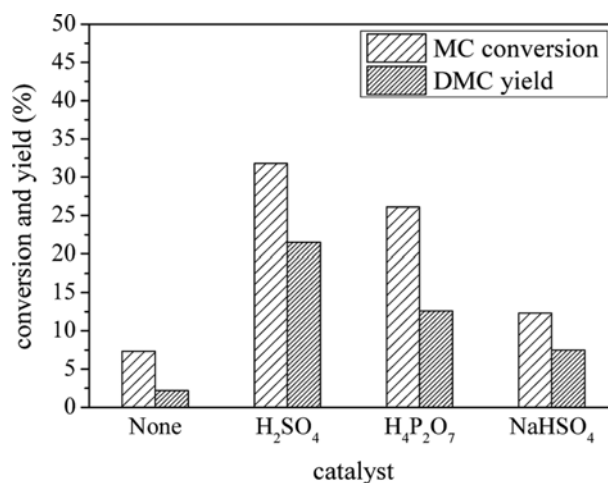


Fig. 1. The catalytic performance of Bronsted acid.

Table 1. The catalytic activity of HSO₃-MCM-41 prepared by different method

Catalyst	Conversion of MC/%	Yield of DMC/%
MCM-41	13.5	1.3
HSO ₃ -MCM-41(A)	13.1	5.8
HSO ₃ -MCM-41(B)	26.5	14.6
HSO ₃ -MCM-41(C-0.5)	35.0	16.7

were just concerned with MC conversion and DMC yield, all the catalysts were evaluated based on MC conversion and DMC yield in the present work.

1. The Catalytic Activity of Brönsted Acid

As expect, all homogeneous Brönsted acids, except for sodium hydrogen sulfate which is incompletely dissolved in methanol, show favorable catalytic activity as presented in Fig. 1. Without catalyst, only 2.2% of DMC yield and 7.3% of MC conversion can be obtained. Sulfuric acid as a homogeneous Brönsted acid catalyst exhibits the best catalytic activity with DMC yield of 21.5% and MC conversion of 31.8%. Pyrophosphoric acid with lower acid strength than sulfuric acid shows slightly lower activity. When sodium hydrogen sulfate was used as catalyst, only 7.5% of DMC yield and 12.3% of MC conversion could be obtained. Though sulfuric acid as a strong homogenous Brönsted acid catalyst shows favorable catalytic activity, it is difficult to separate after reaction. Thus, we grafted sulfonic acid groups to MCM-41 using three different methods as described in the experiment part in the following work to realize heterogenization of homogeneous sulfuric acid catalyst.

2. Catalytic Performance of Different Type HSO₃-MCM-41

HSO₃-MCM-41 was prepared by three methods and used to catalyze methanolysis of MC to DMC. As Table 1 shows, HSO₃-MCM-41(C-0.5) exhibits the best activity with DMC yield of 16.7% among the three types HSO₃-MCM-41. The DMC yield and MC conversion were only 1.3% and 13.5%, respectively, when MCM-41 was used as catalyst. HSO₃-MCM-41(B) shows activity near to that of HSO₃-MCM-41(C-0.5). HSO₃-MCM-41(A) shows the lowest activity with just 5.8% of DMC yield. The reason may be that the acid amount of HSO₃-MCM-41(A) is small because -SH was oxidized incompletely or was oxidized to disulfide species in the oxidation step [28,29]. Since HSO₃-MCM-41(C) showed the best catalytic activity, it was further studied by FT-IR and XRD. Though HSO₃-MCM-41(C-0.5) shows favorable catalytic activity, it may not be the best. The catalytic activity of HSO₃-MCM-41(C) may have some relations with its acid amount. To illustrate this relation, we prepared HSO₃-MCM-41(C) using different ratio of ClSO₃H volume to MCM-41 mass, determined its acid amount by acid-base back titration and investigated the relation of its acid amount and catalytic activity.

3. Characterizations of HSO₃-MCM-41(C)

The successful synthesis of HSO₃-MCM-41(C) without destroying the structure of MCM-41 was confirmed by FT-IR spectra and XRD patterns. The FT-IR spectrum of calcined MCM-41 (Fig. 2(a)) shows several typical IR vibration signals of Si-MCM-41, such as the peaks at 1,101 cm⁻¹ (the asymmetric stretching vibrations of Si-O-Si) and 467 cm⁻¹ (the bending vibration of Si-O-Si) [30]. The bands at 906 cm⁻¹ and 734 cm⁻¹ in Fig. 2(a) can be attributed to the

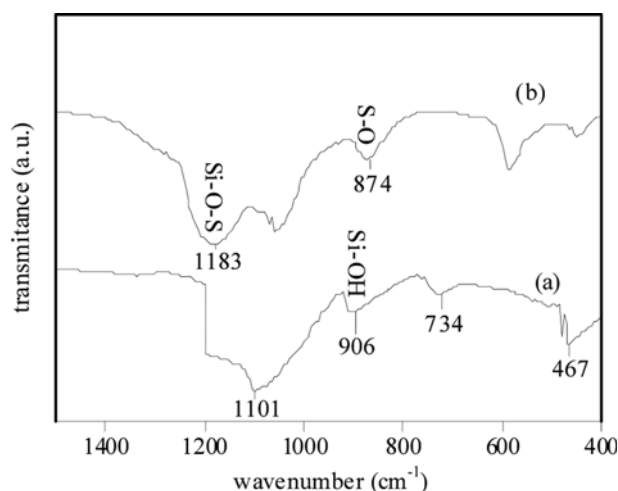


Fig. 2. The FT-IR spectrum of (a) calcined MCM-41 and (b) HSO₃-MCM-41(C-2.0).

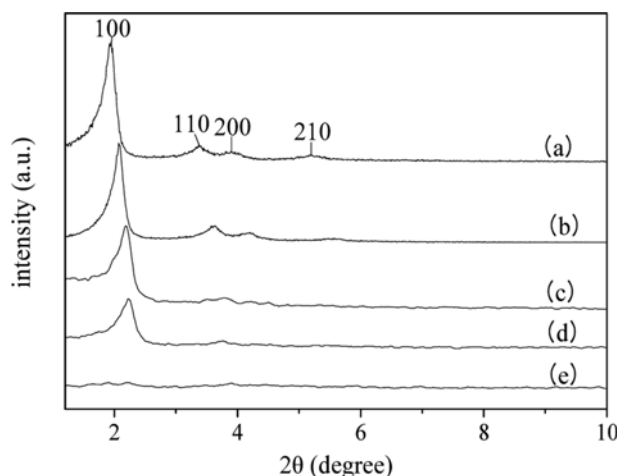


Fig. 3. XRD patterns of (a) MCM-41 without calcined, (b) calcined MCM-41, (c) HSO₃-MCM-41(C-0.4), (d) HSO₃-MCM-41(C-0.5) and (e) HSO₃-MCM-41(C-1.0).

symmetric stretching vibration of Si-O-Si and the bending mode of Si-OH, respectively. The success of grafting sulfonic acid groups to MCM-41 was confirmed by the presence of the signal at 1,183 cm⁻¹ (the symmetric vibration of Si-O-S) and 874 cm⁻¹ (the symmetric stretching vibration of S-O) in Fig. 2(b) [31]. Furthermore, the disappearance of the signal at 906 cm⁻¹ (the bending vibration of Si-OH) can prove indirectly that the sulfonic acid groups were grafted successfully (Fig. 2(b)).

All the XRD patterns in Fig. 3 except for Fig. 3(e) exhibit an intense signal at around 2θ=2.2° (the 100 plane) and three small signals between 3.5° and 6.0° (the 110, 200 and 210 plane respectively). The four peaks confirm the presence of a hexagonal unit [20]. These results indicated that the structure of MCM-41 retains intact after calcination or sulfonating at the condition that the ratio of ClSO₃H volume to MCM-41 mass is less than 0.5 ml/g. However, the four typical peaks disappear when that ratio increases to 1 ml/g, which indicates that the structure of MCM-41 almost has been destroyed

Table 2. Acid amount and sulfur content of SO₃H-MCM-41 sulfonated with different amount of ClSO₃H

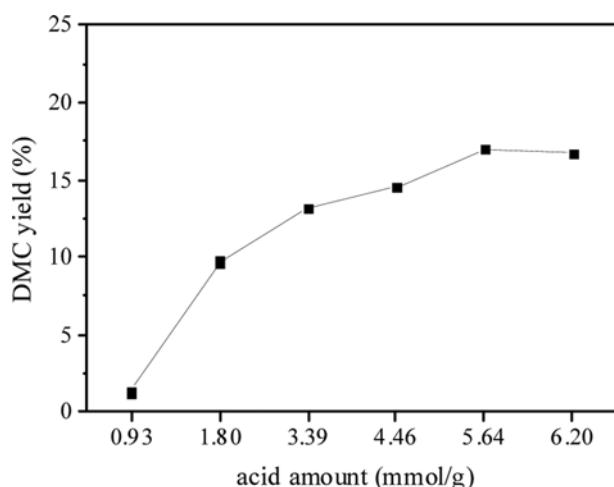
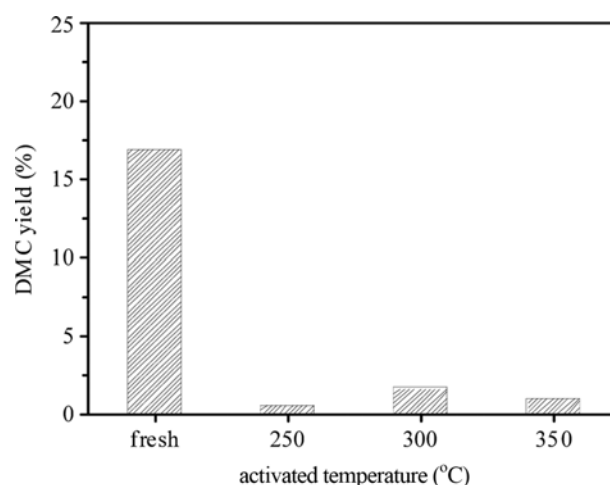
Amount of ClSO ₃ H/ (ml/g)	Acid amount/ (mmol/g)	Sulfur content/ (mmol/g)
0	0.93	-
0.1	1.80	1.04
0.2	3.93	1.81
0.3	4.46	2.38
0.4	5.64	2.91
0.5	6.20	3.07

completely (Fig. 3(e)). Thus, the largest ratio of ClSO₃H volume to MCM-41 mass used to prepare HSO₃-MCM-41(C) to investigate the effect of acid amount on DMC yield was not higher than 0.5 ml/g.

The acid amount of SO₃H-MCM-41(C-x) was determined by acid-base back titration and the corresponding sulfur content was tested by ICP-AES. As shown in Table 2, the acid amount of SO₃H-MCM-41(C) increases with the increase of the ratio of ClSO₃H volume to MCM-41 mass. The acid amount of MCM-41 without sulfonation was just 0.93 mmol/g. However, when MCM-41 was sulfonated under the condition that the ratio of ClSO₃H volume to MCM-41 mass was 0.5 ml/g; the acid amount can reach 6.20 mmol/g. The sulfur content tested by ICP-AES ranged from 1.04 mmol/g to 3.07 mmol/g from HSO₃-MCM-41(C-0.1) to HSO₃-MCM-41(C-0.5), which is consistent with their acid amount.

4. The Influence of Acid Amount of HSO₃-MCM-41(C) on its Catalytic Activity

The catalytic performance of SO₃H-MCM-41(C-x) for the synthesis of DMC from MC and methanol is shown in Fig. 4. The results showed that the catalytic activity of SO₃H-MCM-41(C) is positively correlated with its acid amount. The acid amount of 5.64 mmol/g, which corresponds to that of HSO₃-MCM-41(C-0.4), shows the best catalytic activity with 17.0% of DMC yield. When the acid amount was increased from 5.64 mmol/g to 6.20 mmol/g, DMC yield almost remained unchanged. Since HSO₃-MCM-41(C-0.4) showed the

**Fig. 4.** The effect of acid amount of SO₃H-MCM-41(C) on DMC yield.**Fig. 5.** The catalytic activity of HSO₃-MCM-41(C-0.4) activated at different temperature.

best catalytic activity, it was selected to investigate its reusable performance.

5. The Recycling of HSO₃-MCM-41(C-0.4)

HSO₃-MCM-41(C-0.4) was activated by drying at different temperature after reaction. Since ammonium sulfate begins to deaminate at 250 °C and decompose at 350 °C, we chose to activate HSO₃-MCM-41(C-0.4) by drying at 250 °C, 300 °C and 350 °C, respectively. As shown in Fig. 5, the activated HSO₃-MCM-41(C-0.4) almost lost all catalytic activity. As Fan [32] reported, the process of ammonia sulfate denitrification often accompanies the conversion of sulfur. It would be part of the reason for the activated HSO₃-MCM-41(C-0.4) with low catalytic activity. To investigate the stability of HSO₃-MCM-41(C-0.4) in methanol under reaction temperature, the sulfur content of reaction liquid with HSO₃-MCM-41(C-0.4) as catalyst was tested by ICP-AES. The result indicated that the sulfur content of the reaction liquid was 0.12 mmol/ml. However, if all the sulfonic acid groups were leached from HSO₃-MCM-41(C-0.4), the sulfur content of the reaction liquid should be 0.30 mmol/ml. It indicated that part of sulfonic acid groups leached from HSO₃-MCM-41(C-0.4) after reaction and that HSO₃-MCM-41(C-0.4) was unstable in methanol under reaction temperature. Though HSO₃-MCM-41(C-0.4) achieves heterogenization of homogeneous sulfuric acid with little loss of the catalytic activity, it was unstable in methanol under reaction temperature and could not be reused. Thus, we would focus on its activating method and make effort to enhance its stability in the future work.

CONCLUSIONS

The homogeneous Brönsted acids catalyst investigated showed favorable activity to methanolysis MC to DMC. The sulfonic acid groups were successfully grafted to MCM-41 to realize heterogenization of homogeneous sulfuric acid catalyst. SO₃H-MCM-41(C), which was unstable in methanol under reaction temperature, showed the best activity among the three heterogeneous SO₃H-MCM-41. The investigation of the effect of the acid amount of SO₃H-MCM-41(C) on its catalytic performance indicates that the catalytic activity

of SO₃H-MCM-41(C) is positively correlated with its acid amount.

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