

Selective synthesis of dimethyl carbonate from urea and methanol over $\text{Fe}_2\text{O}_3/\text{HMCM-49}^\dagger$

Cheng Zhang, Bin Lu, Xiaoguang Wang, Jingxiang Zhao and Qinghai Cai*

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The supported material $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ was prepared and characterized by XRD, FT-IR and NH_3 -TPD. This material was tested for the catalytic synthesis of dimethyl carbonate (DMC) from methanol and urea in a batch reactor without any specially designed equipment. The results showed that $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ is an effective catalyst, exhibiting 34.2% conversion of urea and 97.4% selectivity to DMC at 453 K. Furthermore, the catalyst can be recovered due to its heterogeneous nature and reused three times without a significant loss in its activity and the reaction mechanism *via* mutual activation of urea and methanol was proposed.

1. Introduction

Dimethyl carbonate (DMC), as an environmentally benign building block, is becoming increasingly important in the chemical industry.^{1,2} It is mainly used as a carbonylating and methylating reagent substituting dimethyl sulfate and phosgene, which are corrosive and toxic agents.³ In addition, it is also a promising octane enhancer.⁴ Currently, DMC synthesis techniques internationally reported mainly include phosgenation of methanol, oxidative carbonylation of methanol^{5,6} and transesterification of cyclic carbonate with methanol.⁷ Each of the aforementioned processes has commercial or technical and environmental disadvantages. Phosgenation of methanol has been phased out because of the extreme toxicity of phosgene. The oxidative carbonylation of methanol suffers from low production rate, need for corrosion resistant reactors, toxicity and potential explosion of carbon monoxide.^{8,9} Besides, major disadvantages of the transesterification method are high energy consumption, high investment and production costs due to the requirement of the intermediate separation.¹⁰ Recently, carbon dioxide, a readily available, inexpensive and environmentally acceptable material, has widely been investigated as raw material for DMC synthesis.^{11–18} But, the direct synthesis of DMC from methanol and carbon dioxide is still unsatisfactory due to the difficulty in activation of carbon dioxide, deactivation of the catalyst and thermodynamic limitation.

The alcoholysis of urea for producing DMC is one kind of new process developed, which is widely considered as indirect

synthesis of DMC from CO_2 and methanol since the released NH_3 can be recycled to produce urea by reaction with CO_2 . There are several advantages, such as abundant resource and low cost of urea and methanol, no formation of ternary azeotrope of methanol–water–DMC resulting in easier separation of DMC. Several researchers reported the synthesis of DMC from methanol and urea in the presence of organotin, simple basic compounds such as K_2CO_3 , CH_3ONa , CaO , MgO , *etc.*,^{19–22} but the DMC yield in these systems is very low. However, in the research work reported by Sun and co-workers,²³ 29.0% yield was attained by using a ZnO catalyst. Sun *et al.*²⁴ reported that polyphosphoric acid was an effective catalyst in the DMC synthesis by the alcoholysis of urea with 67.4% yield of DMC. The latter suffers from low selectivity due to the formation of several byproducts such as *N*-methyl urea, methyl carbamate, *N*-methyl methyl carbamate and it needs a corrosion resistant reactor. Yang *et al.*²⁵ have reported the synthesis of DMC from urea and methanol catalyzed by metallic compounds at atmospheric pressure. 29% yield was obtained, but this method also has disadvantages such as low selectivity to DMC, complicated procedure and the difficulty in the separation between the product and the catalyst. Very recently, mixed oxides from hydrotalcite-like compounds,²⁶ Zn/Fe mixed oxide²⁷ and lanthanum compounds²⁸ were found to have high activity for the synthesis of DMC from methyl carbamate and methanol. The low selectivity to DMC is also the main problem in these processes. Zhao *et al.*²⁹ have further reported the catalytic nature of ZnO used as the precursor for homogeneous catalytic synthesis of DMC from urea and methanol. Our group has disclosed highly selective synthesis of DMC from urea and methanol catalyzed by metal-chloride ionic liquids in a homogeneous system.³⁰ Zinc-chloride ionic liquids represented high selectivity and activity for this reaction. As our continuous research work, here, we wish to report effective synthesis of DMC over a supported catalyst $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ in a batch reactor. As compared with the reported

Key Lab for Design & Synthesis of Functionalized materials and Green Catalysis, School of Chemistry and Chemical Engineering, Harbin Normal University, No. 1 Shida South Road Limin development Zone, Harbin 150025, P. R. China.
E-mail: qinghaic@yahoo.com.cn; Fax: +86-451-88060580;
Tel: +86-451-88060580

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literature, this report on highly selective synthesis of DMC by heterogeneous catalysis is very rare up to now.

2. Experimental

2.1 Materials

Chemicals used in this study include methanol (A. R.) and ethanol (A. R.), which were obtained from Tianjin Fuchen Chemical Reagent Company. Iron nitrate (A. R.) was provided by Tianjin Guangfu Institute of Fine Chemicals and urea (A. R.) was obtained from Shenyang Third Reagent Company. All the chemicals were commercial reagents with purity greater than 99 mass percent. MCM-49 zeolite (Si/Al = 22) was provided by Shanghai Novel Chemical Technology Co., Ltd. The standard DMC sample ($\geq 99.0\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

2.2 Preparation and characterization of the catalyst

HMCM-49 was prepared by the following procedure: 3.0 g of MCM-49 was added to 150 mL of 2.0 mol L^{-1} NH_4NO_3 aqueous solution. The resulting mixture was heated to 353 K in a water bath and stirred at this temperature for 12 h. After cooling to room temperature, the mixture was filtered under reduced pressure, affording a white solid. The solid was then dried at 373 K for 5 h after washing with deionized water, followed by calcination at 823 K for 3 h in an oven. The above procedure was repeated two times. At last a white HMCM-49 was obtained.

A typical procedure used for preparing $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ was as follows: 1.0 g HMCM-49 was impregnated with 5.8% $\text{Fe}(\text{NO}_3)_3$ solution in ethanol and stirred at room temperature for 12 h. Thereafter, the resulting mixture was filtered, affording a solid material and the solid was dried at 373 K for 3 h after washing with deionized water, followed by calcination at 773 K for 2 h. $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ was obtained after cooling to room temperature.

The XRD of the samples was performed on a Bruker-D8 Advance X-ray diffractometer with Cu $\text{K}\alpha$ radiation (40 kV and 36 mA). FT-IR spectra of the samples were recorded on a vertex 80 infrared spectrometer (Bruker Company). The loading of Fe_2O_3 on HMCM-49 was determined by 7500CE ICP-MS (Agilent Company).

2.3 Catalytic tests

The catalytic reaction was conducted in a stainless steel 0.5 L autoclave with an electric heater and a mechanical stirrer. In a typical procedure, 68 mL (1.68 mol) of anhydride methanol, 0.632 g (0.0105 mol) of urea and 0.3 g of the catalyst ($\text{Fe}_2\text{O}_3/\text{HMCM-49}$) were charged into the reactor in turns. After purging three times with N_2 gas, the reactor was heated to 453 K with a stirring rate of 500 rpm and the reaction was carried out for 8 h. At the end of the reaction, the mixture solution was filtered to remove the catalyst and the filtrate was analyzed by GC and GC-MS.

3. Results and discussion

3.1 Catalyst characterization

Fig. 1 illustrates XRD patterns of HMCM-49 and $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ as compared with that of MCM-49. The materials

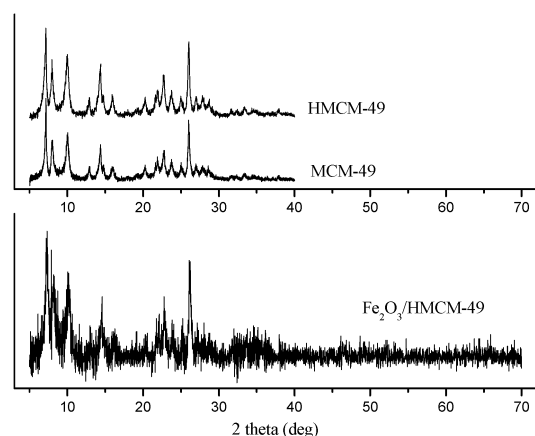


Fig. 1 XRD patterns of MCM-49, HMCM-49 and $\text{Fe}_2\text{O}_3/\text{HMCM-49}$.

HMCM-49 and $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ basically retain the original structure of MCM-49, although addition of iron has a negative effect on the crystalline structure. Moreover, no diffraction peak corresponding to crystalline iron oxides could be observed in the XRD pattern of $\text{Fe}_2\text{O}_3/\text{HMCM-49}$. Possibly, the particle size of iron oxides in the sample was too small to be detected by X-ray diffraction. When the loading of iron onto HMCM-49 was increased from 0.69% to 5.04%, two characterization peaks at 33.5° and 35.3° corresponding to highest peaks of $\alpha\text{-Fe}_2\text{O}_3$ (hematite form) were observed in the XRD pattern (not listed here), which suggested that iron has been supported on the materials in the $\alpha\text{-Fe}_2\text{O}_3$ style. Furthermore, the brown color of the obtained solid materials and chemical analysis of the supported materials by ICP-MS verified the existence of iron species in the sample.

TPD profiles of NH_3 adsorbed on MCM-49, HMCM-49, SBA-15, ZSM-5, HY and $\text{SO}_4^{2-}/\text{ZrO}_2$ were recorded (Fig. 2). Two broad desorption peaks were observed on MCM-49 and HMCM-49 at 523 K and 639 K, which represent the weak and strong acid centers on the molecular sieves, respectively. However, the two peaks on HMCM-49 are remarkably stronger than that on MCM-49, suggesting that the exchange of NH_4^+ with Na^+ on MCM-49, that is, the preparation of HMCM-49 was successful. A very low desorption peak on SBA-15 was observed at 498 K, which implied that SBA-15 possesses much weaker acidity as compared with the two molecular sieves,

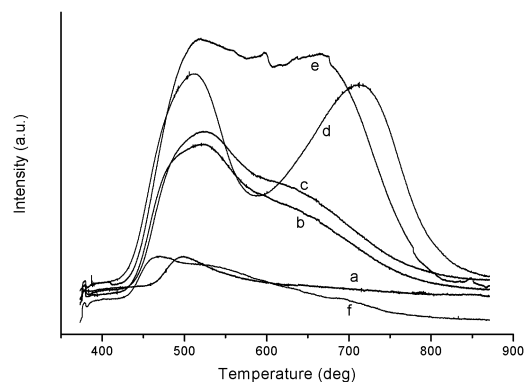


Fig. 2 NH_3 -TPD profiles of SBA-15 (a), MCM-49 (b), HMCM-49 (c), ZSM-5 (d), HY (e) and $\text{SO}_4^{2-}/\text{ZrO}_2$ (f).

Table 1 Catalytic performance over various catalysts

Entry	Catalyst	Yield (%)
1	SBA-15	0
2	MCM-49	3.7
3	HMCM-49	4.1
4	Fe ₂ O ₃	2.4
5	Fe ₂ O ₃ /SBA-15	10.0
6	Fe ₂ O ₃ /MCM-49	14.7
7	Fe ₂ O ₃ /HMCM-49	20.5
8	Fe ₂ O ₃ /HY	7.0
9	Fe ₂ O ₃ /HZSM-5	3.2
10	Fe ₂ O ₃ /SO ₄ ²⁻ /ZrO ₂	2.4

MCM-49 and HMCM-49. Comparatively, ZSM-5 and HY zeolites possess stronger acidity than HMCM-49 does and a very weak desorption peak was found on the solid superacid SO₄²⁻/ZrO₂ although it usually possesses strong acidity.

3.2 Catalytic performance of various catalysts

The alcoholysis of urea for producing DMC over various catalytic materials MCM-49, HMCM-49, SBA-15, α -Fe₂O₃, Fe₂O₃/SBA-15, Fe₂O₃/MCM-49, Fe₂O₃/HMCM-49, Fe₂O₃/HY, Fe₂O₃/HZSM-5 and Fe₂O₃/SO₄²⁻-ZrO₂ was tested and the results are shown in Table 1. In blank reactions, the pure microporous molecular sieves, MCM-49, HMCM-49 and α -Fe₂O₃, exhibited very low activity (entries 2–4), while pure mesoporous SBA-15 was completely inactive for the reaction (entry 1). In contrast, the Fe₂O₃ supported materials Fe₂O₃/SBA-15, Fe₂O₃/MCM-49 and Fe₂O₃/HMCM-49 were found to be more active than the above simple catalysts (entries 5–7). It was noted that Fe₂O₃/HMCM-49 exhibited the highest activity for DMC synthesis from methanol and urea with 20.5% yield of DMC and about 98.0% selectivity, as compared with Fe₂O₃/MCM-49 and Fe₂O₃/SBA-15. The differences in the catalytic activity between the simple and supported catalytic materials might be explained on the basis of the highly dispersed Fe₂O₃ on porous materials, also the acidity on the surface of the materials plays a key role in the activation of urea and methanol. For example, the activity order of these catalysts is: Fe₂O₃/HMCM-49 > Fe₂O₃/MCM-49 > Fe₂O₃/SBA-15 for supported materials and HMCM-49 > MCM-49 > SBA-15 for simple ones, which is consistent with their activity order. In order to explore the role of the surface acidity, other iron supported catalysts Fe₂O₃/HY, Fe₂O₃/HZSM-5 and Fe₂O₃/SO₄²⁻-ZrO₂ with stronger acidity than Fe₂O₃/HMCM-49 were tested and they exhibited very low activity for the reaction (entries 8–10). This result suggested that strong acidity on the material surface is disadvantageous for the synthetic reaction, which may cause the strong interaction with NH₂ in the urea molecule to restrain its further reaction. Therefore, the catalyst with medium acidity could effectively activate urea and methanol and interact with NH₃ gas released in the reaction to promote shift of the reaction equilibrium to the direction producing DMC, which is validated in the following sections.

3.3 Effect of reaction conditions

3.3.1 Effect of the catalyst dose. The effect of catalyst (Fe₂O₃/HMCM-49) dose on the yield and selectivity to DMC was studied by varying its amount from 0.1 to 1.0 g at 453 K with

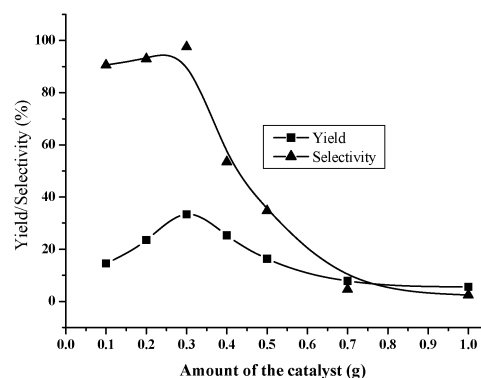


Fig. 3 Effect of the catalyst dose. Reaction conditions: methanol/urea ratio 160 : 1; reaction temperature 453 K; time 8 h; loading of Fe 0.69%.

0.69% loading of iron, as shown in Fig. 3. The yield was increased from 14.5% to 33.4% with increase in the catalyst amount from 0.1 to 0.3 g, which should be due to increase in the amount of acidic sites. Thereafter, the yield declined rapidly as the catalyst amount continuously increased. The excess amount of the catalyst could cause the reactants or the product DMC to further convert into some byproducts, *i.e.* *N*-methyl urea, *N*-methyl methyl carbamate. As a result, the selectivity to DMC inevitably decreased, leading to the sharp fall of the yield.

3.3.2 Effect of reaction temperature. The effect of reaction temperature on DMC yield is shown in Fig. 4. It could be seen that the DMC yield increased as the temperature increased in the range of 423–453 K, and then it decreased when the reaction temperature exceeded 453 K. Since the reaction is an endothermic reaction, it is greatly advantageous for the synthesis of DMC from urea and methanol at a higher reaction temperature from a viewpoint of thermodynamics. In the viewpoint of kinetics, raise of the reaction temperature can accelerate the reaction and shorten the time to approach the equilibrium. Therefore, the yield increased with rising temperature in the range from 423 to 453 K. Nevertheless, it was known that urea begins to decompose into NH₃ and isocyanic acid HNCO at a temperature of 408 K under ambient pressure. The formation of active species HNCO is

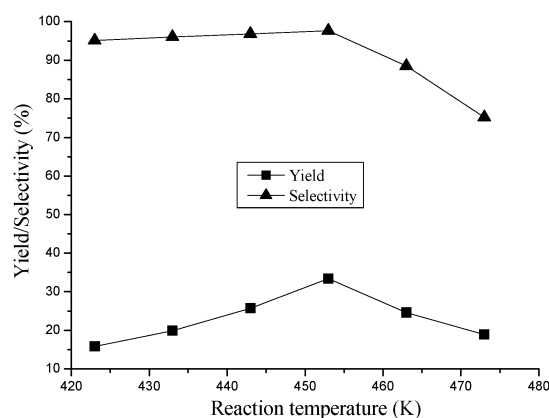


Fig. 4 The effect of reaction temperature on DMC yield. Reaction conditions: methanol/urea ratio 160 : 1; reaction time 8 h; amount of catalyst 0.3 g; loading of Fe 0.69%.

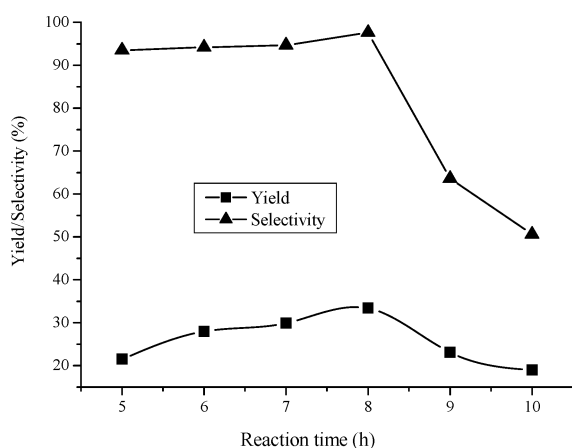


Fig. 5 The effect of reaction time on DMC yield. Reaction conditions: methanol/urea molar ratio 160:1; reaction temperature 453 K; amount of catalyst 0.3 g; loading of Fe 0.69%.

advantageous for the synthesis of DMC as reported by Wang *et al.*³¹ At the same time, the rapid decomposition of urea at high temperature can lead to reaction of HNCO with urea or DMC to generate byproducts. Thus, the rapid decline in the DMC yield observed over 453 K was due to the sharp decline in selectivity.

3.3.3 Effect of reaction time. The yield/selectivity–time profile of the reaction was also examined in the range of 5–10 h. As seen in Fig. 5, the yield increased with reaction time up to 33.4% at 8 h. Then the yield declined when the reaction proceeded continuously. However, the selectivity to DMC was almost unchanged in the time range from 5 to 8 h. When the reaction time exceeded 8 h, the selectivity was sharply decreased due to further reaction of DMC with urea to produce byproducts, which leads to the decline in yield.

In short, the effect of various reaction conditions on the catalytic synthesis of DMC from urea and methanol was investigated and the optimal operational conditions were obtained: reaction temperature 453 K, reaction time 8 h, CH₃OH/urea molar ratio 160/1 and amount of the catalyst 0.3 g with 0.69% loading of Fe. 34.2% conversion of urea with TON of 284.1 mol per mol_{Fe} and about 98% selectivity are achieved, giving 33.4% yield of DMC under the optimal conditions. To our knowledge, this is the highest activity for DMC synthesis from urea and methanol in the batch reactor among the reported results in literature.

3.4 Reusability of the catalyst

In order to further evaluate the performance of the catalyst, recovery and reuse of the catalyst were explored. At the end of the reaction, the reaction mixture was centrifuged and the catalyst was separated. After being calcined at 773 K for 2 h it was reused in the next run under the same conditions. The results shown in Table 2 indicate that the activity of the catalyst was almost not affected even at the fourth run, but the selectivity to DMC was greatly dependent on the number of times it was reused. The selectivity remarkably declined after the catalyst was reused three times, which may be ascribed to iron species agglomeration of small particles on the surface of the catalyst. This was affirmed by the XRD patterns of fresh and reused Fe₂O₃/HMCM-49 (Fig. 6). In the

Table 2 The reusability of the catalyst

Times	Conversion (%)	Selectivity (%)	Yield (%)
1	34.2	97.6	33.4
2	33.6	90.2	30.3
3	27.8	81.9	22.8
4	30.0	42.6	12.8
2 ^a	14.5	93.0	13.5

^a Reused once without calcination.

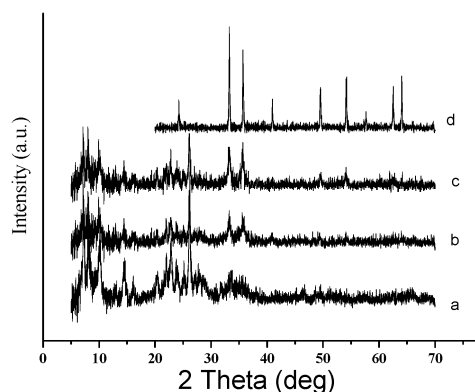


Fig. 6 XRD patterns of reused catalysts (a) fresh; (b) after first reuse; (c) after second reuse; (d) α-Fe₂O₃.

XRD pattern the characteristic peaks of α-Fe₂O₃ were obviously observed for the catalysts after used two or three times, verifying iron species agglomeration on the surface. It is the bulk iron oxide on the surface that causes by-reactions to occur due to the activity of Fe(III) on the compounds containing nitrogen in the molecules, resulting in the decrease of the selectivity. In addition, the catalyst used for the second time without calcination showed low activity for the DMC synthesis, which was likely ascribed to Fe₂O₃/HMCM-49 absorbing NH₃ produced in the reaction to form Fe₂O₃/NH₄MCM-49. The FT-IR spectrum of the used catalyst verified the existence of NH₄⁺ (Fig. 7). In the spectrum, the absorption bands observed at 2958.1 and 2858.9 cm⁻¹ were attributed to the stretching vibrations of the N–H bond and the bands at 1687.3 and 1485.6 cm⁻¹ were likely due to the bending vibration of N–H and N⁺–H bonds. This result also suggested that the catalyst

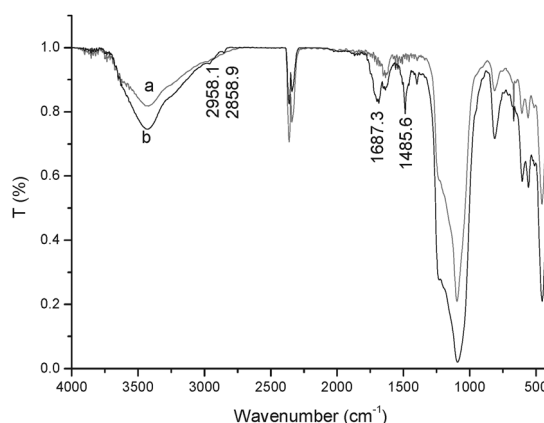
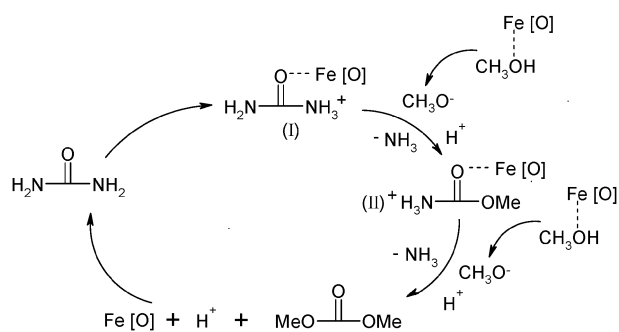


Fig. 7 FT-IR spectra of fresh (a) and reused (b) catalyst.



Scheme 1 Reaction mechanism.

can absorb the released NH_3 to shift the reaction equilibrium to the direction producing DMC.

In addition, the leaching of $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ was investigated after the reaction. The Fe^{3+} content in the reaction mixture was not detected, which implied that the Fe^{3+} content in the reaction mixture is lower than 10^{-10} according to ICP-MS precision although the iron species agglomeration on the surface was found for the reused catalyst. This confirmed that the catalytic process is really heterogeneous.

3.5 Reaction mechanism

It was known that the complexes were easily formed by urea molecules coordinating to metal ions through the oxygen as well as the nitrogen atoms.^{32,33} On the basis of these facts, as well as the experimental results obtained in this case, the reaction mechanism of DMC synthesis from urea and methanol catalyzed by $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ was proposed and is shown in Scheme 1. This reactive procedure involves the mutual activation of urea by Fe [O] and H^+ on the catalyst surface to form activated intermediate I and the activation of methanol by Fe [O] to generate methoxide anion CH_3O^- . Then, methoxide anion CH_3O^- attacks the positively charged carbonyl carbon in the molecule of the intermediate I to generate the intermediate II, which is methyl carbamate coordinated to Fe [O] and H^+ . Finally, the activated methyl carbamate reacts with another CH_3O^- to produce the target product DMC and release Fe [O] and H^+ realizing the catalytic cycle. In this mechanism, it was worthy to note that the two activated particles, CH_3O^- and activated methyl carbamate, in the reaction, possess high reactivity to form DMC, which may make the selectivity of DMC reach too high due to the fast rate of the second step of the synthesis reaction.

4. Conclusions

The prepared $\text{Fe}_2\text{O}_3/\text{HMCM-49}$ was found to be an effective catalyst for the DMC synthesis from urea and methanol, exhibiting a high conversion of 34.2% with a TON of 284.1 mol per mol_{Fe} and a selectivity of 97.4%. This high catalytic activity for the reaction was verified to be dependent on the medium acidity of the surface and highly dispersed Fe_2O_3 on the surface of the catalyst. The catalyst was easily recovered and reused. The catalytic activity of the reused catalyst was almost not affected even at the fourth run, but the selectivity to DMC was greatly dependent on the number of times it was reused. The investigation showed that this decline in the selectivity may be ascribed to iron species

agglomeration of small particles on the surface of the material. Besides, on the basis of the previous report in literature and the experimental results obtained in this case the mechanism of the synthesis reaction *via* the mutual activation of urea by Fe [O] and H^+ was proposed.

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