



## Non-phosgene route for the synthesis of methyl phenyl carbamate using ordered AISBA-15 catalyst

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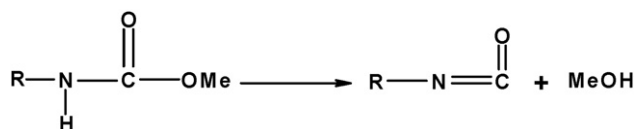
### ABSTRACT

Methyl phenyl carbamate (MPC) has been synthesized under liquid phase conditions from dimethyl carbonate and aniline by using mesoporous AISBA-15 catalyst. The catalyst with different Si/Al ratio was synthesized by isomorphous substitution of aluminium into the framework of siliceous SBA-15. The structural integrity of the catalyst system was diagnosed with the help of various characterization techniques such as X-ray diffraction, surface analysis, and the acidity measurement has been done by TPD using ammonia as probe molecule. AISBA-15 (Si/Al = 10) exhibited highest catalytic activity in the synthesis of MPC under the reaction conditions studied. The effect of parameters such as molar ratio of reactants, catalyst concentration, reaction temperature and time on the conversion of aniline was investigated. The results demonstrated that an aniline conversion of 99% and MPC selectivity of 71% were achieved when the reaction was carried out at 100 °C, DMC to aniline mole ratio of 10 with 5% of catalyst (wt% of total reaction mixture) for 3 h.

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### 1. Introduction

There has been significant interest in the manufacture of carbamates (isocyanate precursors) due to their commercial value as intermediates [1] for the synthesis of pesticides, fungicides, herbicides [2,3], medical drugs [4,5], polyurethane foams. In organic synthesis, carbamates are often used as protecting groups for amine functionality [6]. The important and extensive application of carbamates has made them compounds of great interest. Moreover they can be transformed into isocyanates by thermal cracking as shown below.



Isocyanates are used as precursors to polyurethane elastomers, agrochemicals, adhesives and reaction injection mouldings [7,8]. Originally carbamates were almost exclusively synthesized by the reaction of amines with phosgene or its derivatives [9]. This procedure had several drawbacks, among which the extreme toxicity of phosgene and generation of byproduct HCl is the main. So, sev-

eral efforts have been made for the preparation of the carbamate compounds using non-toxic reagents and for the development of novel environmentally friendly methodologies. Carbamate synthesis has been accomplished by oxidative carbonylation of aromatic amines [10–13], reductive carbonylation of aromatic nitro derivatives [14–16], and methoxycarbonylation of amines [17–22] and substituted urea [23,24]. Compared to different methods, methoxycarbonylation of amines has been less studied because DMC has long been synthesized from methanol and phosgene. DMC is now industrially produced on large scale by oxidative carbonylation of methanol with CO<sub>2</sub> [25] which have lowered its cost of production. Thus, the use of alkyl carbonates is becoming an attractive route for the synthesis of carbamates.

Various homogeneous catalysts are reported for synthesis of MPC from aniline and DMC. Most of the catalysts used are zinc [26–30] and lead [18,31] compounds. Zinc acetate was found to be the most active for MPC synthesis. Gurgilio [27] prepared MPC over zinc acetate and achieved 99.8% selectivity. Baba et al. [32] used zinc acetate as catalyst in synthesis of mono and dicarbamate while Xue et al. [29] used the same catalyst for synthesizing toluene-2,4 dicarbamate. Among the lead compounds Fu et al. [17] used Pb(OAc)<sub>2</sub>. Pb(OH)<sub>2</sub> as catalyst and achieved 95% carbamate selectivity. Toshihide et al. [18] used Pb(NO<sub>3</sub>)<sub>2</sub> for methoxycarbonylation of aliphatic amines. Though zinc and lead compounds exhibit high conversion and selectivity, they possess certain drawbacks. It was found that zinc acetate easily lost its activity because its change to ZnO after being used once only. Lead compounds in spite of their

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excellent catalytic activity could not be used due to their toxicity and environmental non-friendliness. Besides this, product separation and recovery of homogeneous catalysts are also difficult. To overcome the aforementioned shortcomings, synthesis of MPC was studied using solid acid catalysts. Li et al. [33] used  $\text{In}_2\text{O}_3/\text{SiO}_2$  but the catalytic activity was low and MPC yield was only 59.4%. But Li et al. [34] used  $\text{ZrO}_2/\text{SiO}_2$  and at a temperature of 443 K for 7 h, the conversion of aniline was 98% with 79.8% MPC selectivity. However, these claims have not been proved to be successful in large scale MPC production.

Aluminium containing mesoporous silica was expected to show high catalytic performance for the reaction of relatively large molecules since the isomorphous substitution of aluminium into mesoporous framework of MCM-41 and SBA-15 induces the Brønsted and Lewis acidity [35]. However, only a few applications of mesoporous aluminosilicate to acid catalyzed reaction have been realized. Katada et al. [36] have studied the use of AIMCM-41 for the synthesis of carbamates but unfortunately activity of the material was found to be less and low yield of carbamate was obtained. Due to lower hydrothermal stability of AIMCM-41 and low yield of carbamate we tried to explore this reaction with AISBA-15 having larger pore diameter, thicker pore walls, and higher hydrothermal stability. In the present paper, we have demonstrated the effective use of AISBA-15 for the synthesis of methyl phenyl carbamate from dimethyl carbonate and aniline. Our results presented in this manuscript demonstrate a non-phosgene route for the synthesis of MPC via methoxycarbonylation of aniline with DMC using an ordered heterogeneous AISBA-15 catalyst under liquid phase reaction conditions.

## 2. Experimental

### 2.1. Materials

Aniline was purchased from Merck India Ltd., dimethyl carbonate was purchased from Spectrochem India Ltd. aluminium chloride, tetraethyl orthosilicate (TEOS), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight, 5800) were procured from Aldrich, USA. All the chemicals were of research grade and were used after drying following standard procedures.

### 2.2. Catalyst preparation

**Synthesis of AISBA-15:** The synthesis of mesoporous silica SBA-15 was first reported by Stucky and co-workers [37]. In a typical synthesis, 4 g of amphiphilic triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight, 5800) was dispersed in 30 ml of water, and 120 g of 2 M HCl solution was added while stirring. 8 g of TEOS was then added to the homogeneous solution with stirring. This gel mixture was continuously stirred at 40 °C for 24 h and finally crystallized in a Teflon-lined autoclave at 100 °C for 2 days. After crystallization, the solid product was filtered, washed with distilled water, and dried in air at room temperature. The material was calcined in static air at 550 °C for 24 h to decompose the triblock copolymer and obtained a white powder SBA-15.

SBA-15 was used as the parent material to synthesize AISBA-15 via a post-synthesis route similar to that reported elsewhere [38]. Series of AISBA-15 catalysts (with Si/Al ratio ranging 10–40 taken in stoichiometric compositions during synthesis) were prepared using SBA-15. In a sample preparation, SBA-15 (1 g) was combined with 25 ml of dry ethanol containing different amounts of  $\text{AlCl}_3$  with magnetic stirring at 80 °C for 10 h. The solid material was then filtered, washed vigorously with dry ethanol, and dried at room

temperature in air to give AISBA-15. It was then calcined in static air at 550 °C for 5 h.

### 2.3. Characterization

Low-angle X-ray diffraction patterns of mesoporous samples were collected on a Philips X' Pert Pro 3040/60 diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), a nickel filter, and an X'celerator as a detector, using the real time multiple strip (RTMS) detection technique. XRD patterns were collected in the range of  $2\theta = 0.5\text{--}5$ .

The specific surface area of the catalysts was measured by  $\text{N}_2$  physisorption at liquid nitrogen temperature with an Omnisorb 100 CX (Coulter). Samples were dried at 300 °C in a dynamic vacuum for 2 h before the  $\text{N}_2$  physisorption measurements. The specific surface area was determined using the standard BET method on the basis of adsorption data. The pore size distributions were calculated from both adsorption and desorption branches of the isotherms using the BJH method and the corrected Kelvin equation. Pore volume values were determined using the  $t$ -plot method of De Boer.

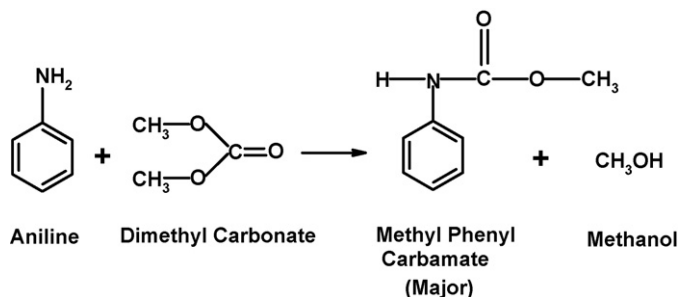
Acidity of the sample was measured by TPD of adsorbed  $\text{NH}_3$  (Micromeritics, Autochem 2910). The standard procedure for TPD measurements involved the activation of the sample in flowing helium at 500 °C (3 h), cooling to 25 °C adsorbing  $\text{NH}_3$  from a stream of  $\text{He-NH}_3$  (10%  $\text{NH}_3$  in  $\text{He}$ ), removing the physically adsorbed  $\text{NH}_3$  by desorbing at 100 °C for 1 h in  $\text{He}$  and finally carrying out the TPD experiment by raising the temperature of the catalyst at 10 °C/min.

### 2.4. Catalytic activity measurements

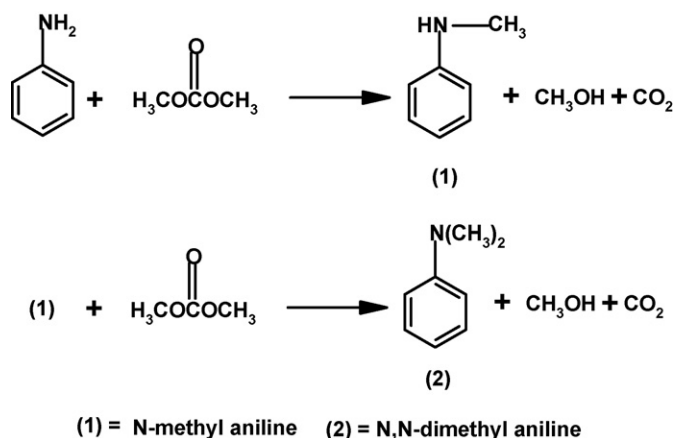
Experiments were carried out in a Parr autoclave with a capacity of 50  $\text{cm}^3$ . In a typical reaction, aniline (1.5 g), dimethyl carbonate (14.5 g) and catalyst (0.8 g, activated at 500 °C prior to use) were placed in the vessel. Samples were withdrawn at regular intervals of time and analyzed by gas chromatography (Shimadzu 14B) equipped with a cross-linked 5% diphenyl-95% dimethylpolysiloxane capillary column (30 m) and a flame ionization detector. The identities of products were confirmed by GCMS (Shimadzu GCMS QP 5000) equipped with an identical column and a mass selective detector. Conversions were calculated with respect to weight percentage of aniline since DMC was used in excess.

## 3. Results and discussion

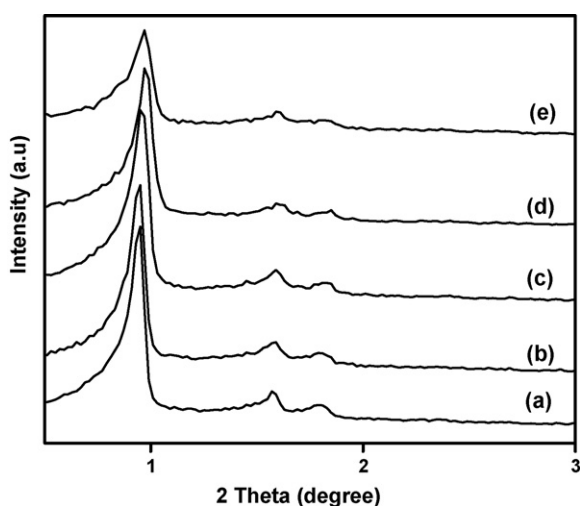
Methoxycarbonylation of aniline by DMC to give methyl phenyl carbamate (Scheme 1) was chosen as a model reaction to test the performance of AISBA-15 catalyst and comparing its activity with reported catalyst system, i.e. AIMCM-41. In this reaction MPC was formed in a major amount under the reaction conditions studied, whereas *N*-methyl aniline (NMA) and *N,N*-dimethyl aniline (DMA) were the minor products (Scheme 2).



**Scheme 1.** Synthesis of methyl phenyl carbamate from aniline and dimethyl carbonate.



**Scheme 2.** Possible side reaction in the reaction of aniline and dimethylcarbonate.



**Fig. 1.** Low-angle XRD patterns of (a) SBA-15, (b) AISBA-15 (10), (c) AISBA-15 (20), (d) AISBA-15 (30) and (e) AISBA-15 (40).

### 3.1. Characterization of the catalysts

XRD patterns of SBA-15 and calcined AISBA-15 catalysts with different Si/Al ratios shown in Fig. 1 ((a)–(e)) consist of three well-resolved peaks in the  $2\theta$  range of 0.8–1.8 correspond to the (1 0 0), (1 1 0), (2 0 0) reflections, which are associated with  $p6mm$  hexagonal symmetry in the materials. Isomorphous substitution of Al into the framework of siliceous SBA-15 by the post-synthesis method did not show any changes in the XRD pattern implying that the hexagonal mesoporous structure is retained after modification.

Textural properties such as specific surface area, specific pore volume, and mesopore size distribution are shown in Table 1.

**Table 1**  
Physicochemical properties of catalysts and their catalytic activities

Catalyst <sup>a</sup>	Si/Al (XRF)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (Å)	Total acidity (mmol g <sup>-1</sup> )	Aniline conversion wt (%)	Selectivity (%)	
							MPCC	NMA + DMA
SBA-15	∞	745	1.03	66.6	0.08	05	–	–
AISBA-15 (10)	17	685	1.31	76.7	0.23	86	67	33
AISBA-15 (20)	26	730	1.16	66.3	0.20	49	68	32
AISBA-15 (30)	36	720	0.99	63.5	0.16	27	82	18
AISBA-15 (40)	43	620	0.98	63.4	0.12	12	91	9
AlMCM-41 <sup>[36]</sup>	–	969	0.60	24.6	0.28	10	–	–

DMC: dimethyl carbonate, MPC: methyl phenyl carbamate, NMA: N-methyl aniline, DMA: dimethyl aniline, TRM: total reaction mixture weight = 16 g.

<sup>a</sup> Conditions: temperature = 100 °C, DMC/aniline mole ratio = 10, catalyst weight = 0.8 g (5 wt% of TRM), time = 2 h.

AISBA-15 showed a narrow pore size distribution with average mesopore size of 77 Å and high surface area of 685 m<sup>2</sup>/g. The overall N<sub>2</sub> adsorption amounts decreased depending on the aluminum loading though no particular trend was observed. Aluminating of SBA-15 did not affect the original pore structure of the parent SBA-15 while the surface areas slightly decreased with increase in aluminium loading (Table 1).

Our earlier studies confirmed the successful synthesis of AISBA-15 with retention of its periodicity and hexagonal arrangement of mesopores [39].

The acidities of the AISBA-15 (different Si/Al ratios) and SBA-15 samples were measured by NH<sub>3</sub>-TPD method and results are shown in Table 1. Total acidity increased with decrease in Si/Al ratio. This is due to the increase in number of acid sites on AISBA-15 with a decrease in Si/Al ratio. It is to be noted that pure mesoporous silica is acidic in nature (total acidity of 0.08 mmol/g of NH<sub>3</sub>) though the acidity is low compared to AISBA-15. These experiments clearly showed that acid sites were formed after aluminating on the surface of the solid.

### 3.2. Catalytic study

MPC synthesis from DMC and aniline has been carried out using AISBA-15 (with different Si/Al ratio). The results are compared with AlMCM-41 as reported by Katada et al. [36]. The characteristic data and catalytic activities of these catalysts are depicted in Table 1 along with the reaction conditions. AISBA-15 (Si/Al = 10) gave the highest activity with 86% aniline conversion with 67% selectivity to MPC and the others followed as AISBA-15 (20) (49%), AISBA-15 (30) (27%) and AISBA-15 (40) (12%). The results indicate that the conversion increases with decrease in Si/Al ratios, i.e. increase in acidity. The yield for MPC using AISBA-15 (10) was 58% whereas the yield for MPC was only 10% with AlMCM-41. It was found that AlMCM-41 in spite of its high surface area and acidity resulted in poor catalytic activity. This is due to its small pore size (24.6 Å) as compared to AISBA-15 (10) (76.7 Å) which hinders the accessibility to the acidic sites. Researchers have demonstrated that SBA-15 has thicker pore walls, higher hydrothermal stability than MCM-41. Additionally the pore diameter of SBA-15 can be tuned without disrupting its hexagonal channels, whereas enlarging the pore diameter of MCM-41 leads to diminished mesoscopic ordering [40]. These findings show the superiority of SBA-15 to MCM-41. Hence the difference in catalytic activity can be attributed to the difference in textural properties of SBA-15 and MCM-41. The acid sites inside the mesoporous cavities of AISBA-15 are more accessible than AlMCM-41 due to a larger pore size leading to a high conversion of substrate and Lewis acidity of aluminium leads to the formation of MPC.

MPC synthesis from aniline and DMC was studied by varying the temperatures (90–120 °C), keeping constant catalyst 0.16 g (1% of the total reactant weight) and aniline to DMC mole ratio as 1:10. The results are shown in Fig. 2. The results show that the

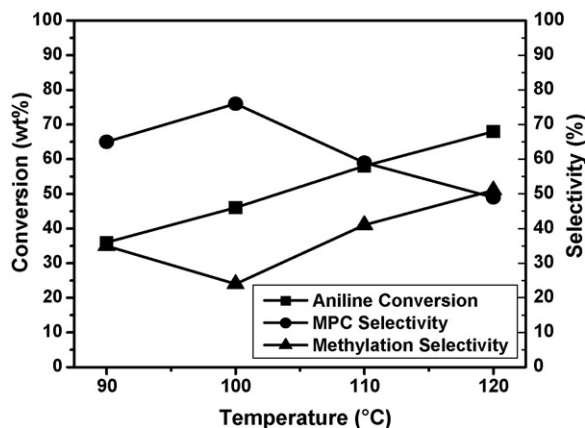


Fig. 2. Effect of reaction temperature on MPC synthesis.

activity (conversion of aniline) of the catalyst increases substantially with increasing reaction temperature. At 90 °C, the conversion was only 36%, which increased to 70% at 120 °C in 2 h of reaction. However, the distribution of the products show that selectivity of MPC increases with temperature up to 100 °C and the decreases apparently. At higher temperature (>100 °C), the side reactions are accelerated (Scheme 2) and *N*-methylation is more favorable than carbamate formation.

The reaction was also carried out with aniline to DMC molar ratios ranging from 1:5 to 1:20 keeping catalyst weight (0.16 g) and temperature (100 °C) constant and the results are shown in Fig. 3. The results show that the conversion of aniline increased from 12 to 67% on varying the molar ratio from 5 to 20 over a period of 2 h. This is because excess of DMC ensures complete conversion of aniline and is favorable to the reaction (Scheme 1) shifting towards the right side. However, the selectivity of MPC increased up to aniline to DMC mole ratio 1:10, and then decreased slightly. Thus the optimal aniline to DMC mole ratio is 1:10.

The effect of catalyst concentration on aniline conversion was studied at 100 °C with aniline to DMC mole ratio 1:10 for a period of 2 h (Fig. 4) by varying its concentration from 1 to 7 wt%. It shows that as the catalyst concentration increases, the conversion of aniline increases for more active sites provided by the catalyst. When the catalyst weight is 5% of the total reaction mixture weight, aniline converts almost completely and MPC selectivity reaches the maximal value (65%). With further increase in catalyst weight MPC selectivity decreases.

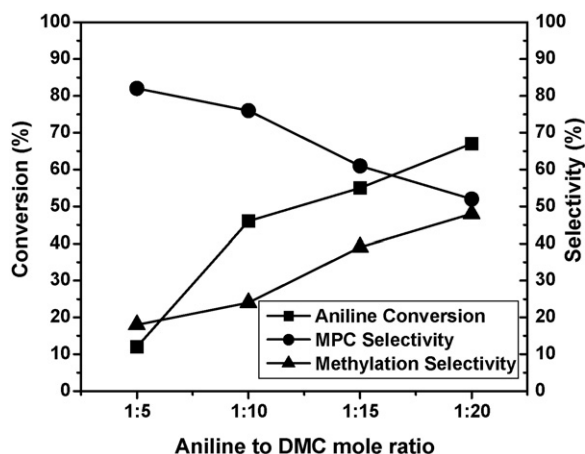


Fig. 3. Effect of aniline to DMC mole ratio on MPC synthesis.

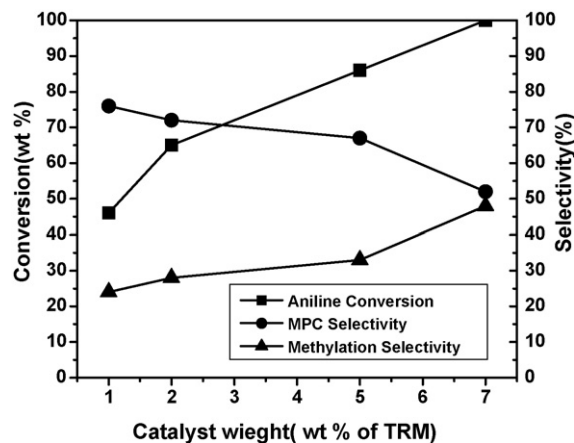


Fig. 4. Effect of catalyst concentration on MPC synthesis.

The effect of reaction time on the activity of the catalyst was studied at 100 °C with aniline to DMC mole ratio 1:10, catalyst weight 5%. The results are shown in (Fig. 5). The conversion of aniline increases with time and aniline converts completely in 3 h. MPC selectivity increases with reaction time and reaches the maximum (71%) in 3 h almost does not change afterwards. At optimized reaction conditions; 100 °C, aniline to DMC molar ratio of 1:10, catalyst weight 0.8 g and total reactant weight 16 g, the conversion of aniline was found to be 99% with 71% selectivity for MPC after 3 h.

In order to check the leaching of framework Al into the reaction mixture during the course of the reaction, reaction was carried out for 2 h under selected reaction conditions. The reaction was then stopped and catalyst was separated by filtration of hot reaction mixture and same reaction mixture was stirred further 6 h. The results are shown in the (Fig. 6). It was found that in the absence of the catalyst, there was no further increase in the conversion of aniline, which indicated the absence of leaching of Al. The above study ensured that the methoxycarbonylation is purely a heterogeneously catalyzed reaction.

The recyclability of AISBA-15 (10) catalyst was tested in the synthesis of MPC from DMC and aniline by conducting five runs (~86% conversion after 2 h) using selected reaction conditions. After each run, the catalyst was repeatedly washed with DMC, dried at 120 °C for 2 h and calcined at 550 °C in air for 4 h. It was then used with a fresh reaction mixture. The result is shown in (Fig. 7). It was found

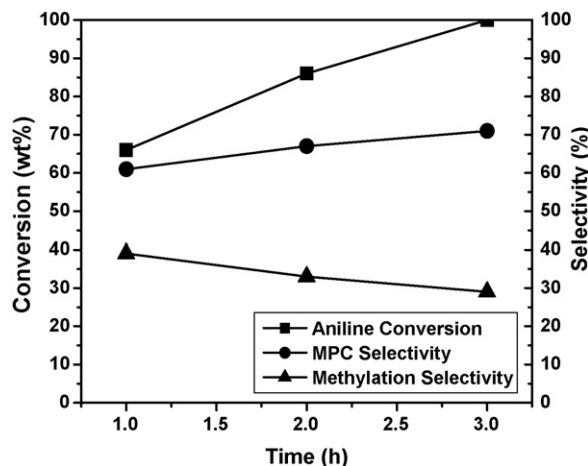


Fig. 5. Effect of reaction time on MPC synthesis.

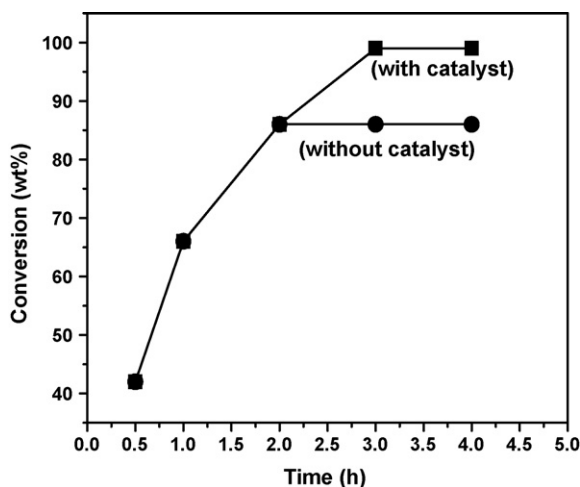


Fig. 6. Leaching of the catalyst.

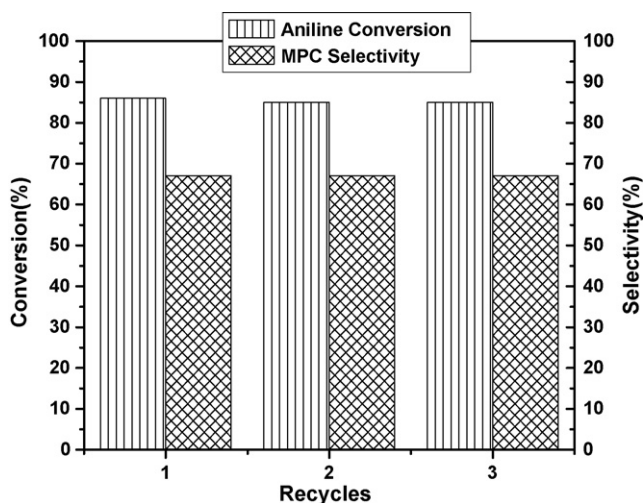


Fig. 7. Recyclability of the catalyst.

that the conversion of aniline was practically the same in all the five cycles.

#### 4. Conclusions

Here, we are reporting an environmentally benign method for synthesizing methyl phenyl carbamate from dimethyl carbonate and aniline using mesoporous AISBA-15 as solid acid catalyst. AISBA-15 was successfully synthesized by isomorphous substitution of aluminium into SBA-15 framework, which induces the Brønsted and Lewis acid sites in the material. Compared to other

conventional catalyst system, AISBA-15 showed higher catalytic activity due to its larger pore diameter, which could make the acid sites better accessible for the substrates.

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#### References

- [1] P. Adams, F.A. Baron, *Chem. Rev.* 65 (1965) 567–602.
- [2] W. Thai-The, J. Huang, N.D. Arrington, G.M. Dill, *J. Agric. Food Chem.* 35 (1987) 817–823.
- [3] P. Piccardi, *Chim. Ind.* 68 (1986) 108–117.
- [4] I. Vauthey, F. Valot, C. Gozzi, F. Facche, M. Lemaire, *Tetrahedron Lett.* 41 (2000) 6347–6350.
- [5] J. Barthelemy, *Lyon Pharma.* 37 (1986) 249–263.
- [6] T.W. Greene, P.G.M. Nuts, *Protective Groups in Organic Synthesis*, 3, J.W. Wiley Sons, 1999, pp. 503–550.
- [7] R. Moore, W.C. Welch, D.D. Russel, *Polyurethane World Congress* 991, 863.
- [8] S. Ozaki, *Chem. Rev.* 72 (1972) 457–496.
- [9] H. Eckert, B. Foster, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 894–895.
- [10] S. Kanagasabapathy, A. Thangaraj, S.P. Gupte, R.V. Chaudhari, *Catal. Lett.* 25 (1994) 361–364.
- [11] S. Fukuoka, M. Chono, M. Kohno, *J. Chem. Soc. Chem. Commun.* 6 (1984) 399–400.
- [12] S. Fukuoka, M. Chono, M. Kohno, *J. Org. Chem.* 49 (1984) 1458–1460.
- [13] Ber Chan, et al., *Green Chem.* 5 (2003) 484–489.
- [14] E. Alessio, G. Mestroni, *J. Organometall. Chem.* 291 (1985) 117–127.
- [15] A. Bassoli, R. Rindone, S. Tollari, *J. Mol. Catal.* 60 (1990) 155–163.
- [16] F. Ragaini, S. Cenini, *J. Mol. Catal. A: Chem.* 161 (2000) 31–38.
- [17] Z.H. Fu, Y. Ono, *J. Mol. Catal.* 91 (1994) 399–405.
- [18] T. Baba, M. Fujiwara, A. Oosaku, A. Kobayashi, R.G. Deleon, Y.S. Ono, *Appl. Catal. A: Gen.* 227 (2002) 1–6.
- [19] S.B. Halligudi, R.V. Choudhari, L.K. Doraiswamy, *Ind. Eng. Chem. Process Des. Dev.* 23 (1984) 794–801.
- [20] M.M. Taqui Khan, S.B. Halligudi, S.H.R. Abdi, S. Shukla, *J. Mol. Catal.* 48 (1988) 325–333.
- [21] M.M. Taqui Khan, S.B. Halligudi, S. Shukla, *J. Mol. Catal.* 57 (1990) 301–305.
- [22] M.M. Taqui Khan, S.B. Halligudi, N.S. Rao, *J. Mol. Catal. A* 59 (1990) 303–309.
- [23] J. Wang, Q. Li, W. Dong, M. Kang, X. Wang, *Appl. Catal. A* 261 (2004) 191–197.
- [24] K. Hwang, Y. Chen, H. Liao, *Eur Patent* 0709363 (1996).
- [25] D. Delledone, F. Rivette, U. Romano, *Appl. Catal. A* 221 (2001) 241–251.
- [26] Y. Wang, X. Zhao, F. Li, S. Wang, J. Zhang, *J. Chem., Technol. Biotechnol.* 76 (2001) 857–861.
- [27] A.E. Gurgilio, *U.S. Patent* 4,268,683 (1981).
- [28] X. Zhao, Y. Wang, S. Wang, H. Yang, *J. Ind. Eng. Chem. Res.* 41 (2002) 5139–5144.
- [29] W. Xue, J. Cong, F. Li, X. Zhao, Y. Wang, *Acta Petrol. Sin.* 18 (2002) 50–54.
- [30] T. Baba, A. Kobayashi, T. Yamauchi, H. Tanaka, *Catal. Lett.* 82 (2002) 193–197.
- [31] W. Kang, J. Yao, G. Wang, C. Hu, X. Jing, *J. Mol. Catal. (China)* 17 (2003) 136–139.
- [32] T. Baba, A. Kobayashi, Y. Kawanami, K. Inazu, A. Ishikawa, T. Echizenn, K. Murai, S. Aso, M. Inomata, *Green Chem.* 7 (2005) 159–165.
- [33] Q. Li, J. Wang, W. Dong, *Chin. J. Catal.* 24 (2003) 639–642.
- [34] F. Li, J. Miao, Y. Wang, X. Zhao, *Ind. Eng. Chem. Res.* 45 (2006) 4892–4897.
- [35] R. Ryoo, S. Jun, J.M. Kim, M.J. Kim, *Chem. Commun.* (1997) 2225–2226.
- [36] N. Katada, H. Fujinaga, Y. Nakamura, K. Okumura, K. Nishigaki, M. Niwa, *Catal. Lett.* 80 (2002) 47–51.
- [37] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* 279 (1998) 548–552.
- [38] Z. Luan, M. Hartmann, D. Zhao, W. Zhou, L. Kevan, *Chem. Mater.* 11 (1999) 1621–1627.
- [39] G.V. Shanbhag, S.M. Kumbhar, S.B. Halligudi, *J. Mol. Catal. A* 284 (2008) 16–23.
- [40] D. Zhao, Q. Huo, J. Fena, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.