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Fabrication of Amine and ZrO₂ on MCM-41 as Acid-Base Catalysts for the Fixation of Carbon Dioxide

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Abstract: Highly porous catalysts based on MCM-41 with both acidic and basic sites such as ZrO_2 as an acid and amino propane triethoxy silane (APTES) as mild base are fabricated and characterized thoroughly XRD, SEM, TGA, TPRDO, BET, EDS, XPS and IR analysis. This catalyst shows synergistic effect for the activation of epoxide as well as carbon dioxide to synthesize cyclic carbonates. The presence of the free amine functional group activates the carbon dioxide molecule by absorption while the presence of zirconium metal activates the epoxide ring. The effect of amine loading and catalyst loading on cycloaddition reaction studied. Additionally, the cycloaddition reactions proceeds under solvent free, at mild reactions condition and the catalysts are recyclable in nature.

Introduction

The carbon dioxide (CO₂) molecule is the heat-consuming molecule and the increasing concentration of CO₂ on the earth surface causes the serious environmental treats. In recent days, great efforts have been carried out for the fixation of carbon dioxide to the value added chemicals. $^{\left[1\right] }$ The CO2 is thermodynamically stable and kinetically inert and hence require catalysts for the activation. To fix CO₂, the synthesis of five membered cyclic carbonates from epoxide and CO2 by cycloaddition reaction is one of the prominent reactions. It replaces the use of traditional toxic phosgene and provides 100 % atom economy.^[1a] Several catalysts for this reaction are reported previously, including metal oxides,^[2] porphyrin,^[3] salen metal complexes,^[4-6] alkali metal salts,^[7-8] transition-metal complexes,^[9-10] quaternary ammonium or quaternary phosphonium salts,^[12-13] ionic liquids,^[14] organocatalysts,^[15-16] MOFs^[17] and so on. Among them the porous heterogeneous catalysts are highly demanded and taking intense interest.^[18] Still there is a need to develop the heterogeneous catalysts which are stable to air, water, chemicals and temperature as well as functionalization of catalysts to make them catalytically more active.

MCM-41 is the form of mesoporous silica with diameters ranging from 2 to 10 nm having hexagonal arrangement of one dimensional mesopores.^[19] The MCM-41 works as an excellent support material, but it lacks any active sites and functional sites on its surfaces. Taking into consideration, researchers are paying much attention towards grafting of MCM-41 surface by different functional amine groups as well as by grafting various metal inside the MCM-41.^[19b] The organic component was trapped within the silica channel that forms an inorganic-organic

Anusandhan University, Khandagiri, Bhubaneswar-751030, Odisha, India Supporting information for this article is available hybrid material. This type of hybrid material containing organic functionalities on the surfaces of MCM-41 is well reported and utilized for the practical application in carbon capture and catalysis.^[20] While, the introduction of the various amine functional group into these materials, makes them highly potent catalysts and CO₂ adsorbents.^[21] While the presence of the zirconium metal with silica also makes the material acidic in nature.^[21f] With the aim of finding the efficient and heterogeneous catalysts for the CO₂ fixation, we anticipated the fabrication of the amine as well as zirconia metal on to the MCM-41 provides the acid base nature to activate the starting materials. In continuation of our research to the development various catalytic systems for the CO₂ fixation,^[22] herein, we report the synthesis, characterization and application of APTES modified ZrO₂-MCM-41 as heterogeneous bi-functional catalysts for the synthesis of cyclic carbonates from CO2 and epoxide. The various wt% of amine functional mesoporous silica with zirconium metal were tested for the synthesis of cyclic carbonates at milder reaction conditions. This developed methodology shows superior activity towards the synthesis of cyclic carbonates under mild and solvent free conditions, additionally this system is recyclable in nature.

Experimental

The Synthesis and characterization of APTES modified mesoporous ZrO₂-MCM-41 composite

Mesoporous ZrO₂ synthesized by a sol-gel mechanism using zirconium butoxide as a zirconia source and CTAB as a structure-directing agent. The pH maintained at 11.5 by adding NH₄OH solution. The rate of hydrolysis of zirconium butoxide was controlled by using the acetyl acetone and ethanol. In the first step 0.025 mol of CTAB were dissolved in 4 mol of water and 0.03 mol of NH3 and stirred for 1 hour. Next 0.1 mol of zirconium butoxide, 0.05 mol of acetyl acetone and 0.5 mol of ethanol added to the template slowly and again the mixture stirred for 3 hour. The as prepared mixture refluxed under stirring for 48 hours at 90°C. The resulting solid filtered, washed with acetone and dried for 10 hours at 100°C. Lastly, the final sample calcined in air at a ramp rate of 1°C min⁻¹ to 450°C for 5 hour to remove the surfactant species. The 2.4 gram of CTAB dissolved in 120 ml of deionized water under ambient condition. 8 ml of aqueous NH₄OH added after complete dissolution. Then 10 ml of trietoxy silane (TEOS, silica source) was added to the solution under vigorous stirring for 1 hour by keeping the Si/Zr=10. The mixture was filtered, and then air-dried at 80°C for 12 h. Different amounts of APTES (0.25 ml to 1.56 ml) were added to get different wt% of APTES modified mesoporous ZrO₂-MCM-41. A white precipitate obtained after stirring for 2 h at 80°C. The above products filtered hot, washed with water and ethanol. The as synthesized material treated with ethanol and conc. HCI (100:1) at 80°C for 6 h to remove the surfactant. The sample then filtered, washed with ethanol and dried at 60°C. The synthesized materials were denoted as x wt% Amine modified mesoporous ZrO₂@MCM-41 (x = 3.2, 6.4, 12.8, and 16.0 wt% respectively) (Scheme 1).

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As prepared composite APTES modified ZrO₂-MCM-41 were characterized by PXRD, BET surface area, FT-IR, SEM-EDX, temperature programmed desorption (TPD) and TGA/DTA analysis technique.

X-Ray Diffraction Analysis:

The phase and crystallinity of catalysts were identified by the powered XRD analysis. The high angle X-ray diffraction pattern of as prepared samples (mesoporous ZrO_2 -MCM-41 and different wt% APTES@ZrO_2-MCM-41) were analyzed in the range (2 Θ =100 to 700) shown in Figure 1. The sharp peaks are clearly visible in mesoporous crystalline ZrO_2. The reflection peaks are observed at 30.280, 35.40, 50.40, 55.30 and 60.10 corresponds to (111), (200), (122), (013), and (302) planes could be attributed to monoclinic phase of ZrO_2 (PDF. No. 00-003-0515).²⁴ More peaks are obviously disappeared, also the intensity seems not decreased. This may be due to the multilayer modification of amine on the surface of mesoporous ZrO_2-MCM-41 support. It affects the long range ordering and crystallinity of all the materials and shows the amorphous nature.



Figure 1 High angle XRD of (a) mesoporous ZrO_2 -MCM-41, (b) 3.2 wt%, (c) 6.4 wt%, (d) 12.8 wt% and (e) 16 wt% APTES@ZrO2-MCM-41 and inset low angle XRD (a) mesoporous ZrO_2 -MCM-41, (b) 16 wt% APTES@ZrO_2-MCM-41.

The low angle XRD pattern of mesoporous ZrO₂-MCM-41 and 16wt% modified APTES@ZrO₂-MCM-41 are shown in the Figure 1 (inset). The three diffraction peaks at d100, d110 and d200 shows that all the three samples reveal the mesoporosity and the presence of a periodic hexagonal arrangement of the channel was suggested.²⁵ MCM-41 has a long-range order of pore entrances, which confirms the highly ordered hexagonal structure. The in situ incorporation of mesoporous ZrO₂ into the MCM-41 to obtain mesoporous ZrO₂-MCM-41 support and after the APTES modification into mesoporous ZrO₂-MCM-41 the peaks are slightly shifted. The long-range ordering retained in all the modified sample and exhibits the hexagonal order.

N2 adsorption-desorption isotherm:

N₂ adsorption and desorption studies has been carried out to measure the surface area and physico-chemical properties of APTES modified mesoporous ZrO2-MCM-41 composites by BET method shown in supporting information (ESI, Figure S-1). The different textural properties (BET surface area, pore diameter and pore volume) of MCM-41, mesoporous ZrO₂, mesoporous ZrO₂-MCM-41 and APTES@ZrO₂-MCM-41 (16 wt%) are derived from the N_2 adsorption-desorption measurements are incorporated in Table S1 (ESI, Table S-1). The N₂ adsorptiondesorption isotherms of 16 wt% APTES represents the type IV isotherm with a hysteresis loop, indicating the presence of ordered mesoporosity, which is well-defined by Brunauer et al (ESI, Figure S-2).^[27] The surface areas of mesoporous ZrO₂ and ZrO2-MCM-41 were 80 m²g⁻¹ and 780 m²g⁻¹ respectively.²⁸ After modification of the support with APTES, the surface area of composite decreases slightly to 482 m²g⁻¹. This is because of the bonding between organic amine with support, the Si-OH and Zr-OH groups in the framework, which results in blockage of surface area of the composite. The pore-size calculated using the BJH equation from the adsorption branch of the isotherm is shown in Table 1 (ESI, S-1). Continual decrease in pore diameter and pore volume enables that the mesoporous ZrO₂ is well modified with MCM-41 forms support and again it was modified with amine and form composite (APTES@ZrO2-MCM-41) for catalytic application.

FTIR:

Fourier Transform Infrared spectra investigation endorses the existence of different functional groups present in the synthesized materials. In our study FT-IR analysis has been done for meso ZrO2, meso ZrO2-MCM-41, APTES modified different (3.2, 6.4, 12.8 and 16 wt %) meso ZrO₂@MCM-41 (See ESI, S-2). In all the samples, the broad peak at 3150-3650 cm⁻¹ are due to the stretching vibration mode of water adsorbed group. The symmetry and asymmetry stretching bonds of the amine modified samples exhibit the peaks at the range of 2850-2950 cm⁻¹ which express the functionalization of amine on mesoporous substrate. Another small intense peak in 3272 cm⁻¹ peak is attributed to symmetric -NH₂ stretching, and the bending vibrations of -NH in APTES, respectively. The water of hydration assigned to H-OH bending vibration and it is confirmed by the peak near 1648 cm⁻¹ in all the samples. A band near 1051-1250 cm⁻¹ is assigned to Si-O asymmetric stretching vibration in all the composites except meso ZrO2-MCM-41. Presence of a band around 952 cm⁻¹ is due to Si-O vibration in Si-OH group in MCM-41. This peak is absent in meso ZrO2-MCM-41 indicates the successful incorporation of amines into the meso ZrO₂. The successful modification of the surface of neat MCM-41 by amine is confirmed by indicating a peak near 590 cm⁻¹ is due to Zr-O-Si stretching vibrations. The band near 490 cm⁻¹ indicates the presence of zirconia in all the composite.[26]

SEM Study:

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Scanning electron micrographs of mesoporous ZrO_2 -MCM-41 and different wt% (3.2, 6.4, 12.8 and 16) amine functionalized ZrO_2 -MCM-41 are shown in Figure 2. The Scanning electron micrography (SEM) micrographs exhibit a variety of particle



Figure 2 SEM images of catalysts (a) ZrO_2 -MCM-41, (b) 3.2 wt%, (c) 6.4 wt%, (d) 12.8 wt%, (e) 16 wt% APTES@ZrO_2-MCM-41 and (f) EDS analysis of APTES@ZrO_2-MCM-41.

shapes and sizes. It has been seen that all the composites are well ordered and uniformly distributed over the surface of the support. The SEM image of mesoporous ZrO₂-MCM-41 (Figure 2a) revealed the small hexagonal tubular morphology and small agglomeration appears due to the accumulation of some particles together. However, the SEM images of the amine modified mesoporous ZrO₂-MCM-41 catalyst suggests that the material has spherical shaped. It is clearly visible in Figure 2 (d-e).

TGA Analysis:

The thermal gravimetric and differential thermal analysis (TG-DTA) of all the prepared composites (mesoporous ZrO_2 -MCM-41, APTES modified ZrO_2 -MCM-41) are revealed in (ESI, S-6). All the composites displayed loss of weight in all the stages. The first peak below 120°C describes the loss of physically adsorbed water molecule. In amine-modified composites, there is a higher rate weight loss than the mesoporous support ZrO₂-MCM-41 showing the functionalization with mesoporous ZrO₂-MCM-41. The weight loss in next the peak range between 300-400°C is due to the breakdown of APTES-O-Zr or APTES-O-Si. The last stage of weight loss above 500°C is due to the surfactant loss from the composites. The figures (ESI, Figure S-6) depicts the differential thermal analysis curves of mesoporous ZrO₂-MCM-41 and all APTES modified composites (3.2 wt%, 6.4 wt%, 12.8 wt% and 16 wt%). These curves are complementary to TGA curve. They presented three endothermic peaks, which resembles the TGA curves. The first peak around 100°C is due to water loss, the second one around 300-400°C is due the loss of amine and the last peak around 500°C corresponds to the loss of surfactant molecule.

TPD analysis:

The acidic as well as basic nature of synthesized APTES @ZrO₂-MCM-41 (16 wt%) were determined by temperature programmed desorption (TPD) analysis. Before analysis, the sample pre-treated with helium gas from 25 °C to 400 °C for 1.5 h to remove the adsorbed water molecule and impurities. Then, the samples were cooled to room temperature and then saturated with respective gases (NH₃ and CO₂) at 50 °C and TPD was carried out from 25 °C to 1000 °C at temperature ramp of 10 C/min using helium as inert gas at a flow rate of 20 cm³ /min. The ammonia TPD utilized to determine the acidity of the catalyst. This shows two peaks of the desorption of ammonia, a sharp peak at 130°C due to ammonia desorption and second peak near around 600 °C which is due to surfactant loss (ESI, figure S-4). While, to determine the basicity of the APTES@ZrO2-MCM-41(16 wt%) catalysts CO2 TPD was utilized the presence of a broad peak at 640°C is due to the desorption of CO₂ and loss of surfactant (ESI, figure S-5).

Elemental analysis:

The presence C, N, O, Si and Zr elements of the catalyst (16 wt%) further confirmed by using the X-ray photoelectron spectroscopy (XPS) (ESI-S-11) as well as by using the EDS analysis (Figure 2, f).

Results and Discussion

Ensuring the acid-base functionalities together with high surface area of the synthesized catalysts, we decided to perform the cycloaddition reaction of propylene oxide (PO) with CO2 to propylene carbonate (PC) (Table 1). Initially, the solvent free reaction of PO to PC at the 2 MPa pressure of CO2 and at 80°C of temperature the cycloaddition reaction performed without the use of catalyst as well as co-catalysts and no any conversion of PO to PC noted (Table 1, entry 1). Then, we utilized the ZrO₂-MCM-41 as a catalyst along with tetra butyl ammonium iodide (TBAI) as co-catalyst for cycloaddition reaction, moderate conversion of PO to PC noted (Table 1, entry 2). Next, 3.2 wt% APTES@ZrO2-MCM-41 which containing the 3.2 wt% of amine was utilized for the cycloaddition reaction and slightly increased yield of PC noted (Table 1, entry 3). While the use of 6.4 wt% APTES@ZrO2-MCM-41 provided 70% conversion of PO to PC (Table 1, entry 4). Interestingly, it was observed that the use of

12.8 wt% APTES@ZrO₂-MCM-41 catalyst provide excellent conversion of PO to PC (Table 1, entry 5). Next, 16 wt% APTES@ZrO₂-MCM-41 as catalyst provided the excellent conversion among the all studied catalysts (Table 1, entry 6). The sudden change in the activity of catalyst observed, by increasing the amount of amine functional group on the catalyst. This effect may be due to the increased amount amine functional group may absorb the increased amount of CO₂ molecules. Next, the various co-catalysts studied for the cycloaddition reaction (Table 1, entries 7-10). The use of tetra butyl ammonium iodide (TBAB) as co-catalyst also provides the good conversion was observed (Table 1, entry 7). Then, for the epoxide ring opening we utilized the KI as co-catalyst and good conversion of PO to PC was noted (Table 1, entry 8). Next, various tertiary amines as co-catalysts were

Table 1. Optimization of the reaction conditions for synthesis PC. [a] 0 Catalyst CO_2 'n Т. P Selectivity Entry Catalyst wt % Conversion Co-catalyst (%)^[b] 1 ZrO₂-MCM-41 TBAI 51 >99 2 TBAI 3.2% 62 >99 3 6.4% TBAI 70 >99 4 TBAI >99 12 8% 89 5 16% TBAI 97 >99 6 16% TBAB 91 >99 7 16% ΚI 88 >99 8 16% DABCO 51 >99 9 16% DMAP 40 >99 10 16% Traces 11 16% TBAI 48 >99 12^[c] 16% TBAI 46 >99 13^[d] 16% TBAI 39 >99 14^[e] 16% TBAI 80 >99 15^[f] TBAI >99 31 16

Reaction conditions: PO (5.808 g, 0.1 mol), catalyst (10 mg), Temperature (80°C), Pressure (2 MPa), Time (3 h) co-catalyst (10 mg). [b] Determined by GC. [c] Time (1 h). [d] R.T. [e] R.T. for 12 h. [f] pressure 1 atm. Time (12 h) and Temp. 110 °C.

investigated along with 16 wt% APTES@ZrO₂-MCM-41 catalyst (Table 1, entries 9-10). The tertiary amine such as DABCO and DMAP provides moderate conversions as compared to other quaternary ammonium salts. While, without the use of any co-

catalyst very trace amount of conversion of PO was noted (Table 1, entry 11) hence, from above study we observed that the both the catalyst as well co-catalyst are need for the cycloaddition reaction. Next, the effect of time on reaction studied and it found that by decreasing the time, the decreased conversion of PO to PC noted (Table 1, entry 12). Next, the reaction performed at the room temperature up to 12 h. and moderate conversion of PO observed (Table 1, entry 13). Next, we performed the cycloaddition reaction at the room temperature and at 1 atm. pressure of CO_2 , moderate conversion of PO to PC noted (Table 1, entry 13). Next, we performed the atmospheric pressure of CO_2 , good conversion of PO noted (Table 1, entry 15). Next, the use of TBAI only on cycloaddition reaction studied and only 31% of yield of PC noted (Table 1, entry 16).

Next, we studied the effect of the catalysts loading on reaction system and it was found that the catalyst loading is also plays the important role in optimization of reaction condition (Figure 3).





Figure 3 Effect of loading APTES@ZrO₂-MCM-41 (16 wt%) catalyst on the cycloaddition reaction.



Figure 4 Effect of pressure of carbon dioxide on cycloaddition reaction OF PO to PC.

By decreasing catalysts loading from 10 mg to 2 mg decreased yield of PC were noted, hence we concluded that the 10 mg of catalysts loading is optimum loading. Then, the effect of

pressure of CO_2 on reaction system were investigated and it was found that the 2 MPa of pressure provides the excellent conversion, the use of 1.5 MPa of pressure also provide good conversion. By further decreasing the pressure, decreased conversion of PC noted (Figure 4).

After the optimization of reaction condition, we further explored the catalytic activity for the substrate study of epoxides to cyclic carbonates (Table 2). The simple aliphatic epoxides such as propylene oxide, epichlorohydrin and 1,2 epoxybutane were studied and it was found that they provide the excellent yield of corresponding carbonates (Table 2, entries 1-3). Next, the aromatic epoxide like styrene oxide was reacted under the



[a] Reaction conditions: Epoxide (0.1 mol), 16 wt% APTES@ZrO₂-MCM-41 (10 mg), TBAI (10 mg), CO₂ (2 MPa), Temperature (80°C), Time (3 h). [b] Determined by GC.

optimized reaction condition and excellent yield of styrene carbonate was noted (Table 2, entry 4). Then, the functional styrene oxide like *p*-fluoro-styrene oxide reacted and good yield of carbonate was noted (Table 2, entry 5). The chloro and bromo

substituted styrene also provide the good yield of carbonates (Table 2, entries 6-7). Then various aliphatic cyclic epoxides such as cyclopentene and cyclohexene oxide, were also well tolerated at the optimized reaction conditions and provide the good yield (Table 2, entries 8-9). All the epoxides show >99% selectivity towards the cyclic carbonates.

After the substrate study, we investigated the catalytic recyclability of the developed catalyst to evaluate the heterogeneity of the catalyst. Regarding this, the spent catalyst washed with ethanol for several times and then oven dried overnight and reused directly for another run. This catalyst shows high activity towards the cycloaddition reaction and provides up to five consecutive recycle run with negligible loss of yield, this may be the loss of handling (Figure 5). While the TGA analysis before and after the reaction shows the low weight loss in catalysts in after the recycled as compared to the before the reaction this may be due to the removal of water from catalyst (ESI, Figure S-6). Then recycled catalyst characterized by using SEM and TGA analysis to investigate the effect of structural and stability changes of catalysts. The SEM image of before and after the reaction shows that there is no any further changes was found (ESI, Figure S-7). The recycled catalyst further characterized by using the XPS analysis to investigate the any change of the oxidation state of the Zr metal. It was found that there are no further changes occurred on the oxidation state of the Zr metal (ESI, Figure S-9). The XPS spectra of the Zr metal as prepared and after the fifth recycle didn't show any electronically changes. To investigate the leaching of APTES and ZrO₂ metal the hot filtration test was carried out using reported method.^[23] The reaction mixture was evaporated on SEM holder for the elemental analysis (Si) and no leaching of Zr metal as well as APTES was noted hence we concluded that the catalyst is stable and active for this reaction. The leaching of zirconium metal by using the ICP-AES analysis also done and no leaching of zirconium metal detected. To investigate the catalytic activity and heterogeneous nature of APTES@ZrO2-MCM-41 catalyst, the hot filtration method was conducted (ESI, Figure S-8).^[23b] At the optimized reaction conditions the



Figure 5 Recyclability of the APTES@ZrO₂-MCM-41 catalyst for the cycloaddition reaction of PO with CO₂ to PC.

cycloaddition reaction performed and after the completion of one h the reaction mixture was hot filtered and separated the catalyst. Then, the resulting reaction mixture kept for the further reaction, while negligible increased yield of the PC noted.

Based on previous reports the tentative reaction mechanism has been developed by using amine as well as metal catalyst for the synthesis of cyclic carbonates (Figure 6).²⁻¹⁸ The presence of high surface area, zirconia metal and amine functional group play the crucial role for the cycloaddition reaction. The amine functional group activates the CO₂ molecule by absorption to form the carbamate intermediate, while the Lewis acidic nature of zirconium metal is helpful for the activation of the epoxide ring with bonding the oxygen atom. [2b-d,] The activated epoxide ring easily under goes ring opening by alkyl halide to form the haloalkoxy anion, then this haloalkoxy anion easily attacked by the activated CO₂ molecule and halocarbonate molecule is generated. Subsequently, this halocarbonate molecule undergoes to ring closing reaction to yielded cyclic carbonate and halogen ion.



Figure 6 proposed reaction mechanism for the synthesis of cyclic carbonates from epoxide and carbon dioxide catalysed by the APTES@ZrO₂-MCM-41.

Conclusions

In conclusion, we have designed and characterized the APTES@ZrO₂-MCM-41 as acid base bi-functional heterogeneous catalysts and applied for the synthesis of cyclic carbonates from epoxide and CO_2 . The presence of amine as well as ZrO_2 shows synergistic effect for the activation epoxide as well as of CO_2 for the cycloaddition reaction. By the increasing amount of the amine functional group (APTES) by 12.8 to16 wt% increased effect of the catalytic activity noted. By comparing with previously reported systems this methodology utilizes the mild reaction condition such as low temperature short time and low pressure.^[29] Additionally, the reaction proceeds

under solvent free conditions and recycling of the catalyst was shown to be excellent up to five consecutive recycle run.

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Keywords: Cycloaddition • MCM-41• CO₂ transformation • bifunctional• catalysis

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