

## Synthesis of Diphenylmethane and its Derivatives Over Ion Exchange Forms of MCM-22 as Catalyst

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### Abstract

In this work, for the first time benzylation of benzene with benzyl chloride or benzyl alcohol was investigated with catalysts in the form of zeolites (zeolite-X, ZAPO-5, MCM-22) as well its ion-exchange forms. The obtained catalysts were characterized by XRD, SEM, NH<sub>3</sub>-TPD and FTIR. After synthesis of catalysts, synthesis of diphenylmethane and its various derivatives using benzene, toluene and a substituted benzyl chloride, benzyl alcohol was carried out (particularly with H-MCM-22). In this direction catalyst amount, effect of time on chemical reaction and other parameters were screened. After screening the zeolite catalysts for synthesis of diphenylmethane and its derivatives, it is observed that the substrates bearing electron donating groups gives high yield as compared to those with electron withdrawing nature.

**Keywords:** MCM-22; Diphenylmethane; BET; TPD; Catalysis; Zeolite

### Introduction

Diphenylmethane (DPM) is one such chemical fragment which is being used in the fragrance industry in the form of fixative and in the scenting soap [1]. DPM can serve as a synergist for pyrethrin in the pesticides and insecticides. It is also recommended as a plasticizer so as to improve the dyeing properties, as solvents for the dyes. DPM has also been utilized to improve the thermal stability of saturated linear polyesters. Besides, its addition to the jet fuels increases their stability and lubricating characteristics. At the Industrial level, Friedel–Crafts reaction of benzyl chloride with benzene in presence of a Lewis acid catalyst, i.e., AlCl<sub>3</sub> is used to synthesize DPM [1,2]. In organic synthesis, Friedel–Crafts reaction utilizes liquid phase alkylation of aromatic compounds through homogenous acid catalyst [3]. On the other hand, usually used homogeneous acid catalysts (viz. AlCl<sub>3</sub>, BF<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) pretend several problems, such as difficulty in separation and recovery, disposal of the spent catalyst, corrosion, high toxicity, etc. Thus the development of reusable solid acid catalyst is necessary.

Zeolite catalysts present one such alternative. This can be attributed to their shape selectivity, thermal stability and easy separation from the products. Their possibility of regeneration of from deactivated state have been widely used in the

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field of petrochemistry [1,3]. Additionally, there are few more reports replacing homogeneous acid catalysts by heterogeneous solid acid catalysts also exist in literature. These include hetero poly acids, Ga or Fe substituted H-ZSM-5, Ga-containing MCM-41 and GaCl<sub>3</sub>, FeCl<sub>3</sub>, ZnCl supported on clay and Si-MCM-41 [4–7]. Thus in this work, we have tried to replace the homogeneous Lewis acid catalysts by the environmentally friendly solid recyclable catalyst in the form of zeolites, for the synthesis of diphenylmethane and benzyl chloride as alkylating agent (Scheme 1).



Scheme 1. **Synthesis of diphenylmethane using benzene and benzyl alcohol as reactant.**

## Experimental

### Synthesis of zeolites

Synthesis of MCM-22 was carried out according to procedure described in previous reports [8-9] along with some modifications as per literature [10]. The synthetic procedure is as: Sodium metasilicate (40 g) was mixed with deionized water (50 mL) in a beaker. To this mixture, 9.87 mL of HMI was added drop wise under vigorous stirring. The solution was named as A. In the meantime, aluminium sulphate (3.21 g) and 6.14 mL concentrated sulphuric acid was dissolved to 16.5 mL of deionized water, solution named as B. After preparation of A and B, solution B was added drop wise to the solution A. The gels were obtained and then kept in an autoclave at 158°C for 72 hrs. The autoclaves were immersed in the cold water. The obtained materials were washed and centrifuged until pH ≤ 9 and subsequently dried at 110 °C. The obtained sample was calcined in the absence of air at around 540°C for 7 hrs. This was done in order to remove water and organic precursor.

Following the synthesis of zeolites, ion-exchanged materials were prepared by stirring 2 g of calcined MCM-22 with metal nitrate solution (30 mL; 0.1 M) for 12 h at 80°C. The obtained solid was filtered, washed thoroughly with distilled water and dried under ambient conditions. The given procedure was repeated three times, and obtained samples were used for characterization and catalytic studies.

### Characterization

X-ray diffraction (XRD) patterns were collected on the Bruker D8 ADVANCE powder diffract meter using Ni-filtered Cu Ka radiation source at 40 kV and 20 mA, from 5°C to 50°C with a scan rate of 20/min. Crystallinities were calculated by comparing the sums of intensities of the peaks appearing at 7–10° and 24–26° in the calcined samples to those found in the fully crystalline reference material.

Scanning electron microscope (SEM) images were recorded on a QUANTA 200 (FEI). The Brunauer–Emmett–Teller (BET) surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP 2010 analyzer. The samples were degassed at 573 K to a vacuum of 10<sup>-3</sup> torr before analysis. Chemical compositions of samples were obtained using EDS. The FT-IR spectra were obtained on a Nexus 870 FTIR spectrometer. Samples were mixed and ground with KBr for IR measurement in the range of 1400–400 cm<sup>-1</sup>. Ammonium thermal programming desorption (NH<sub>3</sub>-TPD) was performed on Micromeritics ASAP 2920 unit helium as a carrier gas.

### Catalytic test

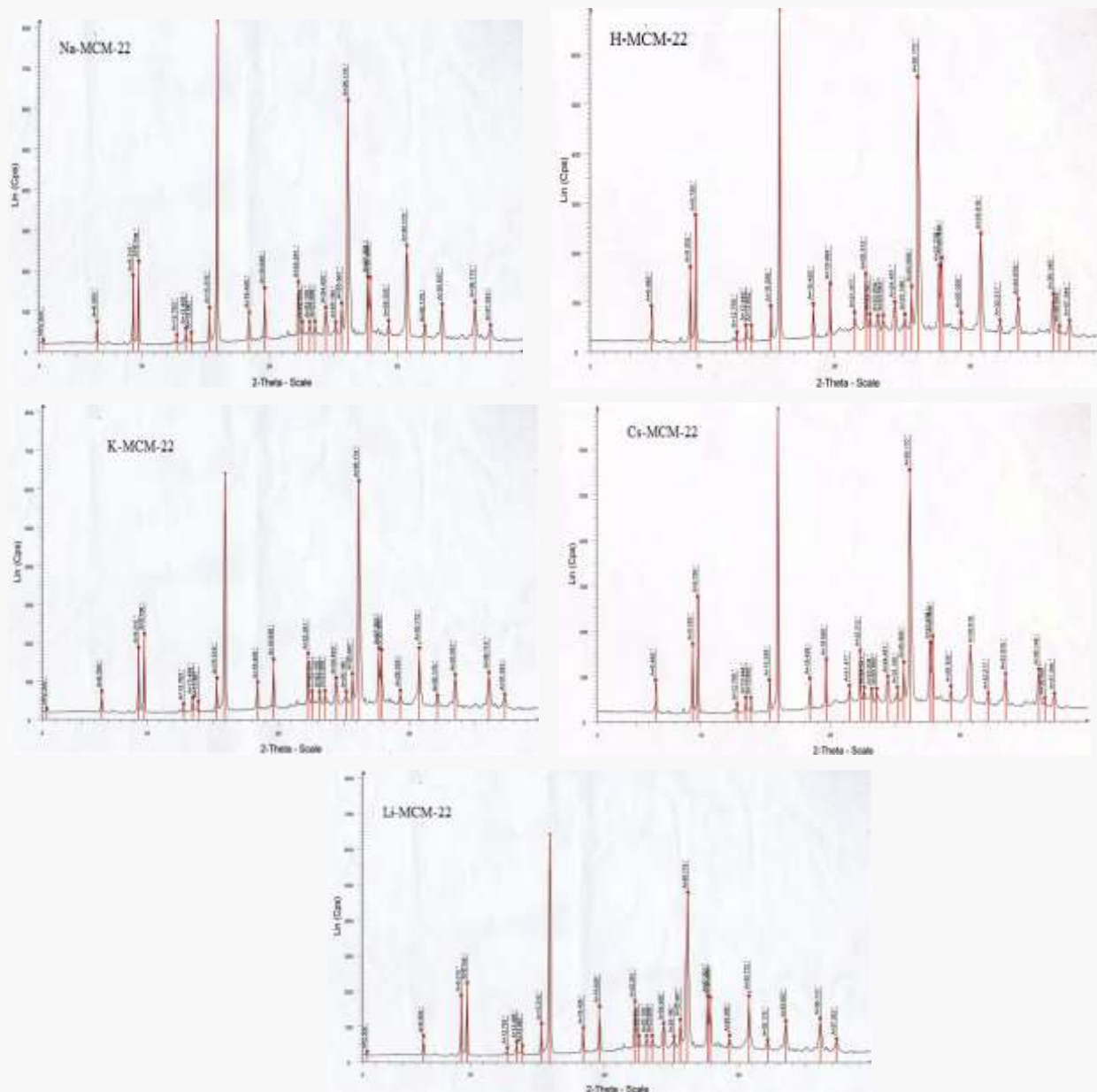
Reactions were carried out in a glass batch reactor. The alkylating reagents used were benzyl alcohol, benzyl chloride. 0.48 mmol of alkylating reagent was reacted with benzene or toluene (2 ml) over H-MCM-22 catalyst, and the ion exchange forms were heated up to reflux conditions. After reaction time was completed, the catalyst was removed by filtration, and the

compounds characterized by <sup>1</sup>H NMR. The conversion rate of the alkylating reagents at different reaction times was determined by gas chromatography.

## Result and Discussion

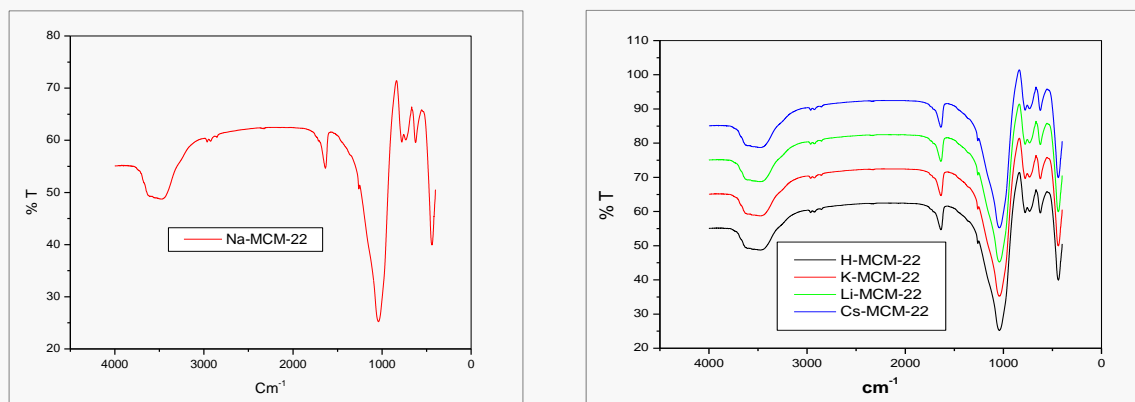
### Characterization

**FIG. 1** shows that XRD patterns of MCM-22 and their ion exchange forms are crystalline and do not contain detectable impure phases. It was also found from XRD that the structure is stable even after calcinations at 550 °C for 8 h in a stream of dry air. All ion exchanged XRD patterns are almost similar to the patterns of parent MCM-22. It can be seen that the peak positions and relative intensities are consistent with the XRD results for MCM-22 observed by Rubin and Chu [8].



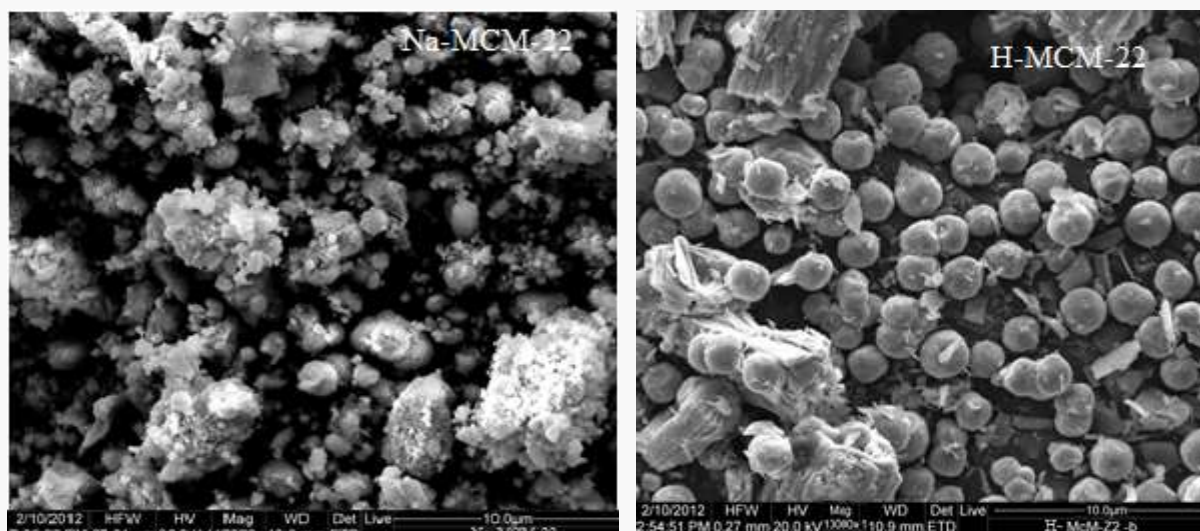
**FIG. 1. X-Ray Diffraction pattern of H-MCM-22 and their ion exchange forms.**

The FTIR spectrum of MCM-22 is shown in the **FIG. 2** (Supplementary Information). Here the presences of bands related to the symmetrical and asymmetrical stretching of O-H band were seen. The band at  $786\text{ cm}^{-1}$  refers to external symmetrical stretching, whilst the band at  $1237\text{ cm}^{-1}$  refers to external asymmetric stretching. The bands at  $1095$  and  $1070\text{ cm}^{-1}$  correspond to internal asymmetric stretching, and the bands around  $594$  and  $550\text{ cm}^{-1}$  are attributed to the presence of double rings in MCM-22 structure. At  $1626\text{ cm}^{-1}$  the band is ascribed to the angular deformation of the N-H bond and water, while as the band around  $449\text{ cm}^{-1}$  could be related to the internal deformation of O-H bands.



**FIG. 2. FT-IR spectra various forms of MCM-22.**

For understanding the surface morphology, Scanning electron micrograms (SEM) of zeolites were taken at 10,000X magnifications. The Zeolites appear to have relatively non- uniform surface and lightly uneven pore morphology. The SEM pictures of MCM-22 and its ion-exchanging forms are shown in **FIG. 3** (Supplementary Information). Catalyst MCM-22 appears under the SEM as small spheres; occasionally with aggregates of  $10\text{-}15\mu\text{m}$ . The SEM pictures of metal ion-exchanged MCM-22 molecular sieves also showed some morphological deformity due to small amount of non-framework oxides inside the pores of these zeolites.



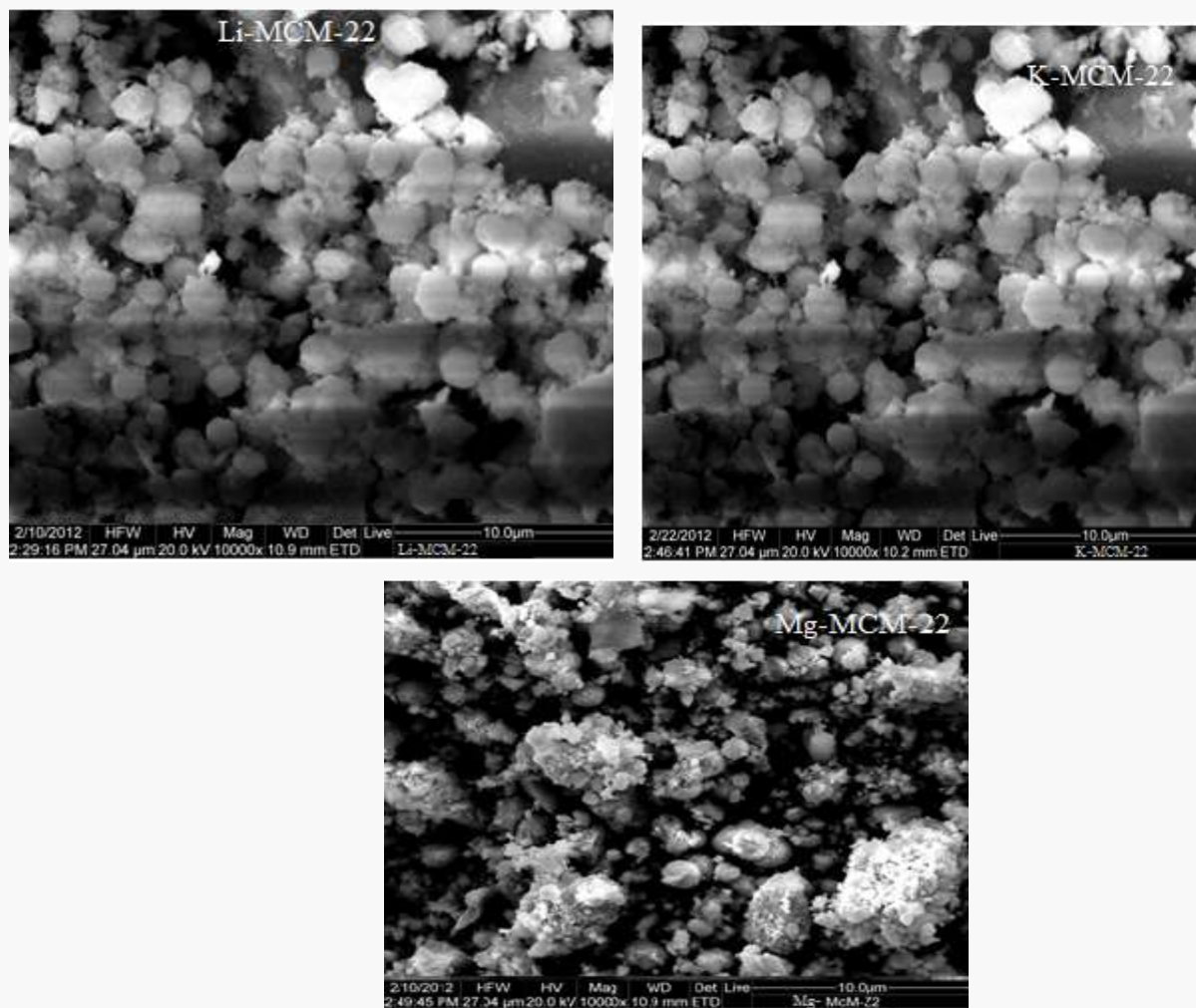


FIG. 3. SEM images of various forms of MCM-22.

The chemical composition of the material was obtained quantitatively from energy dispersive analysis. Results were obtained for elements like Al, Ca, Mg, Na, O & Si. The obtained data revealed that O is present in abundance and is almost half of the overall weight of material **FIG.4** (Supplementary Information) shows that in MCM-22, Si is found in abundance than Al, confirming that the Si/Al ratio is slightly greater than 1. Besides, the elemental ratios are in accordance to the molar composition taken during their synthesis. Electron dispersive spectra in **FIG. 4** (Supplementary Information) also shows the presence of incorporated metal ion in metal ion exchanged forms of MCM-22, thus confirming that the ion-exchange has occurred successfully. Further the Au peak obtained in all the Zeolite forms is due to the fact that these samples were coated with gold before carrying out their energy dispersive analysis.



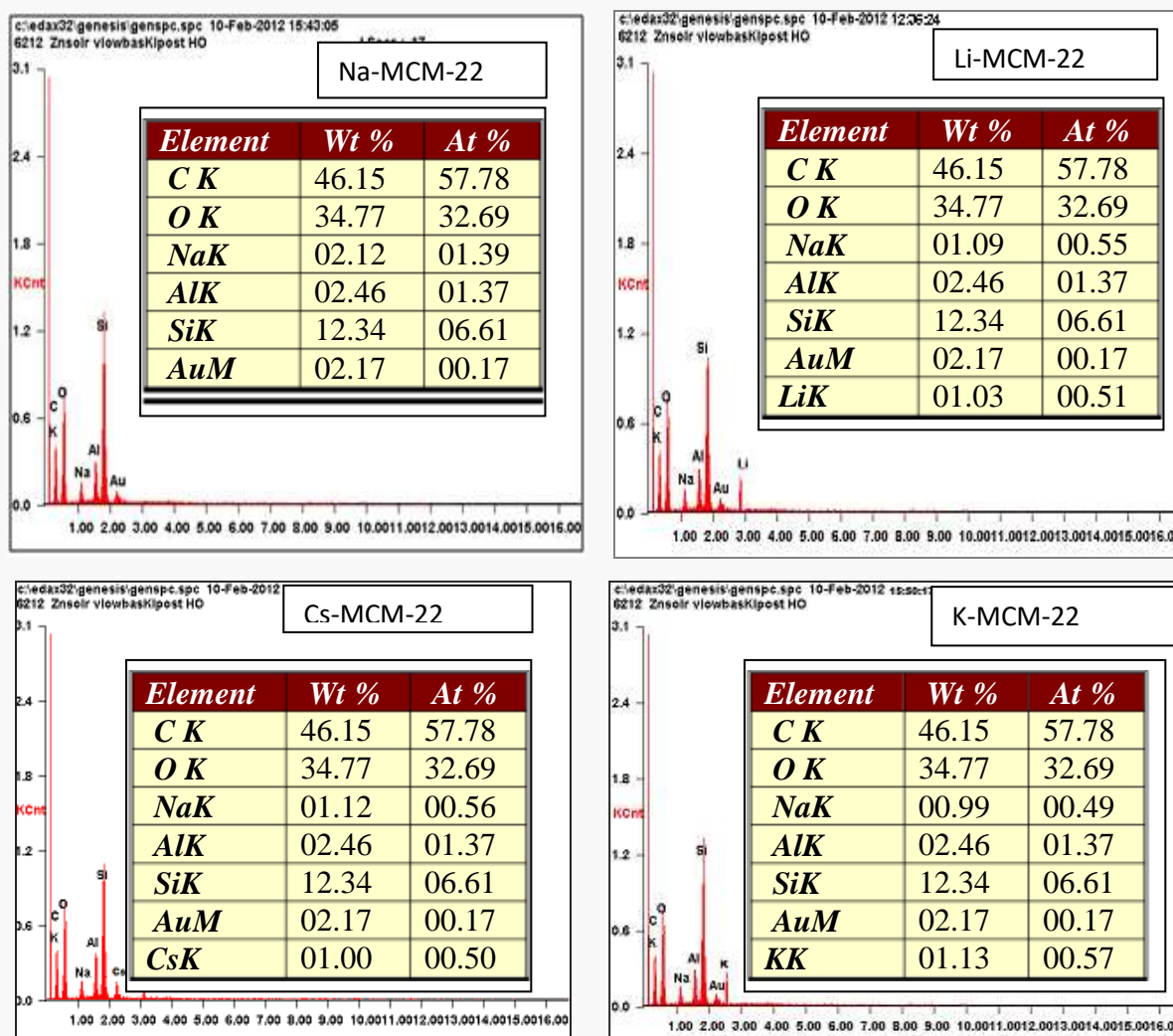


FIG. 4. EDS spectra of various forms of MCM-22.

The BET surface areas of MCM-22 and its ion-exchanged forms were found in the range of 362-390 m<sup>2</sup>/g. The zeolite pore size distribution in **FIG. 5** (Supplementary Information) revealed that MCM-22 exhibit the narrow pore size distribution in the range of 0.7-0.89 nm. These results clearly indicated that the catalysts prepared in this method are nonporous with almost uniform pore size. The BET surface area of all metal ion-exchanged forms is less than that of parent zeolite. This indicates the presence of small amount of non-framework oxides inside the pores of zeolites [11,12].

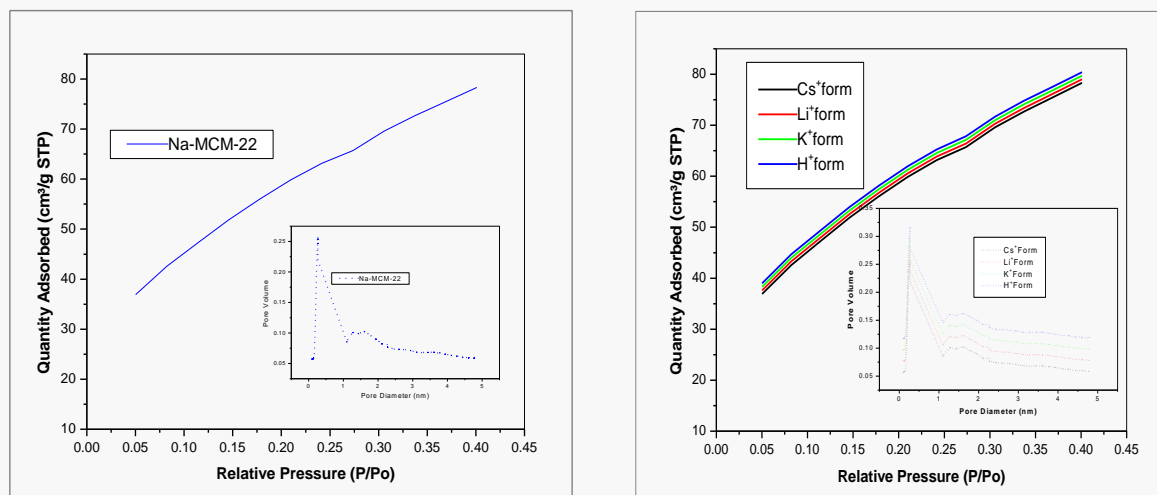


FIG. 5. surface area plot of various forms of MCM-22

In order to locate the adsorption sites on various zeolites, TPD of NH<sub>3</sub> were performed, shown in **FIG. 6** (Supplementary Information). The sharp peak with onset temperature of 30°C with T<sub>max</sub> around 70°C is ascribed to desorption of physisorbed NH<sub>3</sub> confirming the weak adsorption sites. The broad peak with onset temperature of around 150°C is attributed to desorption of strongly chemisorbed NH<sub>3</sub> as well as thermal decomposition, thus confirming the strong adsorption sites. Hence these desorption results reveal that the maximum adsorption capacity could be found above 100°C.

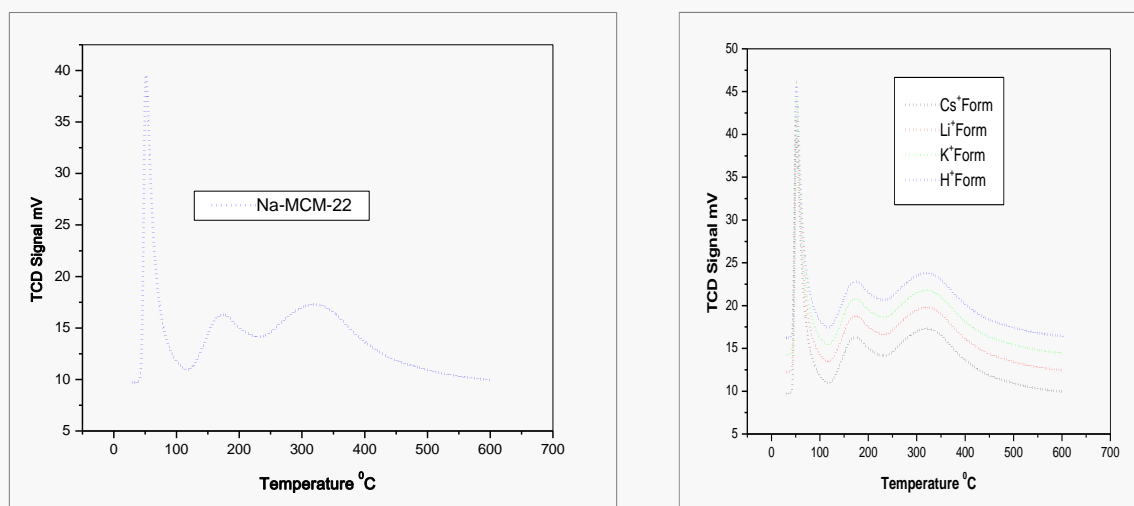


FIG. 6. TPD profile of various forms of MCM-22

## Catalytic study

### Effect of various catalysts

The liquid phase catalytic runs were carried out batch wise in a magnetic stirrer. Here the closed 50 ml glass reactor was fitted with reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, appropriate amounts of benzene and benzyl chloride (1.5:0.5 molar ratios) were charged in the reactor along with 300 mg catalyst. The reaction mixture was heated to 75°C under stirring. Samples were withdrawn periodically and analyzed with a gas chromatograph [Younglin GC-6000 model, SE-30

(10%) capillary column (30 m length, 0.25 mm diameter) with a FID detector and high purity nitrogen as carrier gas] fitted with a flame ionization detector. The identification of the products was done by comparing their gas chromatograph with those of authentic samples.

The results of the catalytic activities of various catalysts such as H-MCM-22 and its ion exchanged forms, Li<sup>+</sup> MCM-22, K<sup>+</sup> MCM-22, Cs<sup>+</sup> MCM-22 in the benzylation of benzene with benzyl chloride are depicted in **FIG. 7** (Supplementary Information). The main product of the reaction is diphenylmethane (DPM). A small amount of higher molecular weight polybenzylated products (others) were also observed, however, the concentration of polybenzylated products depends on the reaction conditions and the type of the catalyst used. As depicted in **FIG. 7**, the catalytic activity of H-MCM-22 was higher due to its large pore size and surface area.

Catalytic efficiency of ion exchange form of MCM-22 follows order as; H<sup>+</sup>>Li<sup>+</sup>>Na<sup>+</sup>>K<sup>+</sup>>Cs<sup>+</sup> as shown in **FIG. 7** (Supplementary Information). The results are consistent with trend of acid strength as measured by NH<sub>3</sub>-TPD. This order of catalytic efficiency is due to small size and high polarizing power of hydrogen ion than other cations. Higher values of the electronegativity of the counter cation according to Sanderson principle create stronger acid sites in the zeolite matrix.

After this, synthesis of DPM over H-MCM-22 catalyst was examined with time. Here **FIG. 8** (Supplementary Information) shows the percentage yield DPM and product distribution at 75°C with respect to the reaction time. It was observed that the percentage yield of DPM increased almost linearly up to 160 minutes of the reaction time. Once optimum time period was reached, no more increase in the yield of DPM was seen.

After studying the synthesis of DPM with H-MCM-22 catalyst, effect of recycling on the synthesis of diphenylmethane was studied at 75°C. In this direction, recycling experiments were carried out in order to find out the activity, stability and reusability of the catalyst material. It was observed that the catalyst was easily separated with the help of centrifuge, and could be further reused after activation at 500°C for 3-4 hrs. It could be easily understood from the **TABLE 1** that after three reaction cycles, loss of catalytic activity is happening. It may be attributed to the loss of catalyst or catalyst structure during the recovery process.



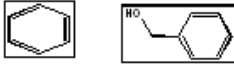

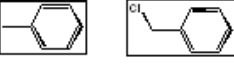
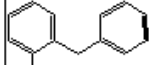



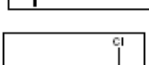
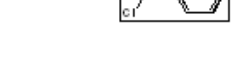
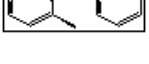
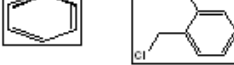
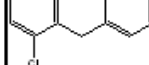

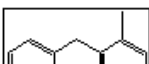
In addition to this, the effect of catalyst amount was also studied. In this regard, varying concentration of catalysts was used in the reaction mixture. It was observed that when catalyst amount increased from 100 to 400 mg, yield of DPM also increased. Below this concentration (100 mg) the yield of DPM was observed to label off. Table 1 shows a good correlation between the yield of DPM and the amount of catalyst, hence the number of acid sites. Therefore, we can say that the number of acid sites in the zeolite catalyst plays a crucial role in this reaction.

**TABLE 1. Effect of amount of catalyst, temperature and recycling on the synthesis of DPM.**

Entry	Amount of catalyst (mg)	Temperature (C)	Recycling	Yield (%)
1	300	75	1st run	82.2
2	300	75	2nd run	81.8
3	300	75	3rd run	79.1
4	300	25	4th run	21.5
5	300	50	5th run	58.5
6	300	75	6th run	82.2
7	300	100	7th run	85.8
8	300	125	8th run	87.6
9	100	75	9th run	25.4
10	200	75	10th run	52.6
11	300	75	11th run	82.2
12	400	75	12th run	89.1



Following the effect of catalyst amount, the effect of temperature on the synthesis of diphenylmethane was studied over a range of 25°C-125°C over H-MCM-22 and results obtained are summarized in the **FIG. 7**. It was seen that lower temperatures does not favor the formation of DPM; however the yield of DPM increased sharply with the increase in reaction temperature, and reached a maximum value at 75°C. As could be seen from the **FIG. 7**, yield increased directly with respect to the reaction temperature. The optimum temperature for all the three zeolites was achieved to be found 75°C.

Entry	Reactants	Product	% Yield H-MCM-22
1			82.2
2			81.3
3			78.7
4			77.9
5			75.5
6			76.8
7			74.9
8			75.3

**FIG. 7. Synthesis of diphenylmethane and its derivatives using H-MCM-22 as catalyst.**

## Conclusions

We conclude by saying that the benzylation of benzene and toluene with benzyl alcohol in liquid phase can be carried out in presence of catalyst H-MCM-22, as well as its ion exchanged forms. The proposed approach results to get good conversion within shorter reaction times. The use of Benzyl alcohol instead of benzyl chloride is advantageous due to the formation of environmentally friendly side product, which is water. Most importantly, the catalyst (zeolite) is reusable and highly stable under ambient conditions.

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