



Alkali/alkaline earth ion-exchanged and palladium dispersed MCM-22 zeolite as a potential catalyst for eugenol isomerization and Heck coupling reactions

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Abstract. Alkali and alkaline earth metal ions (Na^+ , K^+ , Cs^+ , Mg^{2+}) exchanged MCM-22 zeolites were prepared and subsequently palladium (2 wt.%; Pd) was dispersed on above exchanged MCM-22 zeolite materials. All the MCM-22 materials were systematically characterized by FTIR, powder X-ray diffraction, N_2 sorption analysis and temperature-programmed desorption (TPD) of CO_2 . The XRD pattern and FTIR data confirmed the existence of the MCM-22 framework structure even after exchanging bulky metal ions and palladium loading. TPD studies using CO_2 supports that the cesium and magnesium incorporated MCM-22 possess a strong and large number of basic sites. The alkali and alkaline-earth metal ions exchanged MCM-22 catalysts were explored for industrially important eugenol isomerisation, whereas the palladium containing MCM-22 materials were utilised for Heck coupling reaction of styrene with iodobenzene. The Cs-MCM-22 showed the best activity for the eugenol isomerization with the isoeugenol yield of 76%. The Cs/Pd-MCM-22 was shown as promising heterogeneous catalyst for Heck coupling reaction of styrene with iodobenzene and yield 99% stilbene. For both isomerization and Heck coupling reaction, the catalysts retain their activities even after several runs.

Keywords. MCM-22; Cesium exchanged; Eugenol isomerisation; Palladium dispersion; Heck reaction.

1. Introduction

Heterogeneous catalysts play an extremely important role in fine, petrochemical industries, and also in environmental processes with high impact.¹ To our knowledge, the role of platinum on oxidation reaction studied by Faraday was one of the oldest processes using a heterogeneous catalyst.² Among the class of heterogeneous catalysts, zeolites and zeolite like molecular sieve materials have shown great interest since the 1960s, due to their molecular sieve properties and shape-selective in nature.³ The exceptional stability, uniform porosity, and high surface area of these materials lead the researchers to focus on developing synthetic zeolite materials and explore its catalytic behavior.³ Several unique features of these

materials including uniform channels, cavities, tuneable active sites with different strengths, high adsorption capacity, and electronic properties make them viable for commercial applications. In particular, zeolites have been commercially used as catalysts for hydrocarbon conversions in petroleum and petrochemical industries, as well as adsorbents⁴ for small-molecule separation processes, and even as ion exchangers in detergents.⁵

The development of zeolite having unique and wider pore channel accessible with the large surface area is one of the current interests in the area of heterogeneous catalysts. Recently discovered, two-dimensional layered zeolite, *viz.*, MCM-22, with a medium pore opening having an MWW topology is of great interest.⁶ The MCM-22 having framework topology of the material includes two independent

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pore systems - two-dimensional sinusoidal 10-membered ring (10-MR) and 12-membered large super-cages with respective aperture sizes of $4 \text{ \AA} \times 5.9 \text{ \AA}$ and $7.1 \text{ \AA} \times 7.1 \text{ \AA} \times 18.2 \text{ \AA}$.⁷ These super-cages are arranged in such a way that they are stacked one above the other through Double Six-membered rings (D6R).⁸ This unique structure and physicochemical properties make them as potential catalysts in several hydrocarbon transformation processes such as isomerisation, alkylation, aromatisation and cracking.^{9–11}

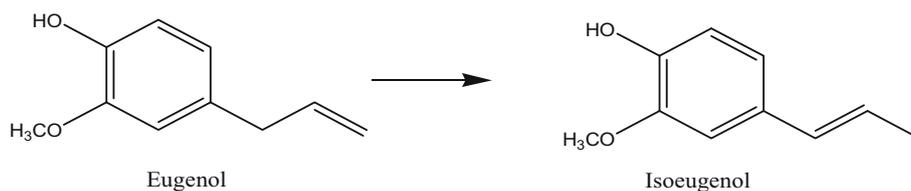
The modification of zeolite surface with different cations and subsequent dispersion of Noble metals broadens the scope of the materials for several fine, petro- and environmental chemical processes.^{9–12} In particular, isomorphous substitution facilitates to tune the surface acidity, whereas the replacement of surface exchangeable cations tunes the surface basicity.¹² The presence of extra framework cations on the channels and cages of the structure, predominantly on different cationic sites¹³ is believed to contribute to the ion exchanging property of these materials. The positively charged cations, such as Na^+ , K^+/H^+ , NH_4^+ are most common charge balancing ions, often the conventionally synthesized zeolite having Na^+ ion.¹² Generally, the number of cations within a zeolite structure depends on the amount of aluminium ions present in the tetrahedral position of the framework and the charge balancing cations can be exchanged with some alkali or alkaline earth metals, which can help to generate basicity on the surface of the zeolites.¹³ To date, a vast number of researchers have focused on the development of zeolite-based solid-acid catalysts,¹⁴ however, not much captivating studies have come up for base catalysts. The design of the base catalyst and exploring its application on base-catalysed reactions have great significance in both academic and industrial researchers. The base-catalyzed reaction is traditionally carried out mostly by the routine alkaline procedure such as KOH in alcoholic solutions at high-temperature, NaOH, organic amines, etc.^{15–17} Numerous studies are known on heterogeneous base catalysts for various base catalysed organic transformations like isomerisation, condensation and dehydrogenations.^{18–20} Among the various base catalysed reaction isomerization of alkene is one of the industrially important base catalysed reaction.^{21,22} In particular, the isomerization of lignin-derived biomass-model compound *viz.*, eugenol isomerization (Scheme 1), results in thermodynamically stable isoeugenol, which has great application in the fragrance and pharmaceutical industries.^{23,24}

On the other hand, applying zeolites materials as solid supports for noble metal catalyst species is known for many years since they play a vital role in several catalytic processes^{25–27} such as hydrogenation, hydrocracking, refining, hydro-isomerisation, etc.^{26,27} Also, numerous studies on literature shows that many of the atomically dispersed Noble metals (Pt, Pd, Re, etc.) and their complexes on zeolites supports have great potential for many chemical processes.^{28–30} For example, a noble metal dispersed zeolite improved the catalytic activity and stability in many petroleum and petrochemical processes.^{26–30} Further, noble metal catalysts were used for many organic coupling reactions *viz.*, Sonogashira, Suzuki, Heck, Stille coupling etc. These were carried out using phosphine ligand containing palladium catalysts in presence of a base.³¹ Djakovitch *et al.*, in 1999 reported the first heterogeneous Pd catalysed Heck reaction using zeolite as the catalyst support.^{31–33} It is found that the use of zeolites as support for Pd particles offers an advantage to overcome the problems of leaching of active sites from the surface under the reaction conditions.^{33–39}

Thus, in this work, the MCM-22 zeolite materials are ion-exchanged with different alkali and alkaline earth metal ions (Cs, K, Mg) and subsequently, palladium was dispersed on the surface and explored for their catalytic applications. The alkali and alkaline earth metal-containing zeolites were explored for the isomerization of eugenol under ambient conditions, whereas the palladium dispersed catalysts were explored for the Heck coupling reaction.

2. Experimental

The chemicals and materials used for the hydrothermal synthesis of MCM-22 involve colloidal silica (Sigma-Aldrich, LUDOX® HS-40; 40 wt.%) sodium aluminate (Sigma-Aldrich, Al_2O_3): 50-56% and (Na_2O) : 37-45%, template (hexamethyleneimine; Alfa Aesar: 98%) and base (sodium hydroxide; SRL 98%). The materials required for subsequent ion exchange as well as impregnation includes cesium nitrate (Alfa Aesar: 99.5%), magnesium nitrate; SRL 98%, potassium nitrate (Sigma-Aldrich; > 99%) and ammonium acetate (Sigma-Aldrich; > 98%). Heck coupling reaction needs such as iodobenzene (spectrochem; 99%), styrene (Sigma-Aldrich; > 99%) and solvent as dimethylformamide (DMF; Sigma-Aldrich 99.8%). Eugenol (spectrochem; > 98%) isomerisation requires eugenol as the starting material along with dimethylformamide as a solvent.



Scheme 1. Isomerization of eugenol to isoeugenol using M-MCM-22; where (M = Na, K, Cs, Mg and NH₄).

2.1 Catalyst preparation

2.1a Synthesis of MCM-22: The MCM-22 samples were prepared as per the procedure described earlier with the following molar gel composition SiO₂: 0.3 NaOH: 0.033 Al₂O₃: 0.5 HMI: 45 H₂O.⁷ First aluminosilicate gel was prepared in presence of alkali (NaOH) and subsequently, the template HMI was introduced and the resultant synthesis gel was transferred to an autoclave and hydrothermally treated for 7 days at 155 °C. After the crystallisation period, the sample was washed with distilled water followed by ethanol to remove excess NaOH and the organic templates. Then it is kept for drying in an air oven. The sample obtained is labelled as as-synthesised MCM-22. The template present in the as-prepared materials was removed by calcination at 550 °C for 6 h in presence of air and the sample is labelled Na-MCM-22.

2.1b Preparation of ion-exchanged MCM-22 samples

2.1.1a. Ion exchange of cesium, potassium, magnesium and ammonium ions on Na-MCM-22 In order to prepare alkali and alkaline earth metal ions exchanged MCM-22 catalysts the following procedure was adopted. For example, the preparation of cesium exchanged MCM-22 was carried out by introducing 30 mL of 1 M solution of CsNO₃ into the round bottom (R.B.) flask containing 1 g of activated (200 °C) Na-MCM-22. The mixture was continuously stirred at 90 °C for 6 h to get cesium exchanged sample. The resultant sample was filtered, washed with distilled water and dried in an air oven, subsequently, it was calcined at 550 °C for 5 h. The resultant sample was labelled as Cs-MCM-22. The potassium, magnesium and ammonium forms of MCM-22 were prepared with a similar procedure described earlier by using 1 M solutions of potassium nitrate, magnesium nitrate, and ammonium acetate solutions respectively. The samples prepared by potassium, magnesium and ammonium were labelled respectively as K-MCM-22, Mg-MCM-22 and NH₄-MCM-22.

2.1.1b. Preparation of Cs-MCM-22 by impregnation method The cesium containing MCM-22 is also prepared by the impregnation method by introducing 10 wt. % of cesium nitrate into the 1 g of Na-MCM-22 sample. First, the water pore volume of MCM-22 was calculated by the incipient wetness method and was found to be 1.5 cm³·g⁻¹.

The required amount of cesium nitrate was dissolved in 1.5 mL of water and introduced into the well-dispersed 1 g of Na-MCM-22 sample uniformly through dropwise addition. After all, the sample gets wet by the cesium nitrate solution, the sample was agitated and is oven-dried at 80 °C for 1 h and subsequently re-calcined at 550 °C for 5 h. This is labelled as Cs-MCM-22(imp).

2.1.1c. Preparation of palladium loaded MCM-22 samples The Pd dispersed on Na, K, Mg, NH₄⁺, Cs and Cs-MCM-22(imp) samples were prepared by using palladium chloride as a palladium source. First, palladium(II) chloride solution with 2 wt. % of palladium was prepared by dissolving in deionized water. The resultant palladium chloride solution (1 mL) was uniformly introduced into the metal-ion exchanged MCM-22 sample (1 g) by incipient wetness method. The resultant sample was agitated, and oven-dried at 80 °C for 1 h and then calcined at 500 °C for 3 h. All the calcined samples were first treated using a 0.1 M NaBH₄ solution and subsequently reduced in H₂ atmosphere at 500 °C for 5 h. The palladium loaded samples are represented as Na/Pd-MCM-22, K/Pd-MCM-22, Mg/Pd-MCM-22, Cs/Pd-MCM-22, and Cs/Pd-MCM-22(imp).

2.2 Physicochemical characterisation of materials

The structural framework features of the samples were analysed using FTIR spectrometer in the range of 400–4000 cm⁻¹ with Perkin-Elmer Spectrum-two using KBr technique. XRD patterns of MCM-22 and all the samples were recorded using Rigaku Miniflex 600 diffractometer using nickel-filtered Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) and a liquid nitrogen-cooled germanium solid-state detector. The patterns were recorded in the 2 θ range of 5–45° with a step size of 0.02°. Brunauer-Emmett-Teller (BET) surface area and N₂ adsorption-desorption of the Na-MCM-22 and Cs-MCM-22 samples were determined at -196 °C by an automatic micropore physisorption analyser (Micromeritics ASAP 2020, USA) after the samples were degassed at 250 °C for 10 h. The BET surface area was calculated in the relative pressure range 0–0.1, over the adsorption branch of isotherm. Barrette-Joyner-Halenda (BJH) pore size distribution was obtained from the desorption branch of isotherm. Other textural properties like, pore volume was elucidated from the isotherm data. TPD profile of CO₂ was performed (BELCAT-M; Japan) from 50

to 800 °C at a heating rate of 10 °C/min with the carrier gas (Ar) flow of about 30 mL/min for all the samples.

2.3 Catalytic studies on ion-exchanged and pd loaded samples

2.3a Isomerisation of Eugenol: To understand the surface basicity, the cations exchanged MCM-22 catalysts were studied for the isomerization of eugenol in a liquid phase autoclave reactor at 200 °C for 6 h. All the alkali metal ion-exchanged samples were applied for the isomerisation of eugenol. Prior to the reaction, the catalysts were activated by heating in an air oven at 70 °C for 1 h. Approximately 0.2 g of eugenol (~0.188 mL) was introduced into the autoclave reactor having 2.5 mL of DMF as a solvent. Then, 0.05 g of the alkali and alkaline earth metal-containing MCM-22 catalyst was added into the reactor. The temperature of the reactor was set to 200 °C and the reaction was continued for 6 h. After the reaction, the catalyst was separated by filtration and the products were analysed by gas chromatography (GC) equipped with ZB-5 capillary column (non-polar column) and a flame ionization detector. The products were confirmed based on the retention time of the authentic samples received commercially.

2.3b Heck coupling reaction: The palladium containing MCM-22 catalyst (M/Pd-MCM-22; where M= Na, K, Mg, Cs, and Cs(imp)) were applied for the Heck coupling reaction. The reaction was carried out in liquid phase medium by introducing iodobenzene (1.4 mmols) and styrene (2.8 mmols) in the ratio 1:2 into the round bottom flask containing 3.56 mmols of potassium carbonate in 2.5 mL of the solvent (DMF). About 0.05 g of M/Pd-MCM-22 catalysts were subsequently added into the round bottom flask containing the above mixture. After the introduction of the catalysts into the reaction mixture, the RB flask was fitted with a water condenser in an oil bath and the reaction was carried out at 150 °C for 6 h. After the completion of the reaction, the catalyst was separated by filtration and washed thoroughly with ethanol and subsequently recycled for several runs. The products obtained in different catalytic reactions were analysed by using gas chromatography equipped with a flame ionizing detector (FID) (Mayura analytical 2100) connected with Zebron ZB-5 column (5% phenyl and 95% dimethylpolysiloxane) of 30 M.

3. Results and Discussion

3.1 Characterization of the catalysts using various techniques

FT-IR spectra of the as-synthesized and ion-exchanged MCM-22 materials are shown in Figure 1. All the samples showed the major vibrational bands, which

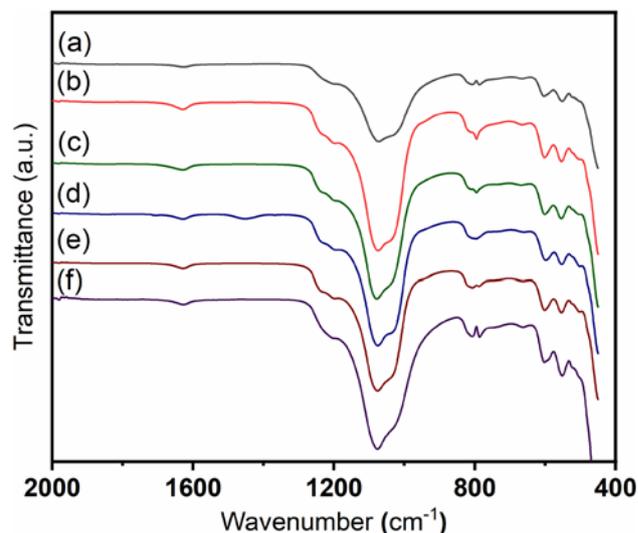


Figure 1. FT-IR spectra of (a) Na-MCM-22, (b) K-MCM-22, (c) Mg-MCM-22, (d) NH_4^+ -MCM-22, (e) Cs-MCM-22 and (f) Cs-MCM-22(imp).

are characteristic of double six-ring (D6R) of MWW zeolite framework structure, a symmetric stretching framework of Si-O-T linkage and as-symmetric framework stretching of Si-O-T vibrations (T = Al or Si).⁴⁰ The vibrational bands appeared for all the MCM-22 samples around 552 cm^{-1} and 600 cm^{-1} correspond to the D6R vibrations of MCM-22.^{4,7,40} The observed band around 810 cm^{-1} is characteristic vibration of symmetric stretching (γ_{sym}) of Si-O-T linkage present in MCM-22 framework.^{4,7,40} The band around 1070 cm^{-1} corresponds to asymmetric (γ_{asym}) Si-O-T internal vibrations and at 1230 cm^{-1} corresponds to asymmetric Si-O-T external vibrations. It is clearly observed that the parent material (Na-MCM-22), as well as the ion-exchanged catalysts (K-MCM-22, Mg-MCM-22, Cs-MCM-22 and NH_4 -MCM-22) showed a similar vibrational spectrum. The accommodation of cations in the framework led to the shifting of stretching vibrational bands towards lower wavenumber is evident. In particular, the introduction of bulk cesium results in a higher shift in framework as-symmetric and symmetric vibration bands toward the lower wavenumber is evident. As the concentration of cesium increases, the wavelength of T-O-Cs band increases and a much higher shift of vibration band towards the lower wavenumber is also evident.⁷

The FT-IR spectra of Cs-MCM-22 prepared by impregnation and ion-exchanged samples are shown in Figure 1(e) and 1(f). Both the samples showed the characteristic feature of MCM-22 framework, the decrease in intensity, broadening of framework vibration and shift in the vibrational band towards lower wavenumber on the Cs-MCM-22(imp) sample

due to incorporation of relatively high cesium loading on the external surface of MCM-22 sample. The XRD pattern of Na-MCM-22 sample is compared with those of ion-exchanged samples and the results are displayed in Figure 2. The parent sample shows sharp and independent peaks on the planes (100), (101), (102), (201), (202), (220), (310) which are characteristic of MWW structure.^{7,40} The presence of well-defined X-ray reflections are characteristics of good crystallinity of MCM-22 material. All the ion-exchanged samples (Figure 2) showed X-ray diffraction characteristic of MCM-22 structure with a line broadening compared to that of the parent sample. The observed line broadening in the X-ray diffraction pattern for the cations-exchanged samples is due to the presence of bulk alkali and alkaline metal ions present in the exchangeable channels and voids of the MCM-22 framework. The exchange of bulk cations in the extra-framework sites also reduces the particle size and further leads to line broadening.^{40–42}

It is clear from Figure 2 that the cesium exchanged sample showed a drastic decrease in the intensity as compared to the ion-exchanged sample. The X-ray pattern of Cs-MCM-22 has more line broadening compared to Cs-MCM-22-(imp) which may be due to strong cesium ion interaction with framework sites on the ion-exchanged sample.

The TPD experiments were conducted on alkali and alkaline earth metal ions exchanged MCM-22 samples and the results are presented in Figure 3. It is clear from the figure that, the cations exchange in zeolite induces specific changes in the basicity. Most of the

TPD patterns show two distinguished desorption peaks with the variation in the distribution of basic sites and strength. The low-temperature peak corresponds to weak basic sites, whereas high-temperature peak is the characteristic of strong basic sites. Among the various cations exchanged samples, the Na-MCM-22, and K-MCM-22 samples showed a broad peak in the temperature range of 200–350 °C which may be due to moderate basicity of the sample. The Cs-MCM-22 sample showed two broad peaks in the temperature range of 100–200 °C and 500–650 °C with the T_{max} of 582 °C which supports the presence of both weak and strong basicity and uniform distribution on the framework. Compared to the Cs-MCM-22 sample, the T_{max} for the Cs-MCM-22(imp) sample showed lower temperature which may be due to a weak interaction of cesium with the support. Among the various metal ion-exchanged samples, the Cs-MCM-22 showed a broad peak with highest T_{max} indicating the strong basicity.

N₂ sorption isotherm of Na-MCM-22 and Cs-MCM-22 is displayed in Figure 4. Both the zeolite materials showed sharp uptake below 0.1 relative pressure (p/p_0), which is typical for type I isotherm and is characteristic of monolayer adsorption on a microporous framework derived from the microporous channel. And both Na-MCM-22 and Cs-MCM-22 show H4 type hysteresis. From the figure, it is clear that the volume of nitrogen adsorbed on Cs-MCM-22 sample decreases noticeably owing to the presence of bulk cesium ions in the channel as well as in the voids of Na-MCM-22 framework. The H4 type hysteresis loop corresponds to the adsorption-desorption in

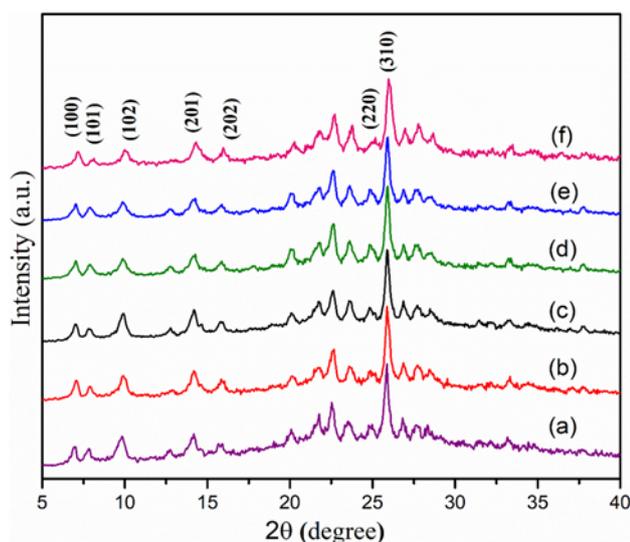


Figure 2. Powder XRD patterns of (a) Na-MCM-22, (b) K-MCM-22, (c) Mg-MCM-22, (d) NH₄⁺-MCM-22, (e) Cs-MCM-22 and (f) Cs-MCM-22(imp).

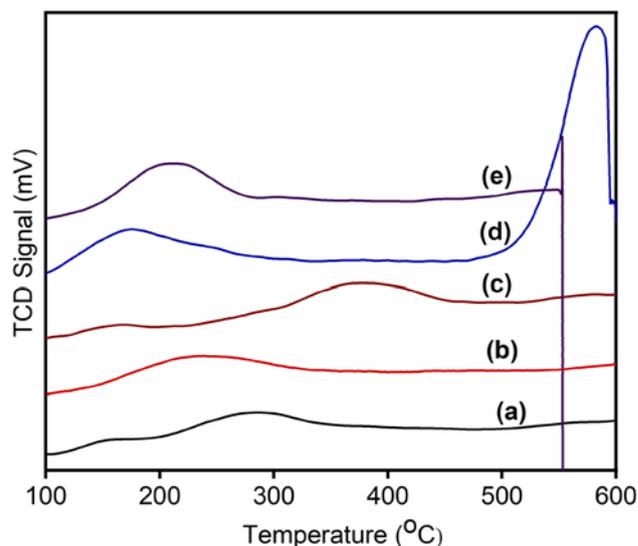


Figure 3. TPD-profile of (a) Na-MCM-22, (b) K-MCM-22, (c) Mg-MCM-22, (d) Cs-MCM-22 and (e) Cs-MCM-22(imp).

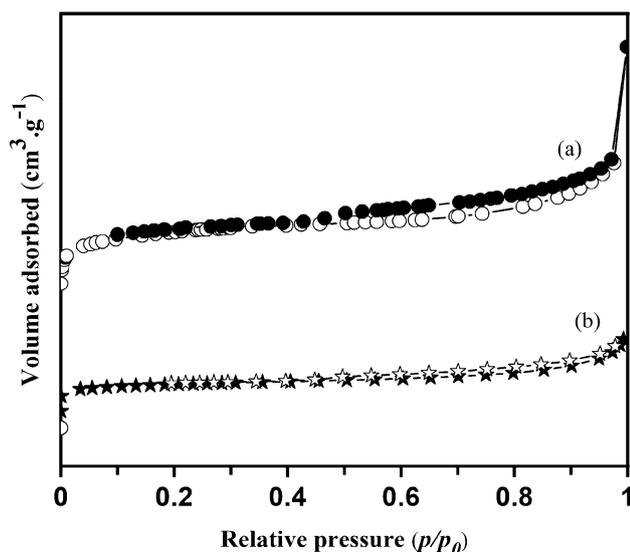


Figure 4. Representative N₂ sorption profile of (a) MCM-22, and (b) Cs-MCM-22.

narrow slit-like interparticle pores in the platelet particles of MCM-22 sample. According to IUPAC classification, all the nitrogen isotherms recorded on MWW samples show this kind of a hysteresis loop.⁴³ Also, the decrease in surface area can be related to the increase in weight of alkali metal cations. The textural properties of the parent and Cs-MCM-22 samples are followed by N₂ sorption studies and the results are summarized in Table 1. The calcined Na-MCM-22 shows BET, the external surface area of 804, 162 m²g⁻¹ with BJH pore volume of 0.42 cm³g⁻¹. After cesium exchanged, it showed BET, the external surface area of 217, 38 m²g⁻¹ with BJH pore volume of 0.10 cm³g⁻¹. A considerable decrease in the surface area and pore volume is shown by the exchanged sample, owing to the bulk cesium ions occupation in the pores and channels of Na-MCM-22.

3.2 Catalytic properties of developed materials

3.2a Eugenol isomerisation: The well-characterized cations exchanged MCM-22 samples were studied for the conversion of eugenol to isoeugenol at 200 °C under liquid phase conditions and the

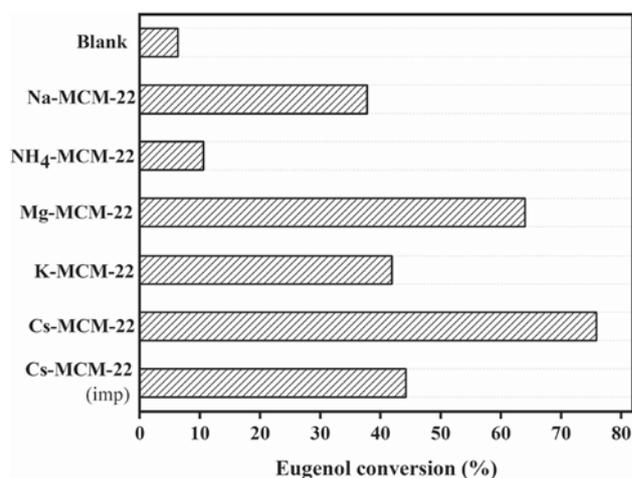


Figure 5. Isomerization of eugenol using different cation exchanged MCM-22 Catalyst. †Reaction conditions: Eugenol (1.2 mmol; 0.2 g); Solvent (DMF) = 8 mL; Catalyst = 0.05 g; Temperature = 200 °C & duration t = 6 h.

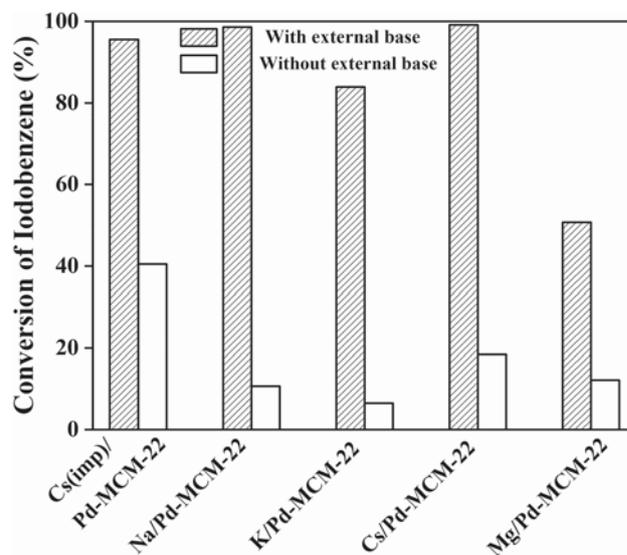


Figure 6. Catalytic activity of palladium containing several metal ion-exchanged MCM-22 with and without an external base. †Reaction conditions: Iodobenzene (1.4 mmol); Styrene (2.8 mmol); K₂CO₃ (3.61 mmol); Solvent (DMF) = 2.5 mL; Catalyst = 0.05 g; Temperature = 150 °C & duration t = 6 h.

Table 1. Textural properties of Na-MCM-22 and Cs-MCM-22.

Sl. No.	Sample name	Surface area (m ² /g)		Pore volume (cm ³ /g)	
		BET	External	BJH	Micropore
1.	Na-MCM-22	804	162	0.42	0.33
2.	Cs-MCM-22	217	38	0.10	0.18

Table 2. Effect of different substrates on Heck coupling using Cs/Pd-MCM-22[†].

Reactant species	Conversion of halo-benzene (%)
Styrene & Bromobenzene	5.2
Methyl acrylate & Iodobenzene	25.0
Methyl acrylate & Bromobenzene	1.2
Ethyl acrylate & Iodobenzene	23.0

[†]Reaction conditions: Halobenzene (1.4 mmol); Substrate (2.8 mmol); K₂CO₃ (3.61 mmol); Solvent (DMF) = 2.5 mL; Catalyst = 0.05 g; Temperature = 150 °C & duration t = 6 h.

results are shown in Figure 5. At first, a blank reaction was conducted without catalyst and the result showed only 6% conversion of eugenol with the exclusive formation of isoeugenol as a product. Among the several cations exchanged catalysts, NH₄-MCM-22 showed only 10% conversion due to poor basicity of the materials. The Na-MCM-22, K-MCM-22 and Mg-MCM-22 showed about 44, 41 and 64% eugenol conversion respectively due to moderate basicity of the catalyst. The Cs-MCM-22 showed a maximum conversion of 76% with the exclusive formation of isoeugenol as a product. Compared to Cs-MCM-22, the catalyst Cs-MCM-22(imp) showed poor conversion may be due to the presence of cesium present as oxide on the external surface. The most active catalyst (Cs-MCM-22) was recovered and reused to see the recyclability of the catalyst. The catalyst showed improved conversion (94%) after recovery may be due to the best dispersion of cesium ion under the reaction conditions that may facilitate the improvement in conversion. In all the cases isoeugenol was obtained as the only product.

3.3 Catalytic activity of palladium loaded Cs-MCM-22 catalyst

The cation exchanged zeolites are modified by introducing palladium and the Pd incorporated samples are explored for the Heck reaction using styrene/methyl acrylate/ethyl acrylate as a nucleophile and iodo-/bromo- benzene as an electrophile. All the reactions are conducted at 150 °C for 6 h (Figure 6). The reaction was studied both in the presence and absence of potassium carbonate as an external base. After each reaction, the catalyst is recovered and checked for reproducibility. The catalyst that yielded the best conversion is further checked for recyclability.

Among the various catalysts studied, the use of Cs/Pd-MCM-22- and Cs/Pd-MCM-22(imp) showed

relatively better conversion of about 40 and 20%, respectively. In all the cases, stilbene is obtained as the major product. The strong basicity and presence of a greater number of basic sites on cesium containing samples resulted in better conversion. Subsequently, the reaction was further studied in the presence of an additional external base. Among the several external bases were studied, the use of potassium carbonate facilitates the complete conversion of halobenzene with the exclusive formation of stilbene. The best result was produced by Cs/Pd-MCM-22 catalyst in the presence of the external base. A conversion of iodobenzene up to 99% was obtained for the reaction conducted under optimum reaction conditions (150 °C; 6 h). The results obtained seem to be in accordance with the order of effective basicity with respect to cations present in the catalyst. The product analysis reveals that the major product formed in all the cases is the trans-stilbene.

The best active catalyst Cs/Pd-MCM-22 was further explored for substrate scope and the results are summarized in Table 2. Among the various reactants, styrene with iodobenzene yielded maximum conversion, whereas the use of bromobenzene and other nucleophiles showed relatively lower conversion.

The above fact is in congruence with the reactivity of halobenzenes that the heavier halogen (I) leaves more easily than the lighter one (Br). The best active catalyst (Cs/Pd-MCM-22) was studied for the recyclability after the catalyst recovery by filtration, washing with ethanol and drying in an air oven. Subsequently, the reaction was studied under similar conditions. The catalyst showed consistent results with the best recyclability for the chosen reaction even after three cycles. The yield (95%) of stilbene remain constant is evident even after the catalyst were reused for three runs. To summarize, we have successfully demonstrated a phosphine free palladium-based heterogeneous catalyst as a promising catalyst for Heck reaction with good yield and recyclability.

4. Conclusions

A series of alkali and alkaline metal ions exchanged MCM-22 zeolites (Cs-MCM-22, Mg-MCM-22, K-MCM-22, and NH₄-MCM-22) were prepared and subsequently palladium dispersed. The resultant materials were systematically characterised using different spectroscopic and analytical techniques. FT-IR spectral studies and powder XRD analysis supported the presence of MWW structure of the catalysts. The powder XRD analysis of different cations exchanged zeolite showed sharp and independent peaks clearly support the retention of high crystallinity of MCM-22 framework even after loading bulk metal ions. TPD of carbon dioxide on the alkali and alkaline metal ions exchanged catalysts showed a broad distribution of basic sites. Among the various metal ions exchanged catalysts, the cesium ion-exchanged catalyst turned out to be the most basic in nature with two distinguished desorption peaks, and one of them at the highest temperature of 550 °C indicating the existence of the stronger basic sites. The decrease in the surface area upon ion exchange with bulk cesium ions corresponds to the accommodation of cesium ions in the pores and channels of MCM-22 framework. The well-characterized cations exchanged MCM-22 samples were studied for the industrially important transformation of eugenol to isoeugenol. The best catalytic activity was obtained in cesium ion-exchanged MCM-22 and showed 76% conversion of eugenol with the exclusive formation of isoeugenol as a product. The Pd dispersed catalysts were explored for Heck coupling reaction of styrene with iodobenzene. Among the various catalysts studied, Cs/Pd-MCM-22 catalyst showed 99% yield of stilbene in the presence of an external base at optimum reaction conditions. Further, the catalytic activity remains intact for both isomerizations of eugenol and Heck coupling reactions.

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References

- Liang J, Liang Z, Zou R and Zhao Y 2017 Heterogeneous catalysis in zeolites, mesoporous silica, and metal-organic frameworks *Adv. Mater.* **29** 1701139
- Corma A 1995 Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions *Chem. Rev.* **95** 559
- Unnikrishnan P and Srinivas D 2016 *Heterogeneous catalysis* In *Industrial Catalytic Processes for Fine and Specialty Chemicals* (Netherlands: Elsevier) pp. 41–111
- Sakthivel A and Baskaran T 2016 Amino-Silane Functionalized MCM-22 Zeolite and Its Application on Nitroaldol Condensation *Adv. Porous Mater.* **4** 206
- Szostak R 1989 *Molecular Sieves* (New York: Van Nostrand Reinhold)
- Rubin M K and Chu P 1990 ExxonMobil Oil Corp *Composition of synthetic porous crystalline material, its synthesis and use* U.S. Patent 4,954,325
- Sahu P, Eniyarppu S, Ahmed M, Sharma D and Sakthivel A 2018 Cerium ion exchanged layered MCM-22: preparation, characterization and its application for esterification of fatty acids *J. Porous Mater.* **25** 999
- Leonowicz M E, Lawton J A, Lawton S L and Rubin M K 1994 MCM-22: a molecular sieve with two independent multidimensional channel systems *Science* **264** 1910
- Thakkar R and Bandyopadhyay R 2017 Preparation, characterization, and post-synthetic modification of layered MCM-22 zeolite precursor *J. Chem. Sci.* **129** 1671
- Bellussi G, Carati A, Rizzo C and Millini R 2013 New trends in the synthesis of crystalline microporous materials *Catal. Sci. Technol.* **3** 833
- Rutkowska M, Díaz U, Palomares A E and Chmielarz L 2015 Cu and Fe modified derivatives of 2D MWW-type zeolites (MCM-22, ITQ-2 and MCM-36) as new catalysts for DeNO_x process *Appl. Catal. B: Environ.* **168** 531
- Corma A, Corell C, Fornés V, Kolodziejski W and Pérez-Pariente J 1995 Infrared spectroscopy, thermogrammed desorption, and nuclear magnetic resonance study of the acidity, structure, and stability of zeolite MCM-22 *Zeolites* **15** 576
- Corma A, Corell C, Llopis F, Marti A and Pe J 1994 Proposed pore volume topology of zeolite MCM-22 based on catalytic tests *Appl. Catal. A: Gen.* **115** 121
- Walton K S, Abney M B and LeVan M D 2006 CO₂ adsorption in Y and X zeolites modified by alkali metal cation exchange *Micropor. Mesopor. Mater.* **91** 78
- Ting A, Goss J M, McDougal N T and Schaus S E 2010 Brønsted Base Catalysts *Top. Curr. Chem.* **291** 145 and references therein.
- Jenicks W P 1972 General acid-base catalysis of complex reaction in water *Chem. Rev.* **72** 705
- Brønsted J N 1928 Acid and Basic Catalysis *Chem. Rev.* **5** 231
- Kishore D and Kannan S 2002 Isomerization of eugenol and safrole over MgAl hydrotalcite, a solid base catalyst *Green Chem.* **4** 607
- Hattori H 2014 Solid base catalysts: fundamentals and their applications in organic reactions *Appl. Catal. A: Gen.* **504** 103 and references therein.
- Hattori H 1995 Heterogeneous Basic Catalysis *Chem. Rev.* **95** 537 and references therein.
- Dunning H N 1953 Review of olefin isomerization *Ind. Eng. Chem.* **45** 551

22. Crossley S W M, Barabé F and Shenvi R A 2014 Simple, Chemoselective, Catalytic Olefin Isomerization *J. Am. Chem. Soc.* **136** 16788
23. Koeduka T, Fridman E, Gang D R, Vassao D G, Jackson B L, Kish C M, Orlova I, Spassova S M, Lewis N G, Noel J P and Baiga T J 2006 Eugenol and isoeugenol, characteristic aromatic constituents of spices, are biosynthesized via reduction of a coniferyl alcohol ester *PNAS* **103** 10128
24. Calvino-Casilda V, Pérez-Mayoral E, Martín-Aranda R M, Zienkiewicz Z, Sobczak I and Ziolk M 2010 Isomerization of Eugenol under ultrasound activation catalyzed by alkali modified mesoporous NbMCM-41 *Top. Catal.* **53** 179
25. Sakthivel A, Iida A, Komura K, Sugi Y and Chary K V R 2009 Nanosized β -zeolites with tunable particle sizes: Synthesis by the dry gel conversion (DGC) method in the presence of surfactants, characterization and catalytic properties *Micropor. Mesopor. Mater.* **119** 322
26. Glaser R and Weitkamp J 2004 *The Application of Zeolite in Catalysis In Basic Principles in Applied Chemistry* M Baerns (Ed.) (Berlin Heidelberg: Springer-Verlag) pp. 161–211
27. Karge H G, Zhang Y and Beyer H K 1992 Preparation of bifunctional catalysts by solid-state ion exchange in zeolites *Catal. Lett.* **12** 147
28. Weitkamp J 2000 Zeolites and catalysis *Solid State Ion* **131** 175
29. Flytzani-Stephanopoulos M and Gates B C 2012 Atomically dispersed supported metal catalysts *Annu. Rev. Chem. Biomol. Eng.* **3** 545
30. Djakovitch L and Koehler K 2001 Heck reaction catalyzed by Pd-modified zeolites *J. Am. Chem. Soc.* **123** 5990
31. Hussain I, Capricho J and Yawer M A 2016 Synthesis of Biaryl via Ligand-Free Suzuki-Miyaura Cross-Coupling Reactions: A Review of Homogeneous and Heterogeneous Catalytic Developments *Adv. Syn. Catal.* **358** 3320 and references therein.
32. Yin and Liebscher J 2007 Carbon-Carbon Coupling Reactions Catalyzed by Heterogenous Palladium Catalysts *Chem. Rev.* **107** 133 and references therein.
33. Djakovitch L and Koehler K 1999 Heterogeneously catalysed Heck reaction using palladium modified zeolites *J. Mol. Catal. A: Chem.* **142** 275
34. Jagtap S 2017 Heck reaction—state of the art *Catalysts* **7** 267
35. Barnard B C 2008 Palladium-Catalysed C-C Coupling: Then and Now *Platin. Met. Rev.* **52** 38
36. Corma A 1997 From microporous to mesoporous molecular sieve materials and their use in catalysis *Chem. Rev.* **97** 2373
37. Corma A, García H, Leyva A and Primo A 2003 Basic zeolites containing palladium as bifunctional heterogeneous catalysts for the Heck reaction *Appl. Catal. A: Gen.* **247** 41
38. Heck R F 1985 *Palladium Reactions for Organic Syntheses* (London: Academic Press) p. 19
39. Henriksen S T, Norrby P O, Kaukoranta P and Andersson P G 2008 Combined experimental and theoretical study of the mechanism and enantioselectivity of palladium-catalyzed intermolecular Heck coupling *J. Am. Chem. Soc.* **130** 10414
40. Sahu P, Ganesh V and Sakthivel A 2020 Oxidation of lignin-derived-model compound: *Iso*-eugenol to Vanillin over Cerium Containing MCM-22 *Catal. Commun.* **145** 106099
41. Pawlesa J, Zukal A and Čejka J 2007 Synthesis and adsorption investigations of zeolites MCM-22 and MCM-49 modified by alkali metal cations *Adsorption* **13** 257
42. Holzwarth U and Gibson N 2011 The Scherrer equation versus the ‘Debye-Scherrer equation’ *Nat. Nanotechnol.* **6** 534
43. Baskaran T, Joshi A, Kamalakar G and Sakthivel A 2016 A solvent free method for preparation of β -amino alcohols by ring opening of epoxides with amines using MCM-22 as a catalyst *Appl. Catal. A: Gen.* **524** 50