



Molybdenum Carbonyl Grafted on Amine-Functionalized MCM-22 as Potential Catalyst for *Iso*-Eugenol Oxidation

Preeti Sahu¹ · Alex Tincy¹ · Awadakkam Sreenavya¹ · Ganapati Shanbhag² · Ayyamperumal Sakthivel¹

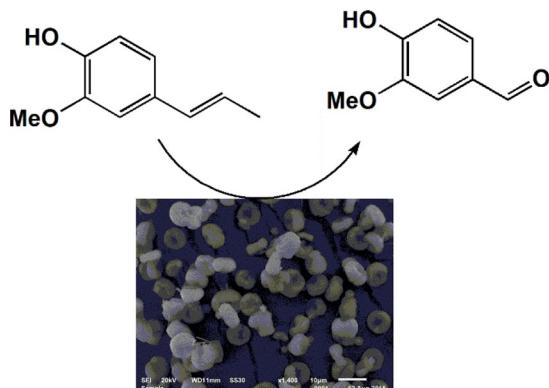
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Abstract

Different concentrations of molybdenum carbonyl were incorporated on the surface of amine-functionalized MCM-22. The obtained samples were thoroughly characterized by Fourier-transform infrared spectroscopy (FTIR), powder X-Ray diffraction (XRD), high-resolution transition electron microscopy (HRTEM), N₂-sorption and thermo-gravimetric analysis (TGA) methods. HRTEM images confirmed the uniform distribution of active molybdenum species on the functionalized MCM-22. The resultant materials were explored for liquid-phase oxidation of *iso*-eugenol at ambient reaction conditions. The catalyst with 6 wt% Mo(CO)₆ loaded materials showed comparable conversion (87%) with vanillin as the major product (selectivity of 61%) for the chosen reaction. The better catalytic activity of MCM-22-DA-Mo catalyst having 6 wt% loading of Mo carbonyl could be due to the uniform distribution of molybdenum species on MCM-22-DA surface. Importantly, the catalyst retained its activity even after several runs.

Graphic Abstract

Molybdenum carbonyl were incorporated on the surface of amine-functionalized MCM-22 by the post-synthesis method. The resultant MCM-22-DA-Mo showed promising activity on iso-eugenol oxidation with a conversion of 87%.



Keywords Zeolites · MCM-22 · Aminosilane grafting · Molybdenum carbonyl · *Iso*-eugenol oxidation · Vanillin

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1 Introduction

The historical significance of catalysis in the industrial processes has been known over the decades [1]. Heterogeneous catalysts play a pivotal role in fine chemicals, cosmetics, biochemical, and petroleum industries [2]. In particular, heterogeneous catalysts based on inorganic oxide, such as silica, alumina, hydrotalcite, clay, zeolites and zeolite-like microporous materials, polymers, and other mesoporous

materials are widely used [3]. Among them, zeolites and zeolite-like molecular sieves have shown a tremendous impact on petroleum and petrochemical industries as well as environmental processes [4]. Zeolites emerge with their capability for the sustainability along with cost-effectiveness and have potential for the innumerable advance applications such as thermal energy storage, biomass conversion, CO₂ capture, air purification redressal, etc. [5]. Besides, the importance of zeolites in the industrial applicability is due to the exceptional versatility that they offer as solid-acid catalysts whose structure and surface properties can be tailored easily [6]. Their shape selectivity and remarkable thermal stability also make zeolites favorable for various selective catalytic processes [7].

Among the range of zeolites, MCM-22 with a medium pore opening is of great importance as it has MW_W topology (MCM-tWent-tWo, Mobil Composition of Matter with sequence number twenty-two) [8]. The framework topology of MCM-22 zeolite includes two independent pore systems: two-dimensional sinusoidal 10-membered ring (10-MR) apertures (4 Å × 5.9 Å) and 12-MR large supercages (7.1 Å × 7.1 Å × 18.2 Å). This unique ordered porous structure shows the potential for ion exchange. The MCM-22 zeolite crystallizes in the form of a precursor that contains a system comprising large external cages with 12 members, deemed “cups” (0.71 nm × 0.70 nm), along with 10-membered sinusoidal channels [9]. The immense attention for MCM-22 as catalyst is due to its unique pore system and acidic nature and thus it has been used for several major reactions like methanol to olefins (MTO) [10], isomerization [11], and oxidation. A new window to the modification of the zeolites framework arises with the discovery of this layered two-dimensional MCM-22 zeolite [12]. The MCM-22 precursor contains vertically aligned layers not covalently connected; upon calcination the interlayer surfactant is removed with simultaneous 3D framework formation, giving rise to the MCM-22 zeolites which are now established as a promising catalyst in the research field [13]. Even though these layered materials show spellbinding properties due to the enhanced accessibility of external surface [14], a huge interest has been developed by the scientists in the preparation of surface-modified molecular sieve materials with the help of organic functional groups such as amine, sulfonic acid, mercapto amide, and halogen as they play an important role as catalysts and adsorbents [15]. Many reports have also shown that modifying the zeolites surfaces has increased their capacity as compared to that of the pristine materials [16]. In particular, the amine-functionalized molecular sieve materials act as linkers for the grafting of various organometallic complexes and showed higher selectivity for CO₂ adsorption in comparison with CH₄ molecule [17, 18]. In this regard, it is worth mentioning

the scope of grafting and tethering of metal complexes inside the pores of zeolites which promotes the reaction much better than the neat materials [19]. Among the various transition metal-based complexes, the molybdenum complexes have wide applications such as epoxidation, polymerization, and hydrodesulfurization [20], thus our interest focuses on heterogenization of molybdenum-based complexes.

Molybdenum complexes are versatile catalysts for various processes such as olefin metathesis, olefin hydrogenation [21], and oxidation of organic substrates, and thus have a remarkable interest. Predominantly, Mo(CO)₆ can exchange one or more CO ligands with other donor ligands, and the dehydroxylated environment of zero-valent Mo in Mo(CO)₆ provides active sites for hydrogenation, and hence it is used as a catalyst for hydrogenation and hydrosilylation reactions [22, 23]. Moreover, Mo species in zero-valent and higher oxidation states have a high affinity for olefin groups and are thus able to catalyze hydrogenation, oxidation, hydrosilylation, and metathesis processes [23]. The predominant characteristics of Mo catalysts are that they positively influence the preservation of the zeolite structures [24], the existence of a very distinct induction period, and the subsequent process of steady catalytic deactivation [25]. On this account, it would be worth attempting to introduce molybdenum ions into the framework and to utilize them for oxidation reactions. Oxidation reactions play a vital role in the chemical industry as it is the second-largest process and contributes to around 30% of the total production in the chemical industry. Moreover, selective oxidation catalysis is also a window to establishing a green and sustainable chemical processes [26].

Non-edible biomass is considered as an appealing and sustainable renewable feedstock for drop-in liquid fuels and bio-products with high carbon efficiency [27]. Catalytic oxidation of biomass-derived intermediates such as furfural, eugenol, and *iso*-eugenol to high-value chemicals has received considerable attention. Among them, we focus on the conversion of *iso*-eugenol to vanillin by the oxidation process. Vanillin (4-hydroxy-3-methoxy benzaldehyde) is a metabolite which is widely used in food, cosmetics, and pharmaceutical products as flavor and fragrance ingredients [28]. Vanilla sugar is used for chocolate manufacturing and in countless commercial products. In addition to the flavor qualities, vanillin also has medicinal value – as an antimicrobial agent [29]. However, the conventional production of vanilla is arduous, and only 1% of the required vanilla is obtained from these natural extractions. In this context, the emphasis has been made on producing vanilla via chemical and biochemical routes. Many reports have shown that 99% of the needed vanillin was produced by the chemical and biochemical techniques successfully [30]. Production of vanillin using

various chemical methods has been reported so far, such as the preparation of vanillin from coniferin [31], sulfite liquor [32], guaiacol and glyoxylic acid, and various lignin products.

Thus, the present study focuses on the preparation of vanillin from *iso*-eugenol using oxidation pathways because of their economic and commercial availability. *Iso*-eugenol is effortlessly obtained from lignin and has a common structural unit with that of vanillin and thus, it is potentially useful for vanillin production via simple oxidation pathways [33]. Moreover, many researchers have claimed that the conversion of *iso*-eugenol has led to several-fold higher vanillin production than that derived from any other products [34]. In this work, a systematic approach has been made on grafting of molybdenum ions into the surface of amine-functionalized MCM-22 zeolite for the oxidation of *iso*-eugenol to vanillin using H₂O₂ as a green and safer oxidizing agent.

2 Experimental Section

2.1 Synthesis of MCM-22

The MCM-22 was synthesized as per the modified procedure reported earlier [35]. All the MCM-22 samples were prepared with the molar gel composition of SiO₂: 0.3 NaOH: 0.033 Al₂O₃: 0.5 HMI: 45 H₂O.

Colloidal silica (silicon (IV) oxide, Alfa Aesar) was used as a silicon source, sodium aluminate (NaAlO₂, Sigma Aldrich) was used as an aluminium source, and hexamethyleneimine (HMI) (Alfa Aesar) was used as a template. The detailed synthesis involved the following step: first preparing solution A by adding 0.456 g of NaOH in 5 mL of water added to 10.01 g of colloidal silica. In parallel, solution B was prepared by adding 0.46 g of sodium aluminate to 5 mL of water. Solution B was added to Solution A with the addition of water. A homogeneous gel was obtained after 1 h stirring. In the subsequent step, the template Solution C was prepared by dissolving 4.602 g of HMI and 0.2 g of NaOH in 2 mL of water. The template solution was added into the prepared silica gel with continuous stirring with the addition of 28 mL of water and stirred continuously for 1 h to get a homogeneous mixture. The resultant gel was transferred to an autoclave and hydrothermally treated for 10 days at 155 °C. After the crystallization period, the sample was washed first with distilled water and then with ethanol to remove excess of NaOH and the organic template. Then it was dried in an air oven. The sample obtained was labelled as the as-synthesized MCM-22. The template present in the as-prepared material was removed by calcination at 550 °C for 6 h in the presence of air and the sample was labelled as MCM-22.

2.2 Preparation of Amine-Functionalized MCM-22

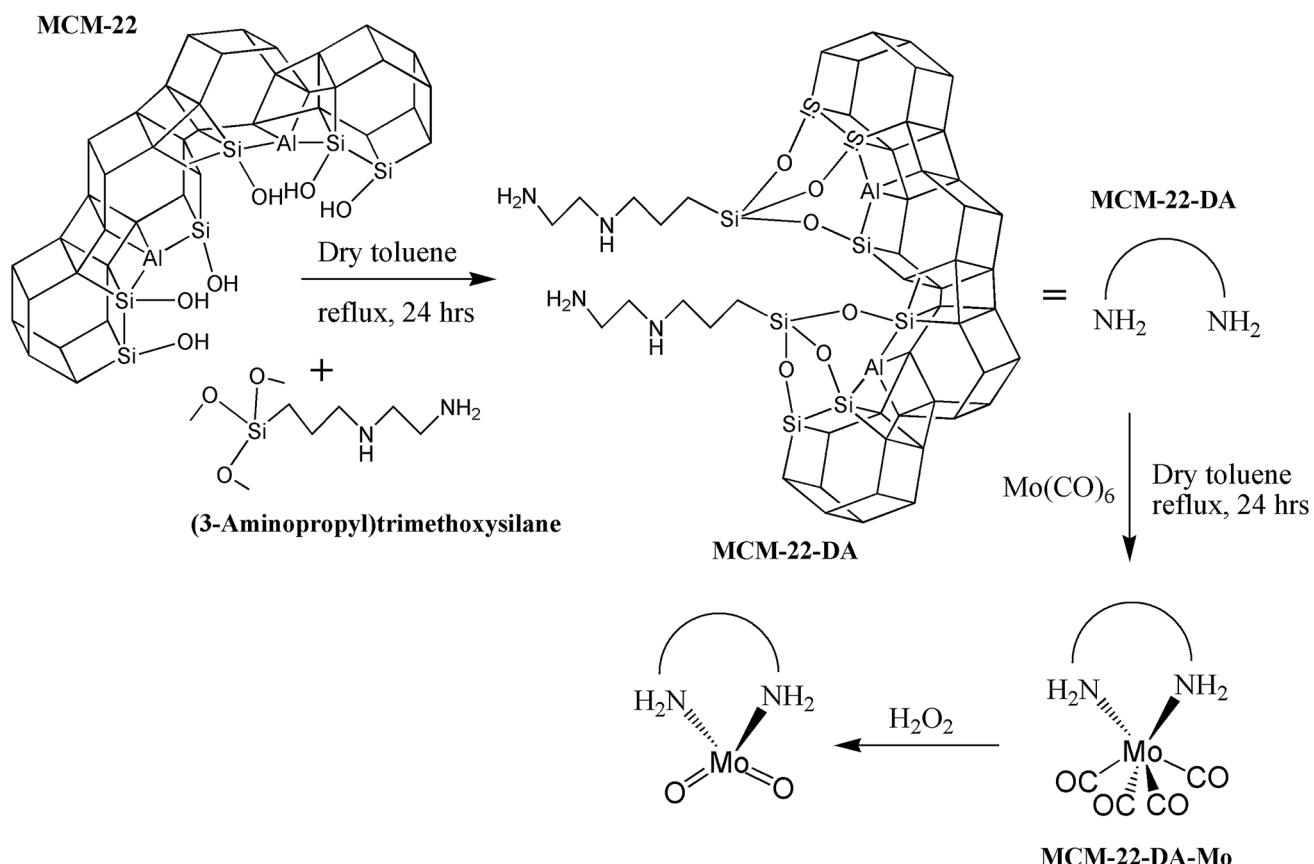
The aminosilane (3-aminopropyltrimethoxysilane) was utilized as received (from Sigma-Aldrich) without any further purification for the functionalization of MCM-22. Before the introduction of aminosilane, MCM-22 was activated at 110 °C overnight. Then the activated material was cooled down to room temperature and the calculated amount of 3-aminopropyltrimethoxysilane (3 mL/g w.r.t. MCM-22 catalyst) was introduced and refluxed using dry toluene (30 mL/g) for 24 h under nitrogen atmosphere at 110 °C (Scheme 1). The procedure was repeated three times, the final reaction mixture was cooled down to room temperature, and toluene was removed by vacuum filtration. The excess diamine was removed by washing with dichloromethane (DCM) several times and the solid was finally dried under vacuum to get amine-functionalized MCM-22 (MCM-22-DA).

2.3 Molybdenum Carbonyl (Mo (CO)₆) Grafting

About 3 mmol (0.792 g) of Mo(CO)₆ was introduced into 1 g of MCM-22-DA material in the presence of dry toluene and was refluxed under N₂ atmosphere for 6 h (Scheme 1). It was then filtered and washed with DCM several times and was dried under vacuum and then represented as MCM-22 DAMo. The different concentrations of molybdenum were introduced to the MCM-22-DA with different weight percent such as 1.5, 3, 5, 6, and 10% and were represented as MCM-22-DA-Mo1.5, MCM-22-DA-Mo3, MCM-22-DA-Mo5, MCM-22-DA-Mo6, and MCM-22-DA-Mo10, respectively.

2.4 Characterization of Material

FTIR spectra were recorded on JASCO-FT/IR 4700 FTIR spectrophotometer using KBr pellets. Spectra were collected with a resolution of 4 cm⁻¹ and 60 scans in the mid-IR (400–4000 cm⁻¹) region. Prior to pellet preparation, all the samples were dried well and uniformly ground to a fine powder. The powder XRD diffraction patterns were recorded using a Rigaku MiniFlex (300/600), Japan X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54059 \text{ \AA}$) in 20 range of 3–70, a scan speed of 3 degrees/min, and a step size of 0.02. Thermogravimetry (TG) measurements were carried out using Perkin-Elmer STA 6000 in the nitrogen atmosphere with a flow rate of 20 mL/min. The weight of the obtained sample was in the range of 2–5 mg and the heating rate of the sample was 10 °C min⁻¹ in the temperature range of 40–900 °C. Silica crucible was used as a sample holder. Higher-resolution transmission electron microscopy (HR-TEM) analysis was performed with a JEOL JEM-F200 to find the dispersion of molybdenum complex on the surface of functionalized MCM-22. N₂ adsorption-desorption measurements were carried out at –196 °C using an automatic



Scheme 1 Schematic representation of diammine functionalization and grafting of molybdenum carbonyl on the surface of MCM-22

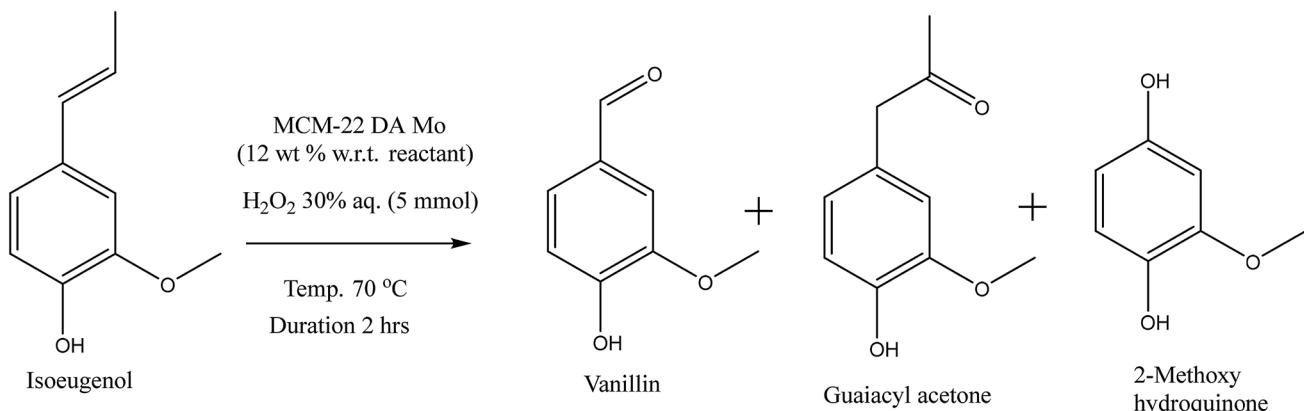
micropore physisorption analyzer (Micromeritics ASAP 2020, USA) after the samples were degassed at 250 °C for at least 10–12 h under 0.133 Pascal pressure before each run. The Brunauer–Emmett–Teller (BET) surface areas were calculated in the relative pressure of 91.9 kPa, over the adsorption branch of isotherm. DRUV–Vis spectra of the MCM-22 DA-Mo and samples loaded with different weight percent were recorded on Shimadzu UV-2700 double-beam spectrophotometer with the help of Teflon disc as reference. Prior to the analysis, all the samples were finely grounded to uniform powder.

2.5 Oxidation of Iso-Eugenol to Vanillin

The oxidation of *iso*-eugenol was carried out using hydrogen peroxide as a green oxidant since the by-product produced using hydrogen peroxide is water which is environmentally green. The probable oxidation products of *iso*-eugenol are presented in Scheme 2.

The catalytic activity of MCM-22-DA-Mo was studied by introducing 1 mmol of *iso*-eugenol (0.152 mL) into a two-necked round-bottom flask containing the catalyst. The reaction flask was fitted with a water condenser

in an oil bath with continuous stirring; when vapors started forming, 5 mmol (0.51 mL) of H₂O₂ (30% aqueous solution) was added dropwise. After complete addition of hydrogen peroxide, the reaction was carried out at stipulated temperature for 2 h. After the completion of the reaction, it was brought down to room temperature. Methanol was added to quench the reaction. It was then transferred to a sample vial and centrifuged and the catalyst was recovered. To the resultant solution, magnesium sulphate was added to remove the excess water from the unreacted H₂O₂. It was again centrifuged and transferred the product solution into a sample vial and was analyzed using 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. The role of various catalytic parameters such as reaction temperature, the catalysts having different molybdenum carbonyl concentrations, oxidant content, and the recyclability of the catalyst were systematically studied. The conversion and selectivity were calculated using the formulae given below after calculating the response factor obtained from the gas



Scheme 2 Pictorial representation of oxidation of *iso*-eugenol using MCM-22-DA-Mo catalyst

chromatogram with the calibration curve, where C_i and C_f are the initial and final concentration of reactant molecule.

$$\text{Isoeugenol conversion \%} = \frac{(C_i - C_f)}{\text{Initial Concentration of Reactant } (C_i)} \times 100$$

$$\text{Vanillin selectivity \%} = \frac{\text{Concentration of vanillin}}{(C_i - C_f)} \times 100$$

3 Results and Discussion

3.1 Materials Characterization

The FTIR spectra of calcined, amine-functionalized, and molybdenum carbonyl grafted MCM-22 are depicted in Fig. 1. The FTIR spectra of MCM-22 materials shows vibrational bands around 593 and 545 cm⁻¹, which are characteristics of zeolite secondary building block of double six-ring (D6R), which is a characteristic feature of MWW zeolite structure [7, 8]. The bands observed around 790 cm⁻¹ correspond to the symmetric stretching of Si—O—T (where T = Si or Al) linkage present in MCM-22 framework material. The band around 1015 cm⁻¹ correspond to ν_{asym} Si—O—Al internal vibrations and 1069 cm⁻¹ correspond to ν_{asym} Si—O—Al external vibrations [8, 9].

All the samples exhibit bands around 1090, 795, 593, and 545 cm⁻¹, which are the characteristics vibrations of the MCM-22 framework. In addition to this, two additional vibrational bands were present around 2923 and 2854 cm⁻¹ for the MCM-22-DA sample, which are correspond to the C—H stretching from the alkyl diamine group present on the ligand. The band around 3480 cm⁻¹ correspond to the N—H stretching vibrations. The vibration spectra of materials freshly grafted by Mo(CO)₆ complex (MCM-22-DA-Mo6 and MCM-22-DA-Mo10) showed a new vibrational band at 1998 cm⁻¹ characteristic of terminal carbonyl group which

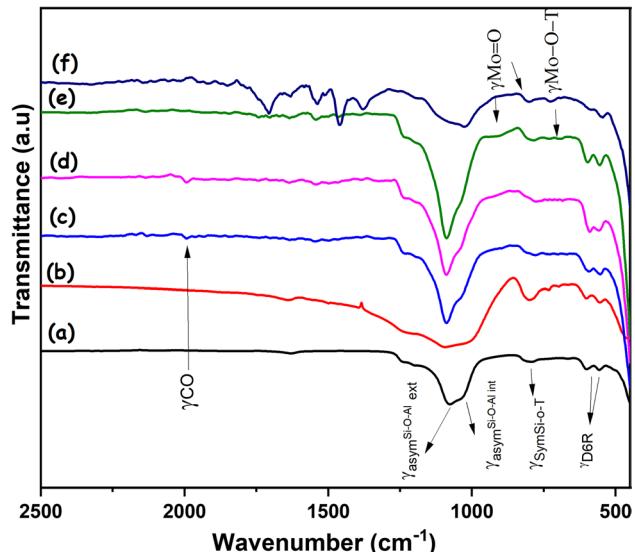


Fig. 1 FTIR characterization of calcined (a) MCM-22, (b) MCM-22-DA, (c) MCM-22-DA-Mo6, (d) MCM-22-DA-Mo10 and (e) MCM-22-DA-Mo6-H₂O₂-treated

confirmed the anchoring of molybdenum species on the diamine surface [20–23]. The molybdenum carbonyl loaded sample (MCM-22-DA-Mo6) when treated with H₂O₂, the additional broad band appeared in the range of 940–840 cm⁻¹, which shows the oxidative conversion of molybdenum carbonyl species in the active Mo(VI) di-oxo-species (Mo=O) [21–23, 36–40]. In addition, a broader and weaker band appeared around 700 cm⁻¹, characteristic of Mo—O—T (T=Mo, Si) moiety [36–40], which further shows that the molybdenum species are well dispersed and present as monomeric form of molybdenum oxo-species on the surface of functionalized MCM-22 material [21–23, 36–40].

The powder diffraction analyses of calcined MCM-22 and amine-functionalized molybdenum carbonyl grafted

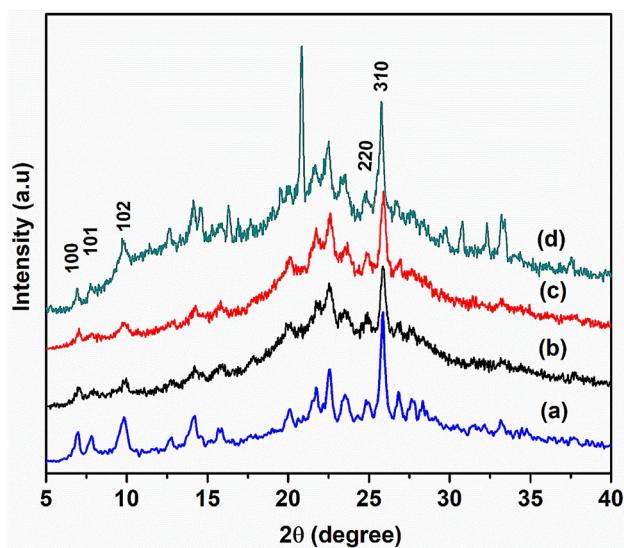


Fig. 2 XRD pattern of (a) calcined MCM-22, (b) MCM-22-DA-Mo6, (c) MCM-22-DA-Mo1.5 and (d) used catalyst

MCM-22 (MCM-22-DA-Mo) amine samples are shown in Fig. 2. All the samples showed sharp and well-defined peaks corresponding to (100), (101), (102), (220), (310) planes, which are typical of MCM-22 framework with MWW structure [8, 9]. The presence of sharp reflections confirms the good crystallinity of MCM-22. The major reflections of all the samples are indexed based on JCPDS data. Further, the molybdenum-grafted MCM-22 samples (MCM-22-DA-Mo1.5 and MCM-22-DA-Mo6) showed slight broadening in their peaks in comparison to the parent MCM-22 due to the introduction of bulk organo-linker (propylamine) and bulk molybdenum carbonyl present in the channel of MCM-22 framework. However, the retention of all the X-Ray reflections confirms that the structure remains intact even after loading higher molybdenum content. Diffused reflectance UV–Visible spectra of MCM-22-DA-Mo prepared with different amounts of grafted molybdenum complex are shown in Fig. 3. The UV–Visible spectra showed two intense absorptions bands around 210 and 230 nm, and the weaker absorption band around 300 nm may be due to the ligand-to-metal charge transfer transitions ($O \rightarrow Mo(VI)$) [23, 36–40], which is formed by the conversion of molybdenum carbonyl species into molybdenum oxo-species by the exposure to atmosphere. The absence of any additional absorption bands in the visible region supports the uniform distribution of molybdenum species on the surface of functionalized MCM-22. HRTEM images of MCM-22-DA-Mo6 and MCM-22-DA-Mo10 samples are shown in Fig. 4. The uniformly dispersed active molybdenum species on the surface

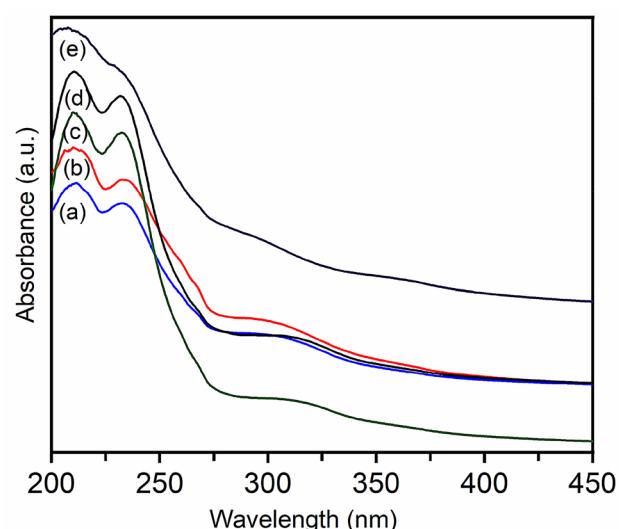


Fig. 3 Diffused reflectance UV–Visible spectra of (a) MCM-22-DA-Mo1.5, (b) MCM-22-DA-Mo3, (c) MCM-22-DA-Mo5, (d) MCM-22-DA-Mo6, and (e) MCM-22-DA-Mo10

of MCM-22-DA-Mo6 samples can be evident from HRTEM [41]. As the concentration of molybdenum increases (MCM-22-DA-Mo10), the aggregation of molybdenum species on the surface (Fig. 4b) is clearly evident.

The TG curves of the as-synthesized MCM-22 and MCM-22-DA-Mo6 samples are shown in Fig. 5. Four-stage weight losses were found in the TG curve of MCM-22a, with the following temperature intervals: 25–150, 150–300, 300–600, and above 600 °C. The first-stage weight-loss corresponds to the loss of 2.5% water present as physisorbed molecules in the channel and cavities. The second- and third-stage weight-losses are related to the removal of the organic template (HMI) and water formed with the condensation of the silanol group. The final weight-loss above 600 °C is due to the loss of residual organic substances. The mass loss in the second and third inflexions is related to the structural organic template (HMI) strongly bound inside the pores of zeolite MCM-22. HMI is found in two different locations: inside the 10-membered channels (strong interactions) and inside the 12-membered sockets (weaker interactions). In the case of MCM-22-DA-Mo6, a gradual weight loss found at the interval 25–150 °C corresponds to the physisorbed solvent molecules present on the surface. The second weight-loss occurring gradually in the temperature range of 150–300 °C may correspond to the degradation of molybdenum carbonyl and the organo-linker (propylamine) present in the surface of MCM-22 framework. The textural properties of the MCM-22 and MCM-22-DA-Mo samples are summarized

Fig. 4 HRTEM images of **a** MCM-22 DA-Mo6 and **b** MCM-22 DA-Mo10

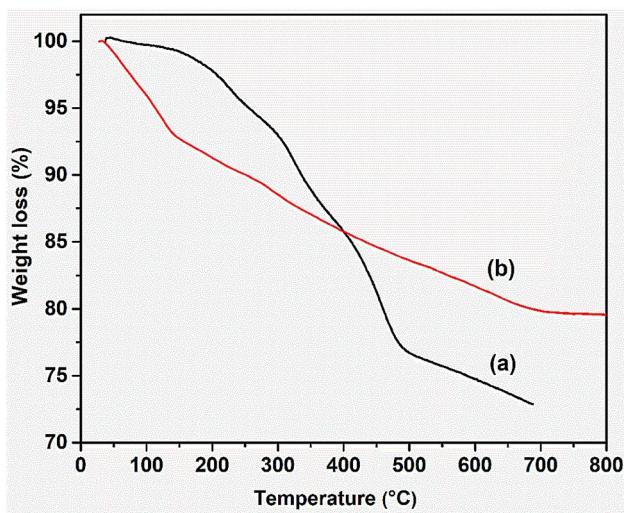
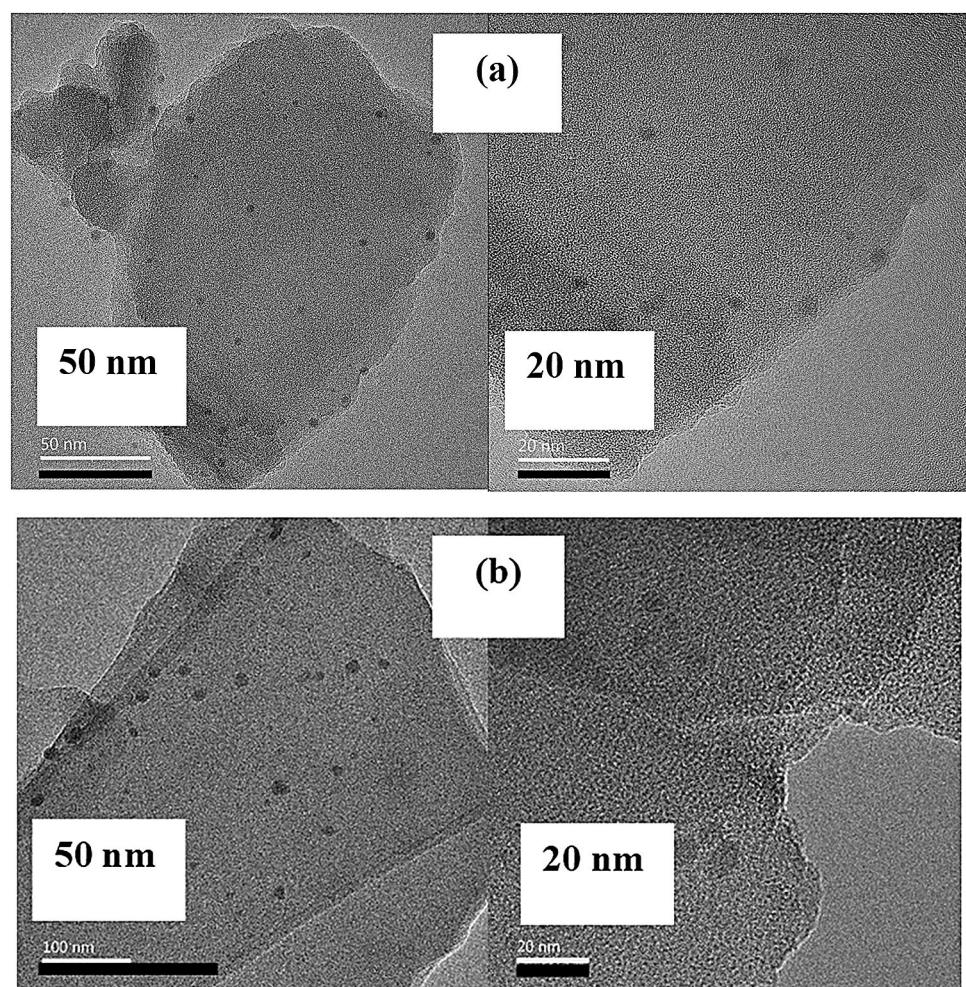


Fig. 5 TGA curve of (a) MCM-22 and (b) MCM-22-DA-Mo6

Table 1 Textural properties MCM-22 and MCM-22-DA-Mo samples

S. No.	Sample name	Surface area (m ² /g)		Pore volume (cm ³ /g)	
		BET	External	BJH	Micro pore
1	MCM-22	802	162	0.420	0.330
2	MCM-22-DA	142	89	0.107	0.096
3	MCM-22-DA-Mo-6	52	33	0.037	0.029

in Table 1. The amine-functionalized molybdenum carbonyl grafted MCM-22 will show a drastic decrease in surface area and pore volume owing to bulk Mo ions occupying the pores and channels of MCM-22 [9, 23].

The catalytic activity of well-characterized MCM-22-DA-Mo was evaluated for the oxidation of *iso*-eugenol with H₂O₂. The reaction was studied with different temperatures, with different amounts of oxidant and catalysts prepared with different weight percents of molybdenum carbonyl loaded on MCM-22-DA. After each run, the catalyst is recovered and the recyclability is evaluated.

3.2 Effect of Molybdenum Carbonyl Loading on Oxidation of *Iso*-Eugenol to Vanillin

The reaction carried out using pure MCM-22 and different weight percent (1.5, 3, 5, 6 and 10) of molybdenum carbonyl loaded on MCM-22-DA support and the resultant catalyst were used for the oxidation of *iso*-eugenol, and the results are depicted in Fig. 6a and b. The reaction did not facilitate without a catalyst and the use of pure MCM-22, which showed only 13 and 16% conversion respectively. The conversion of *iso*-eugenol increased steadily with increase in molybdenum concentration from 1.5 to 5 wt%, and the maximum conversion of about 85% was obtained on catalyst having 5 wt% molybdenum carbonyl (MCM-22-DA-Mo5). With further increase in molybdenum concentration, no appreciable improvement in conversion was evident, which may be due to the uniform distribution of molybdenum species on MCM-22-DA surface till the concentration of molybdenum carbonyl content is about 6 wt% (as evident from HRTEM). The use of MCM-22-DA-Mo6 (6 wt% molybdenum carbonyl-containing catalyst) showed better vanillin selectivity among all the catalysts studied. The in-situ formation of uniformly distributed (Fig. 4) molybdenum oxo- (Scheme 3) and dioxo- species as evident from FT-IR spectra of peroxide treated sample (Fig. 1e) [23] on the surface of MCM-22-DA-Mo6 may facilitate the better selectivity of vanillin (61%). The reaction may proceed by the interaction of peroxide with in-situ formed molybdenum oxo-species into peroxy-species [20–23] and subsequently, interaction of olefinic bond of *iso*-eugenol with peroxy species leads to C–O–Mo intermediates, which finally converted into vanillin with the regeneration of molybdenum dioxo species (Scheme 3).

3.3 Effect of Temperature on the Oxidation of *Iso*-Eugenol

The effect of different reaction temperatures ranging from 50 to 90 °C on the oxidation of *iso*-eugenol to vanillin is studied using MCM-22-DA-Mo6 catalyst and the results are depicted in Fig. 7a and b. The *iso*-eugenol conversion increases initially with temperature and reaches the maximum around 87% at 70 °C. When the reaction temperature is further increased to 90 °C, there is no appreciable change in conversion; however, the selectivity of the vanillin decreases drastically with the formation of guaiacyl acetone, 2-methoxyhydroquinone, and other products. The observed poor selectivity at a higher temperature may be due to the decomposition of hydrogen peroxide and facilitation of other products. The optimum condition to get maximum *iso*-eugenol conversion and vanillin selectivity was at 70 °C with MCM-22-DA-Mo6 catalyst. About 87% conversion and 61% selectivity of vanillin was obtained for the reaction of 2 h.

3.4 Effect of Varying the Concentration of Oxidant on Oxidation of *Iso*-Eugenol to Vanillin

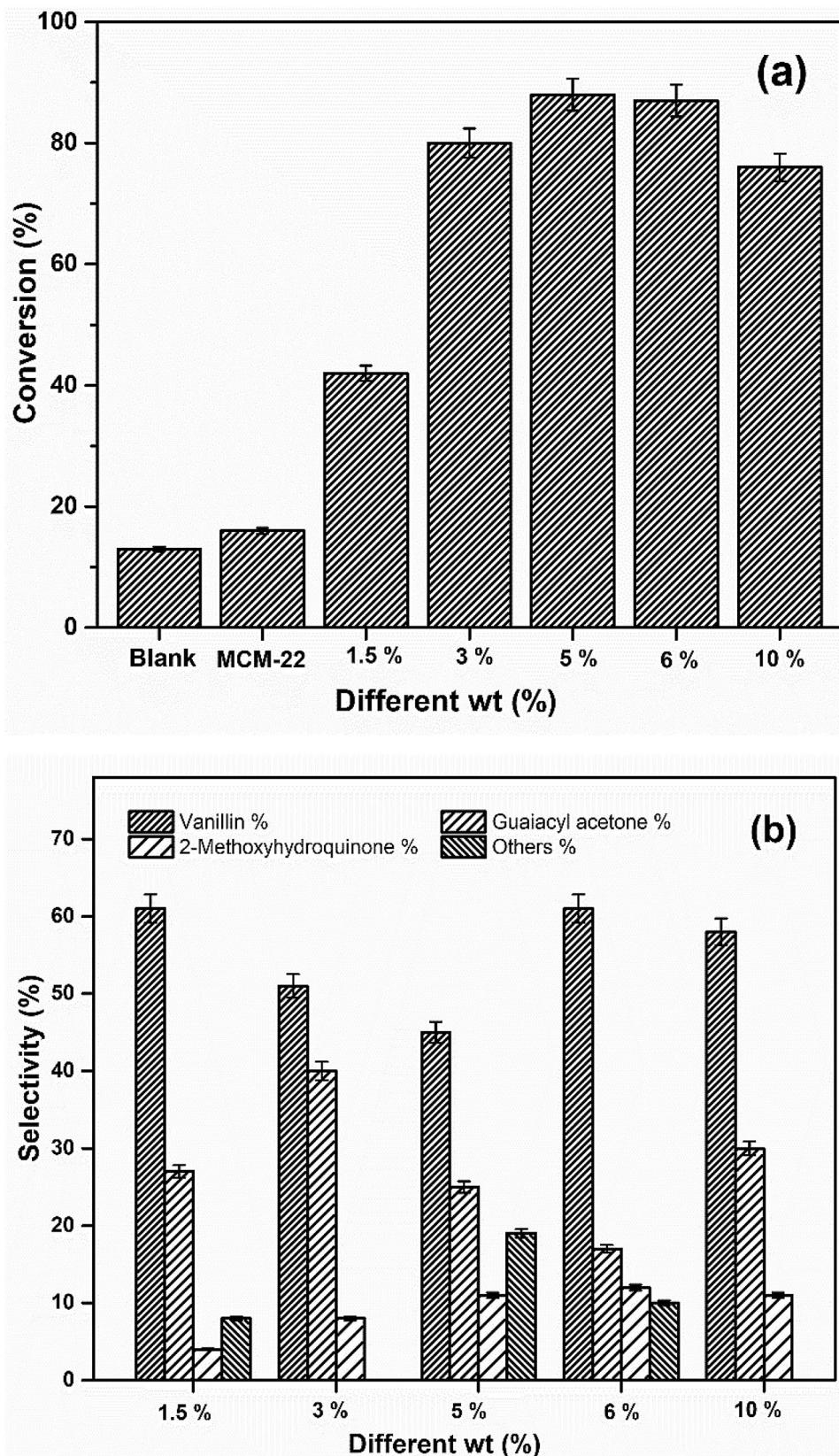
The reaction was further studied using different amounts (molar ratio with respect to *iso*-eugenol) of hydrogen peroxide (2.5, 5, and 7.5 mmol), and the results are summarized in Fig. 8a and b. With increase in H₂O₂ molarity from 2.5 to 5 mmol (1 mmol of *iso*-eugenol), the conversion of *iso*-eugenol increases from 62 to 87%, and a further increase in H₂O₂ molarity to 7.5, the conversion level remains intact, however, the selectivity of vanillin decreases with increase in unidentified products which may be due to over oxidation of *iso*-eugenol in presence of high H₂O₂ concentration.

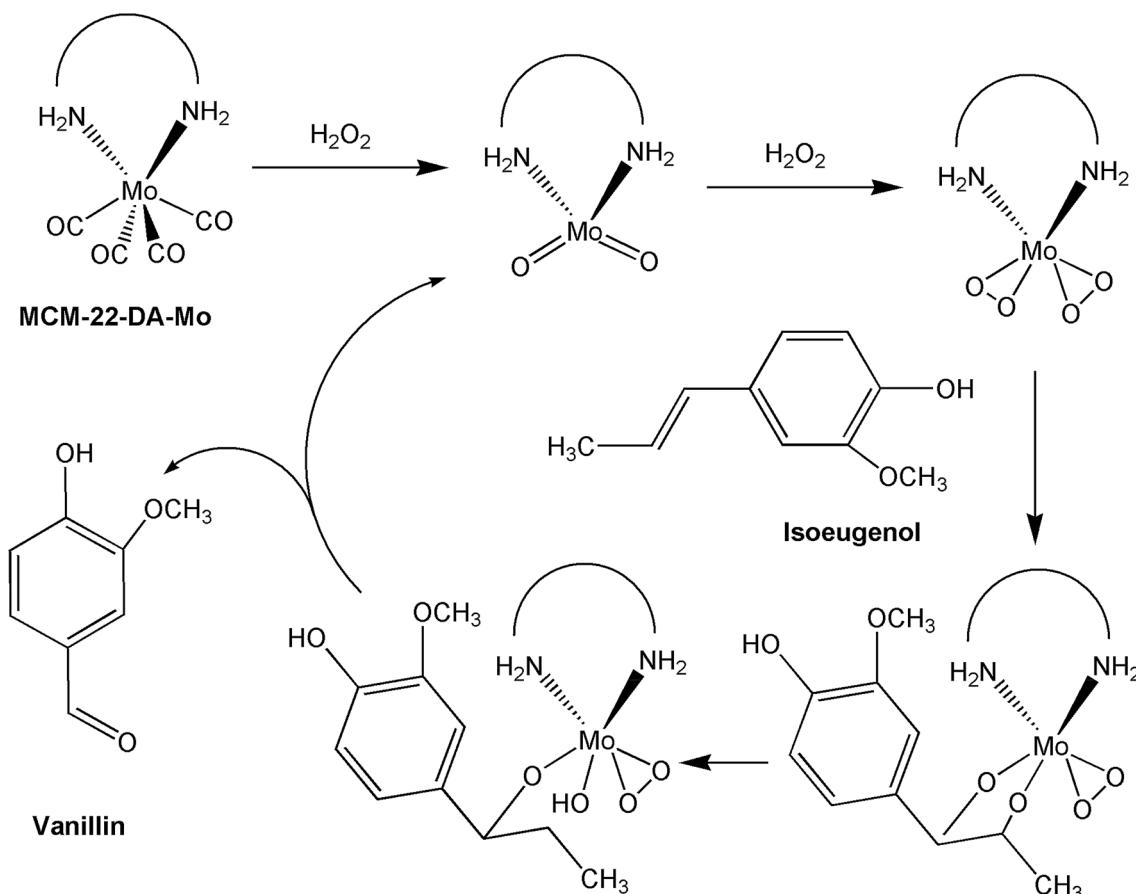
3.5 Recyclability of the Catalyst MCM-22-DA-Mo

The optimized catalyst (MCM-22-DA-Mo6) was further evaluated for recyclability by filtering the catalyst after the reaction, followed by thorough washing with ethanol, and subsequently air drying at 80 °C. The recycled catalyst was followed for several runs under optimum reaction conditions and the results are summarized in Fig. 9a and b. Interestingly, the *iso*-eugenol conversion and the selectivity of vanillin remain intact even after four cycles, which clearly supports that the heterogenized molybdenum catalyst successfully anchored on the surface of aminosilane modified MCM-22 support. Further, in order to understand the stability of the molybdenum species on the surface, a leaching experiment was conducted. In a typical leaching experiment carried out by treating catalyst with the required amount of substrate and oxidant, and the reaction was followed for half an hour. The reaction mixture was then cooled down to room temperature and the catalyst was filtered. Subsequently, the reaction proceeded with the filtrate solution which showed only about 11% conversion. This confirmed that the active molybdenum species is not leached into the filtrate solution and remained intact on the surface.

The textural properties of the used catalyst (MCM-22-DA-Mo6) was followed by FT-IR, powder XRD and BET surface area analysis. FT-IR spectrum of used catalyst (Fig. 1f) retained the broad vibrational bands in the range of 900–840 and 806 cm⁻¹, which are characteristic of Mo=O bond which supports that the active species remain intact on the surface. The additional band appeared around 1540, 1450 cm⁻¹ due to the presence of chemisorbed organic moiety on the surface of the catalyst. The powder XRD pattern of the used catalysts remained intact and showed all the reflections characteristic of MWW structure of MCM-22 (Fig. 2d). Overall, the present study is demonstrated the successful grafting of molybdenum species on amine-functionalized MCM-22 materials and its importance on the conversion of isoeugenol to vanillin.

Fig. 6 Effect of molybdenum carbonyl loading on **a** *iso*-eugenol conversion **b** product selectivity over MCM-22-DA catalyst





Scheme 3 Possible reaction pathway on conversion of isoeugenol to vanillin

4 Conclusions

Amine-functionalized molybdenum carbonyl grafted MCM-22 zeolites (MCM-22-DA-Mo) were synthesized by ion-exchange method, and the resultant materials were systematically characterized using various spectroscopic and analytical techniques. The powder XRD analysis confirmed the high crystallinity and the retention of the MW_W structure of MCM-22-DA-Mo even after the loading of higher molybdenum carbonyl content. FTIR spectroscopy further supports the presence of MW_W structure. TGA curve indicates the distribution of template HMI between the interlamellar regions and sinusoidal channels, which can be removed only by calcination at high temperature. The drastic decrease in surface area and HRTEM images of

MCM-22-DA-Mo6 sample indicates the uniform distribution of bulk molybdenum ions in the pores and channels of MCM-22. MCM-22-DA-Mo materials with different amounts of molybdenum carbonyl grafted were evaluated for the oxidation of *iso*-eugenol using H_2O_2 as the oxidizing agent. The studies revealed that MCM-22-DA-Mo6 shows promising catalytic activity for the oxidation of *iso*-eugenol to vanillin with 87% conversion and 61% vanillin selectivity at 70 °C in less than 2 h. The reproducibility of the reaction was also carried out up to four cycles and the activity remains intact. The observed good conversion and comparable selectivity of vanillin on the materials might be due to retention of active molybdenum oxo-species on the surface of functionalized MCM-22 surface.

Fig. 7 Effect of reaction temperature on **a** *iso*-eugenol conversion **b** product selectivity over MCM-22-DA-Mo6 catalyst

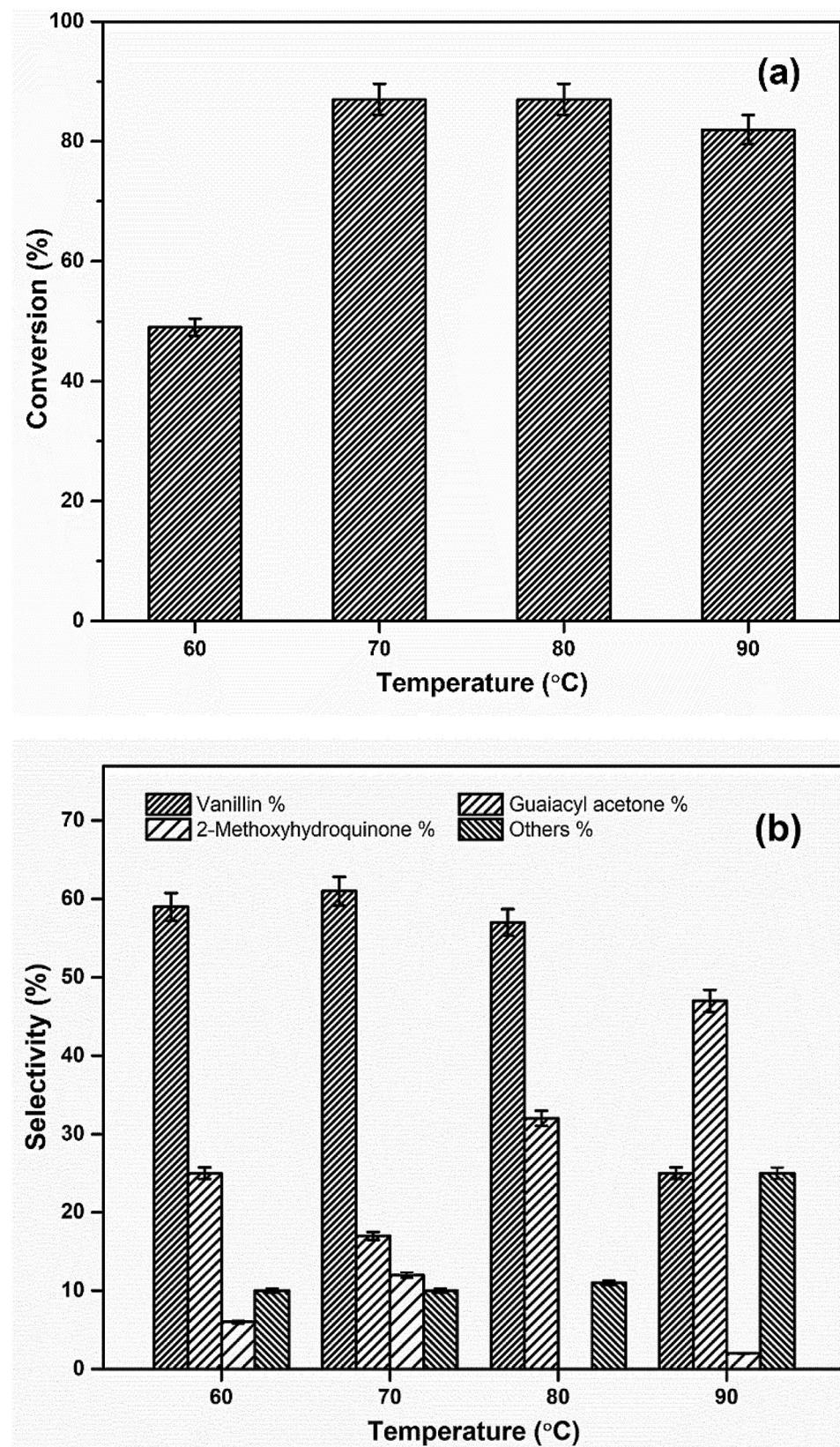


Fig. 8 Effect of oxidant amount variation on **a** *iso*-eugenol conversion **b** product selectivity over MCM-22-DA-Mo6 catalyst

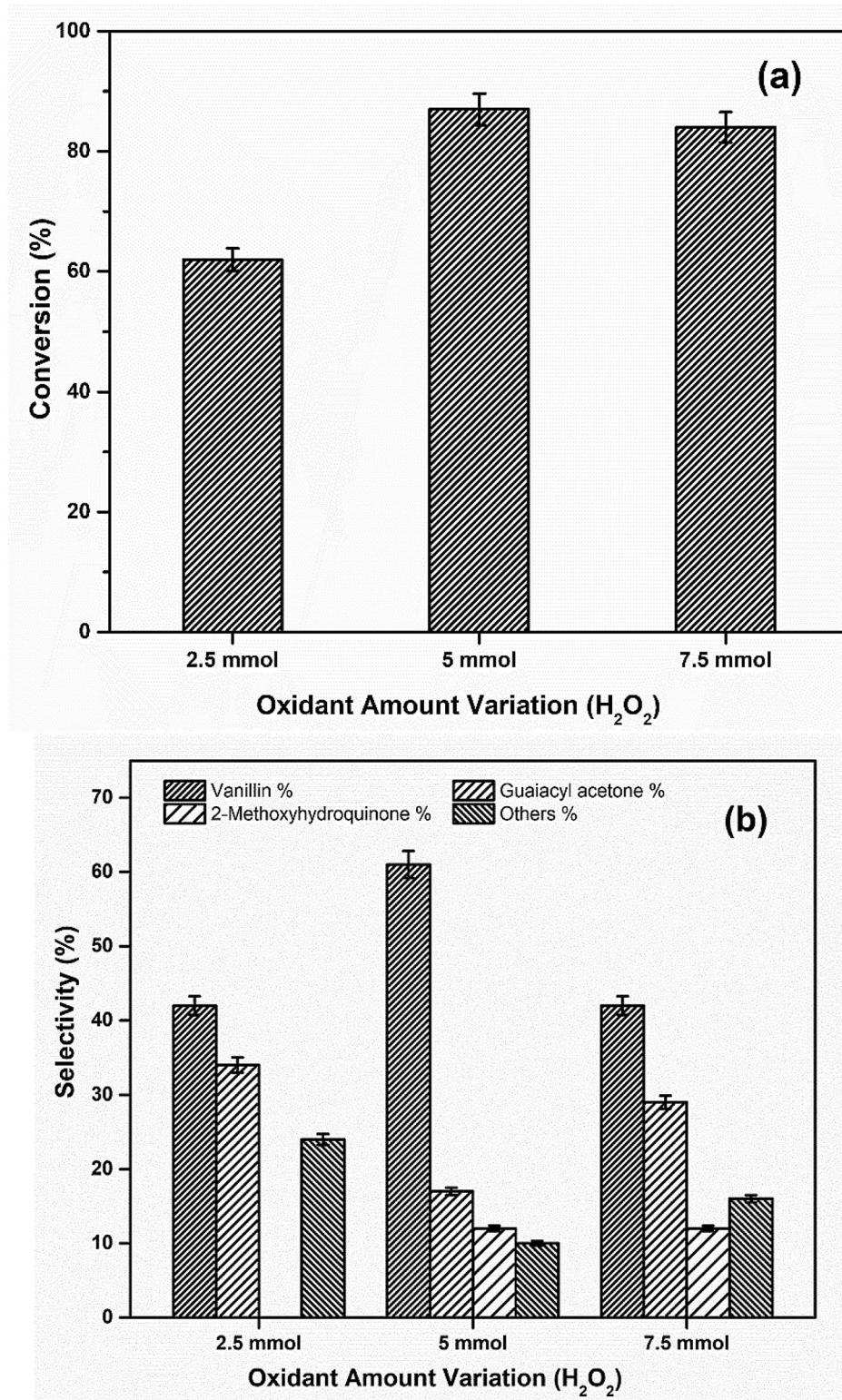
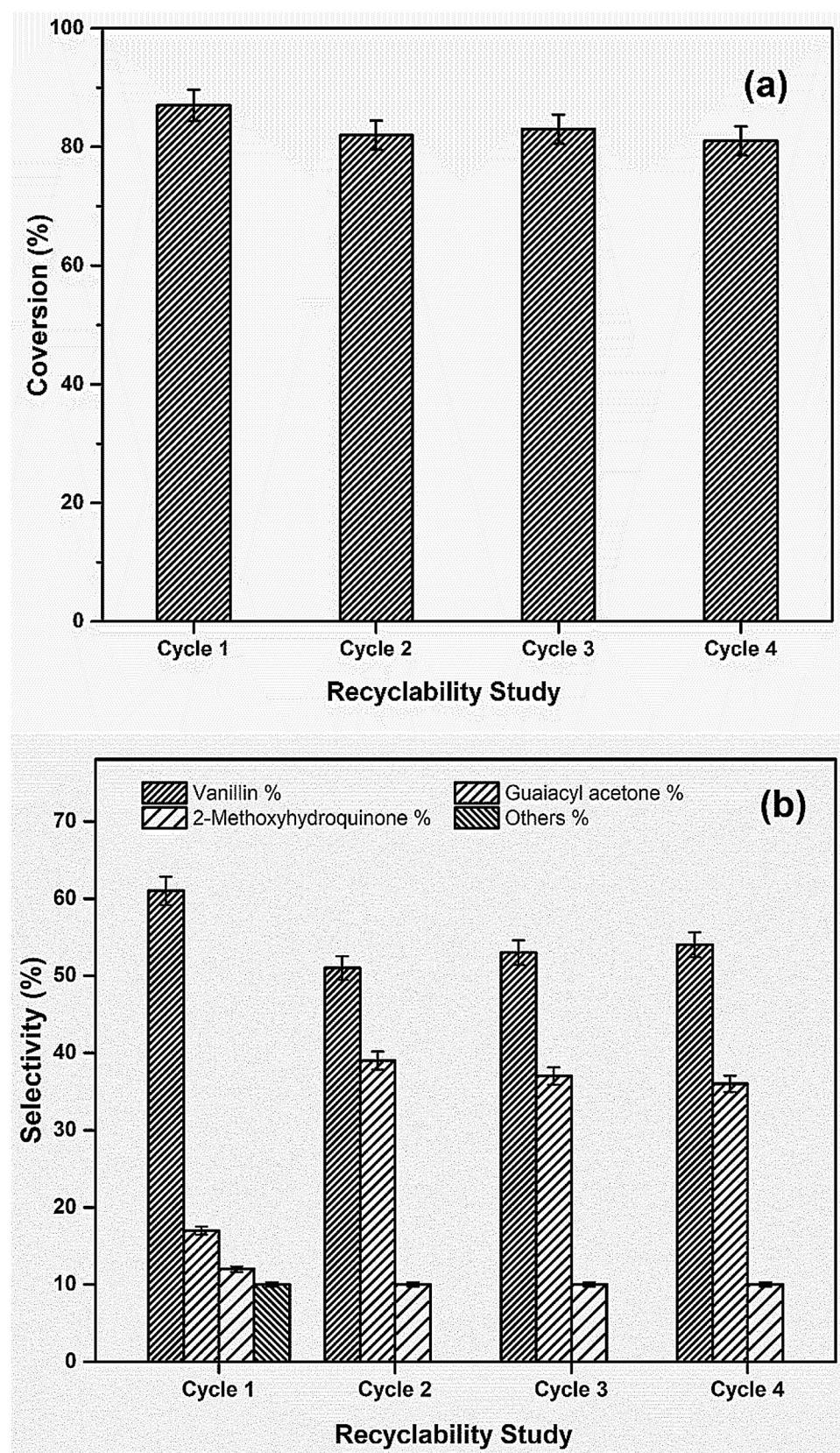


Fig. 9 Recyclability study on **a** *iso*-eugenol conversion **b** product selectivity over MCM-22-DA-Mo6 catalyst



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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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