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Research Note

A highly selective, heterogeneous route to enones from allylic and benzylic compounds over mesoporous CrMCM-41 molecular sieves

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Dedicated to Professor M.M. Sharma, FRS on the occasion of his 70th birthday

Abstract

A unique combination of oxidant, solvent, and catalyst is proposed for the allylic and benzylic oxidation of alkenes to enones with 100% selectivity and good conversion. The proposed catalyst, CrMCM-41, in combination with H_2O_2 is found to be highly active and selective for this purpose. The catalyst is also found to be very useful for selective oxidation of toluene and aniline. It is also proved that the catalyst can be reused several times while maintaining its structural integrity and activity.

Keywords: Chromium; C–H activation; Oxidation; Mesoporous materials; Heterogeneous catalysis

1. Introduction

Selective oxidation of allylic compounds to corresponding ketones is of importance in many applications, ranging from agricultural products to pharmaceuticals [1–3]. A variety of chromium-based (Cr) reagents have been used for this purpose [4–7]. However, the use of large amounts of environmentally undesirable chromium reagents and the large volume of solvent required in these procedures, in combination with the complicated workup, makes such processes inefficient in large-scale productions. The major problem in these oxidation processes is the formation of various products due to uncontrolled oxidation. To overcome these problems, cobalt- and selenium-based catalysts have been reported; however, the demand of single product (enone) not achieved by these catalysts [8,9]. Sheldon et al. [10,11] and Das and Clark [12] also have reported excellent catalytic processes for these types of oxidation with good activity and >90% ketone selectivity. In earlier reports [13–16], we reported the oxidation of few allylic and benzylic compounds to corresponding enones over chromium containing mesoporous MCM-41 molecular sieves (CrMCM-41) with high selectivity. Although the above catalysts give high selectivity to ketones, other compounds are also obtained (e.g., epoxides, alcohols, and alkenes), and complicated processes are needed to separate the products. Here we report the successful conversion of allylic and benzylic compounds to enones using a mesoporous CrMCM-41 catalyst with 100% selectivity and good-to-high conversion, which will overcome the above-stated problems.

2. Experimental

2.1. Catalyst preparation

The CrMCM-41 catalyst was prepared as described previously [14] with a final gel molar composition of: 1 SiO_2:0.27 CTAB (cetyl trimethyl ammonium bromide):0.26 NaOH:0.26 TMAOH (tetra methyl ammonium hydroxide):60 H_2O:0.02 Cr_2O_3 (chromium nitrate as source; Si/Cr = 50). The calcinations were performed at 823 K for 2 h in a flow of nitrogen (N_2), followed by 8 h in air. The as-synthesized CrMCM-41 was light green in color, whereas the calcined CrMCM-41

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was light yellow. The change in color to yellow after calcination of the CrMCM-41 catalyst can be attributed to the surface polychromate-type clusters [17], which are responsible for leaching of the chromium species during reaction. To avoid this problem, the calcined CrMCM-41 (100 mg) was washed with 1 M ammonium acetate solution (30 mL) for 12 h at room temperature under constant stirring. This removed the loosely bound chromium species from the CrMCM-41 catalyst. The yellow color of the calcined sample changed to white after washing, indicating successful removal of the surface chromium species. This washed CrMCM-41 catalyst was used for the oxidation reactions. For comparison, titanium-substituted MCM-41 (TiMCM-41; Si/Ti = 50) was prepared and characterized as described previously [18].

2.2. Reaction conditions

The oxidation of allylic and benzylic compounds (18 mmol) was carried out in the presence of 36 mmol hydrogen peroxide as an oxidant (50% H_2O_2) at 353 K for 12 h under atmospheric pressure using 50 mg of the catalyst and 5 mL of solvent (methanol). In a typical liquid-phase oxidation setup, the above reaction mixture was refluxed in a 50-mL round-bottomed flask fitted with a spiral condenser. The temperature was maintained by an oil bath filled with paraffin oil. Constant stirring was maintained throughout the reaction using a spinning bar. After the reaction, the catalyst was separated and extracted with ether three times, and then the products were analyzed by gas chromatography (GC; Nucon) with OV-101 column. The products were further confirmed using combined GC–mass spectrometry (MS; Hewlett G1800A). The conversion and selectivity presented here are based on the GC calculations using standard reference compounds.

2.3. Quenching studies

To check the leaching of chromium ions from the catalyst, several recycling and quenching experiments were carried out on both calcined and washed catalysts. The quenching experiments were performed by separating the catalyst from the reaction mixture under the reaction conditions, and the reaction was followed on the quenched solution.

2.4. Recycling and washing studies

To check the recyclability of the catalyst, four reaction runs were carried out. For this purpose, after each reaction, the catalyst was separated from the reaction mixture by filtration and washed with acetone, followed by drying at 353 K. The catalyst was activated at 723 K for 6 h in air, to remove the adsorbed molecules, and then the reaction was then carried out on the recycled catalyst.

3. Results and discussion

Powder X-ray diffraction (XRD) patterns (Fig. 1) of as-synthesized and calcined CrMCM-41 shows four well-resolved reflections, (100), (110), (200), and (210), corresponding to a hexagonal lattice [14,17]. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) shows 0.75 wt% of chromium in the washed CrMCM-41 catalyst. The characterization of the catalysts are discussed in detail elsewhere [14].

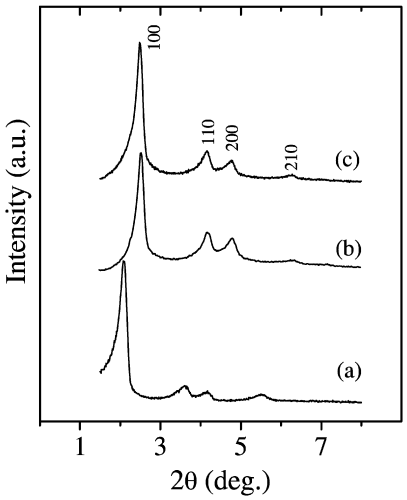
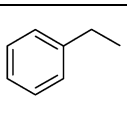
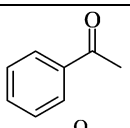
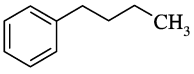
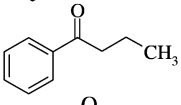
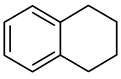
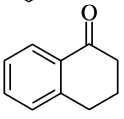
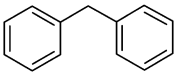
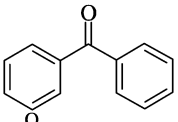
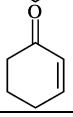


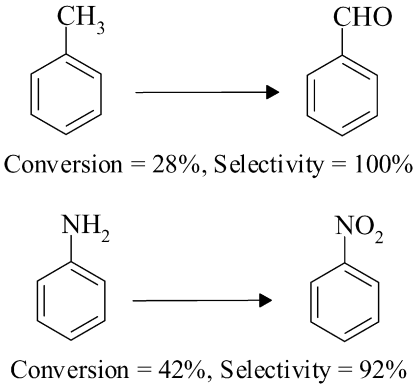
Fig. 1. XRD pattern of (a) as-synthesized CrMCM-41, (b) calcined CrMCM-41 and (c) CrMCM-41 after used for ethyl benzene oxidation reaction.

Table 1
Selective oxidation of allylic and benzylic compounds to corresponding enones[a]

Entry	Substrate	Product	Conversion[b]	Selectivity[b]
1			85.0 (84.2)[c]	100 (100)[c]
2			57.0	100
3			86.5	100
4			53.8	100
5			47.3	100

[a] Reaction conditions: temperature = 353 K; time 12 h; oxidant:substrate = 2:1 (mole ratio); solvent = methanol (5 mL); catalyst = calcined and washed CrMCM-41 (50 mg).
[b] Calculated from GC.
[c] After 3rd recycle.

Table 1 reports the results of allylic and benzylic oxidation of few industrial important organic compounds. The table shows that very good to high conversion is obtained for these compounds. Only corresponding enones are observed in the reaction mixture. Note also that for both pure MCM-41 and without catalyst (blank), the reaction showed only ∼6% conversion of



Scheme 1. Oxidation of toluene and aniline over CrMCM-41 (reaction conditions same as in Table 1).

ethyl benzene. This indicates that the observed high activity of CrMCM-41 could be attributed to the presence of isolated chromium ions in the matrix. *Tert*-butyl hydroperoxide (TBHP, 70%) was also used as an oxidant for the oxidation of ethyl benzene, and 92% conversion and 95% acetophenone selectivity were observed. But even though TBHP gave higher activity for these types of oxidation, H_2O_2 is preferred due to its better selectivity and eco-friendly nature [19,20]. TiMCM-41 catalyst under the same reaction conditions showed 100% acetophenone selectivity but lower activity (67% ethyl benzene conversion) than CrMCM-41.

To check the reusability of the CrMCM-41 catalyst, three recycling experiments for the oxidation of ethyl benzene were carried out over CrMCM-41. The selectivity to enones was 100% even after three recyclings. The filtrate and quenched solution showed only 3–6% ethyl benzene conversion, implying that the homogeneous part of the catalyst makes only a small contribution to the total activity. This observation is well supported by ICP-AES analysis of the filtrates obtained from the reaction mixture, which detected no chromium. Furthermore, the XRD pattern of the recycled CrMCM-41 catalyst (Fig. 1, plot c) shows that the catalyst maintained its structural integrity after the reaction. These results demonstrate the true heterogeneous nature of the catalyst under the specified reaction conditions. Moreover, our preliminary studies also show that the same catalytic system can be used for oxidation of alkylbenzenes (e.g., toluene) and aromatic amines (e.g., aniline), as shown in Scheme 1. In these experiments, aldehydes and nitro compounds were obtained as the major products.

4. Conclusion

CrMCM-41 catalyst in combination with 50% H_2O_2 showed high activity for the allylic and benzylic oxidation of some industrially important model compounds. In most cases, 100% enone selectivity was obtained. Further, the catalyst was found to be heterogeneous in nature. The catalyst also can be used for the oxidation of toluene and aniline. This catalytic process can be very useful in the selective oxidation of some valuable organic compounds in the pharmaceutical industry.

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