Catalysis by Mesoporous Molecular Sieves

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Abstract

Mesoporous metallo-silicate and aluminophoshate molecular sieves exhibit high activity and stability for the liquid-phase oxidation/reduction reactions than the corresponding microporous analogues as well as many other heterogeneous catalysts.

INTRODUCTION

A wide variety of homogeneous metal complexes have been reported for many organic transformations. However, these catalysts are not reusable due to various problems such as deactivation by metal precipitation or ligand degradation, separation difficulties, and so on. On the other hand, the use of heterogeneous catalysts offer several advantages over homogeneous systems with respect to easy recovery and recycling of catalysts as well as minimization of undesired toxic wastes. In this regard, transition metal substituted microporous molecular sieves (silicates, aluminosilicates and alumino-phosphates) have attracted significant attention as promising catalysts for such purpose [1]. However, their application is limited owing to the smaller pore size of the materials.

However, the discovery of mesoporous silicate and aluminosilicate molecular sieves [2,3], designated as MCM-41 and MCM-48, as well hexagonal mesoporous as aluminophosphates (HMA) [4], analogous to disordered MCM-41 structure, has not only broadened the scope of their use in catalysis but also overcome the drawbacks encountered by microporous materials [5-8]. They posses high surface area; large pore size and huge pore Hence, in recent years, numerous volume. heteroions substituted mesoporous silicates and aluminophosphates have been used in many catalytic applications including bulky organic substrates. It is, however, noteworthy here that the mesoporous silicates/metallosilicates posses ordered pores (Fig. 1-4) while the analogous

aluminophosphates have disordered pores (Fig. 5 and 6) [9-34].



Fig. 1. TEM image of VMCM-41 [10].



Fig. 2. ED pattern of VMCM-41 [10].

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At this juncture, it is also important to note that the transition metal incorporated mesoporous molecular sieves [9-34] have drawn significant interest as they can be used to perform certain important organic transformations such as alkylation, oxidation and hydrogenation more efficiently than the corresponding microporous analogues or supported metal oxide systems.



Fig. 3. TEM image of AlMCM-48 [11].



Fig. 4. ED pattern of AlMCM-48 [11].

In this presentation, novel, efficient and ecofriendly metal incorporated mesoporous silicate and aluminiphosphate catalysts are put forward as viable catalysts for a variety of industrially important organic transformations. The results indicate that the transformations occur in elegant and rapid manner with excellent yields. Furthermore, the catalyst can easily be recovered and reused without practically affecting the yields.



Fig. 5. TEM image of FeHMA [12].



Fig. 6. ED pattern of FeHMA[12].

Experimental

The experimental procedures employed for the preparation and characterization of various mesoporous-based molecular sieve catalysts as well as the reaction details are presented elsewhere [10-35]. All the catalysts were hydrothermally synthesized and characterized systematically using various analytical and spectroscopic techniques.

Results and Discussion

The oxidation of ethylbenzene, cyclohexene, cyclohexane over various and chromiumcontaining mesoporous catalysts showed very good substrate conversion and excellent product selectivity. More importantly, the activity is much higher any other chromium-based catalysts reported so far [19-23]. Fig. 7 depicts the results of a representative oxidation reaction of cylcohexane (Scheme 1) over several chromiumcontaining catalysts under mild reaction conditions [32].



Fig. 7. Catalytic activity of chromium-based mesoporous and microporous catalysts [32].

It is clear from this figure that the microporous catalysts, viz., (Cr)APO-5, (Cr)-Beta and (Cr)S-1, showed much lower activity along with a continuous decrease in activity as a consequence of leaching of active chromium ions.

On the other hand, it is interesting to note that only a marginal loss in activity was noticed for the mesoporous catalysts. Thus, the mesoporousbased catalysts opens up new possibility as potential heterogeneous catalysts and that the application of these catalysts can further be extended for bulkier molecules (Scheme 1). The successful oxidation of bulky substrates, viz., cyclooctane. cyclododecane and 2.6-di-tertbutylphenol, exhibited the novelty of the mesoporous catalyst [36]. Further, the activity of TiHMA was compared with TiMCM-41, TS-1, and TiAPO-5 (Fig. 8).



Scheme 1. Oxidation of cycloalkanes [34].



Fig. 8. oxidation of 2,6-di-tert-butylphenol [36].

On the other hand, MeHMA were found to be an excellent catalyst for the various reactions. A remarkable *para*-selectivity (para/ortho = 1.7) was achieved [23], for the first time, for the oxidation of phenol over TiHMA at room temperature (Table 1), and that the catalysts showed excellent activity for substituted phenols (Scheme 2).



Scheme 2. Oxidation of phenols [23].



Catalyst	Conversion (wt %)	<i>para/ortho</i> ratio
TiHMA [†] Calcined Washed Recycled [‡] Filtrate Blank HMA TiAPO-5 TiMCM-41	18.5 18.3 18.5 3.1 2.2 2.6 8.0 14.0 27.0	$ \begin{array}{r} 1.6 \\ 1.7 \\ 1.6 \\ 0.3 \\ 0.4 \\ 0.4 \\ 0.9 \\ 0.8 \\ 1.0 \\ \end{array} $

Table 1. Oxidation of phenol over TiHMA [23].

Selective reduction of nitroarenes (Scheme 3) and carbonyl compounds (Scheme 4) including bulkier molecules was achieved by catalytic transfer hydrogenation method (CTH) using mesoporous-based molecular sieve catalysts [24-27,35]. In addition, they were also found to behave as a truly heterogeneous catalyst as the yield was practically unaffected even after several recycling experiments.



Scheme 3. CTH of aromatic nitro compounds [24].



Scheme 4. CTH of aromatic carbonyl compounds [24].

The catalysts were also used successfully for the regioselective (Scheme 5) and chemoselective (Scheme 6) reduction of certain aromatic nitro and carbonyls compounds.









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