

Catalytic oxidation of alkylaromatics over mesoporous (Cr)MCM-41 *

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Liquid-phase catalytic oxidation of certain alkylaromatics over mesoporous (Cr)MCM-41 molecular sieves in the presence of chlorobenzene and tertiary butylhydroperoxide showed high substrate conversion and excellent product selectivity. The high catalytic activity of the materials is attributed to the complete oxidation of chromium ions to hexavalent chromium and the absence of pentavalent chromium in the mesoporous matrix.

KEY WORDS: (Cr)MCM-41; alkylaromatics; catalytic oxidation; mesoporous materials.

1. Introduction

Aromatic ketones such as acetophenone, butyrophenone, benzophenone, α -tetralone, and aromatic acids like benzoic and toluic acids are widely employed as solvents as well as intermediates in organic synthesis, resin synthesis, antihistamines, hypnotics and injectables [1]. In general, hexavalent chromium catalysts are extensively used for the transformation of alkylaromatics to aromatic ketones and acids in homogeneous phase [2–5]. However, a large excess of the catalyst used in the homogenous medium has an adverse effect owing to the toxic nature of chromium, besides affecting the selectivity significantly. Therefore, in recent years, considerable attention has been focused on the development of heterogeneous catalysts, *e.g.* chromium-incorporated molecular sieves including microporous silicates, aluminophosphate and mesoporous silicates and pillared clays [6–11]. Among these various catalysts, chromium-containing mesoporous MCM-41 molecular sieves show promise for certain oxidation reactions [10,12]. Here we report the results of the oxidation reactions of some industrially important alkylaromatics (scheme 1), over these catalysts in the presence of chlorobenzene solvent and tertiary butylhydroperoxide (TBHP) oxidant.

2. Experimental

The chromium-containing MCM-41 was hydrothermally synthesized according to the procedure outlined elsewhere [13] from a gel having molar composition of $1\text{SiO}_2:0.25(\text{TDTMA})_2\text{O}:0.25\text{Na}_2\text{O}:45\text{H}_2\text{O}:0.01\text{Cr}_2\text{O}_3$.

Tetraethylorthosilicate (TEOS), tetradecyltrimethylammonium (TDTMA) bromide, and chromium nitrate ($\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$; Alfa; 98%) were used as the sources for silicon, template and chromium respectively. For comparison, the samples were also prepared using the usual source of chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$; Alfa; 98.5%). The typical synthesis procedure is as follows. First, a solution of chromium nitrate nonahydrate in water was added to tetraethyl orthosilicate and stirred for 15 min and the resulting solution was designated as A. Another solution, B, was prepared by adding an aqueous solution of NaOH to 27 wt% solution of tetradecyltrimethyl ammonium bromide in water and stirred for 30 min. Solution A was added to solution B and stirred for another 30 min for homogenization. The resulting gel was transferred into Teflon-lined stainless steel autoclaves and kept in an air oven for crystallization at 373 K for 24 h. The solid product obtained was washed, filtered and dried at 373 K overnight.

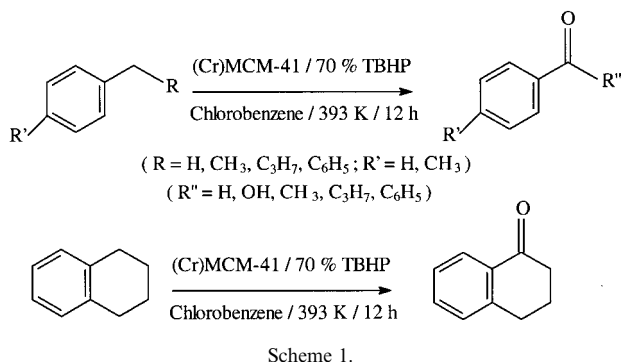
The as-synthesized sample was then calcined in a flow of oxygen at 823 K for 12 h. The samples prepared from chromium nitrate and chromium nitrate nonahydrate are designated Catalyst-1 and Catalyst-2, respectively. Unless otherwise stated, the catalyst used in the present study is Catalyst-1. The siliceous MCM-41 was also synthesized hydrothermally in a Teflon-lined stainless steel autoclave at 373 K for 24 h with a typical gel (molar) composition of $10\text{SiO}_2:1.35(\text{CTA})_2\text{O}:0.75(\text{TMA})_2\text{O}:1.3\text{Na}_2\text{O}:680\text{H}_2\text{O}$ [14–16]. The as-synthesized samples were calcined at 823 K in a flow of N_2 for 1 h, followed by 6 h in air. In this study, the chromium-free siliceous MCM-41 catalyst was also used for comparison.

Powder X-ray diffraction (XRD, Rigaku), thermogravimetry–differential thermal analysis (TG/DTA; Dupont 9900/2100), diffuse reflectance ultraviolet–visible (DRUV-VIS; Shimadzu UV-260), electron paramagnetic resonance (EPR; Varian E-112), silicon magic angle spinning–nuclear magnetic resonance (^{29}Si MAS–NMR,

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Varian number VXR-300s), and inductively coupled plasma–atomic emission spectroscopic (ICP-AES; Labtam Plasma 8440) techniques were used for the characterization. Various analytical and spectroscopic studies indicate the absence of framework chromium ions in MCM-41. Thus, the chromium-incorporated MCM-41 samples are, henceforth, designated as (Cr)MCM-41. In order to remove the non-framework chromium ions present in the mesoporous matrix, the calcined samples were washed with ammonium acetate solution (1M) as per the procedure described earlier [13]. The resulting sample is designated as ammonium acetate washed (Cr)MCM-41. In order to check the leaching of chromium ions (under reaction conditions) from the mesoporous matrix, several recycling and quenching experiments were carried out on both calcined and washed catalysts, as per the procedure given elsewhere [13].

The following six alkylaromatic substrates were chosen for the present investigation: tetralin, ethylbenzene, *n*-butylbenzene, diphenylmethane, *p*-xylene and toluene. The oxidation reactions were carried out in the liquid phase using 50 mg of the calcined (Cr)MCM-41 catalyst and 5 ml of the (chlorobenzene) solvent. A mixture containing the catalyst, solvent, substrate (8 mmol) and oxidant (TBHP, 16 mmol) were taken in a round bottom flask and refluxed at 393 K for 12 h, except for toluene where it was refluxed for 20 h, under constant stirring. For a complete oxidation of toluene and xylene, a stoichiometric molar ratio of (substrate-to-oxidant) 1:3 and 1:6 is required. Hence, these reactions were carried out with the above ratios. After completion of the reaction, the catalyst was filtered and the products were analyzed by gas chromatography (GC, Nucon 5700) employing an SE-30 column. They were further confirmed using combined gas chromatography–mass spectrometry (GC-MS, Hewlett G1800A) with HP-5 capillary column.

3. Results and discussion

The XRD patterns and TG-DTA studies of both as-synthesized and calcined siliceous MCM-41 (not

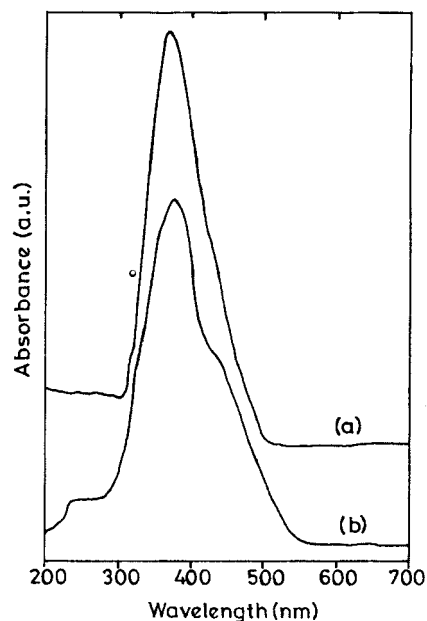


Figure 1. DRUV-VIS spectra of (a) Catalyst-1 and (b) Catalyst-2.

reproduced here) show typical characteristics of mesoporous hexagonal MCM-41 structure [14]. The as-synthesized (Cr)MCM-41 samples were green in colour and changed to yellow upon calcination. The former is due to the presence of trivalent chromium ions and the latter is due to the presence of higher valent chromium ions, namely chromate, dichromate and/or polychromates. XRD patterns (not reproduced here) of both as-synthesized ($d_{100} = 39.41 \text{ \AA}$) and calcined ($d_{100} = 36.14 \text{ \AA}$) samples are consistent with MCM-41 structure [15–18]. The former showed typical absorption bands at ~ 642 , 445 , and 290 nm in the DRUV-VIS spectra (not reproduced here) corresponding to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively. These bands are characteristics of trivalent chromium in octahedral coordination. On the other hand, the calcined samples (figure 1(a)) showed strong charge transfer (oxygen to chromium) bands at 375 nm along with the very weak shoulder at 322 and 430 nm assigned to chromate, dichromate and polychromate species, respectively [13,19]. In the case of Catalyst-2, the bands at 322 and 430 nm are pronounced (figure 1(b)), which is in accordance with earlier observation [13]. Unlike earlier reports, both on microporous [6] and mesoporous [10,13] molecular sieves, where the presence of Cr(V) is always noted, in the present study a complete oxidation of trivalent to hexavalent chromium is evidenced. That is, the EPR spectrum (at room temperature) of Catalyst-1 does not show the signal (figure 2(a)) while the Catalyst-2 (figure 2(b)) shows a clear signal at $g_{\text{eff}} = 1.97$ due to the presence of penta-valent chromium [20]. The ICP-AES results of calcined samples gave 1.17 and $1.23 \text{ wt\%}$ of chromium content in Catalyst-1 and Catalyst-2 respectively. The ${}^{29}\text{Si}$ MAS-NMR studies (figure 3) of calcined samples show distinct signals at -111 and -100 ppm , which are assigned to Q_4

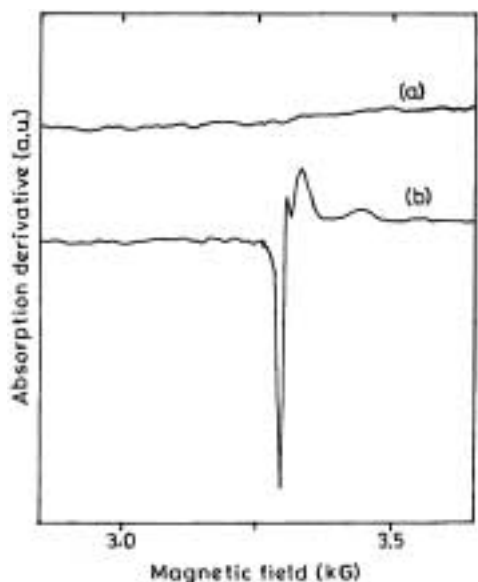
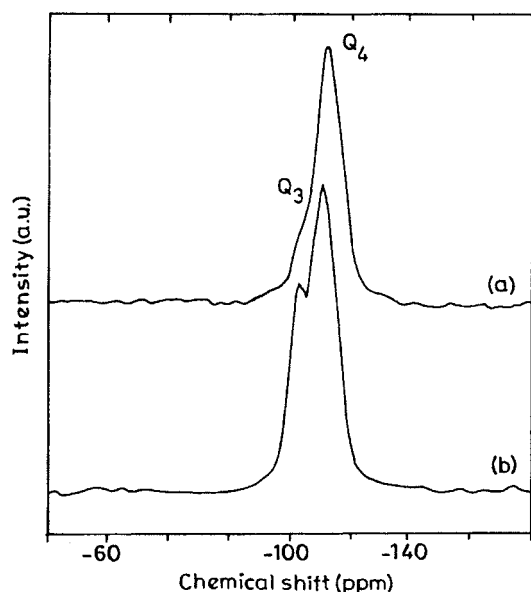
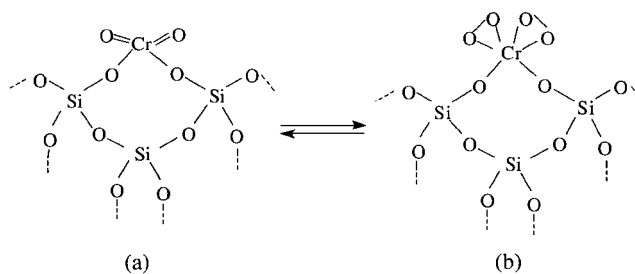


Figure 2. EPR spectra of (a) Catalyst-1 and (b) Catalyst-2.

and Q₃ (silicon) sites, respectively [17]. They reveal that MCM-41 possesses a large amount of silanol groups (Q₃; $\equiv \text{Si}-\text{OH}$), and it is considerably reduced for (Cr)MCM-41 (figure 3(a)). This is a clear indication that the silanol groups present in the matrix play an important role in stabilizing chromate, dichromate or polychromate species (scheme 2) in a similar way to that reported for the chromium supported silica catalysts [21,22] or tetravalent titanium grafted on the walls of MCM-41 [23].

Table 1 summarizes the results of the oxidation reactions carried with various substrates over (Cr)MCM-41 (Catalyst-1). The observed high conversion and selectivity may be explained as follows. Under

Figure 3. ²⁹Si MAS-NMR spectra of (a) (Cr)MCM-41 (Catalyst-1) and (b) MCM-41.

Scheme 2.

the reaction conditions, the hexavalent chromium in the matrix (scheme 2(a)) may interact with TBHP to form catalytically active peroxo-complex (scheme 2(b)). Subsequently, the substrate molecules interact with this reactive intermediate peroxo-species to give the final product, which may proceed through two steps, *i.e.* hydroxylation followed by oxidation at the benzylic position. The reactions were also carried out using siliceous MCM-41 as well as without using the catalyst. In both cases, about 5% conversion was noted, thus indicating that activity is only due to chromium ions. Table 2 summarizes the oxidation of ethylbenzene over (Cr)MCM-41 (Catalyst-2). From tables 1 and 2, it is clear that Catalyst-1 shows higher activity than Catalyst-2. The low catalytic activity of the latter could readily be attributed to the presence of (non-framework) polychromate and (extra-framework) pentavalent chromium ions. It is, however, noteworthy here that a significant decrease in catalytic activity was noted for the first recycling experiments (see table 2), which may be accounted for by leaching of active chromium ions from the matrix. The catalytic activity remains nearly the same after the first cycle or after washing experiments, indicating no further leaching of chromium ions from the mesoporous matrix, which is in good agreement with ICP-AES results of the filtrate/quenched/washed solutions where no chromium was detected. On the other hand, the moderate selectivity of the product for the recycled and washed catalysts may possibly be due

Table 1
Oxidation of alkylaromatics over (Cr)MCM-41 (Catalyst-1)

Reactant	Product	Conversion (wt%)	Selectivity (%)	TBHP efficiency (%)
Tetralin	α -Tetralone	92.5	95.0	93.5
Ethylbenzene	Acetophenone	90.3	89.0	93.8
<i>n</i> -Butylbenzene	Butyrophenone	61.0	90.0	91.6
Diphenylmethane	Benzophenone	48.7	92.0	90.3
<i>p</i> -Xylene ^a	Toluic acid	67.0	95.0	93.6
Toluene ^b	Benzoic acid	65.0	81.0	92.8

Note: Reaction conditions: temperature = 393 K; time = 12 h; substrate : oxidant = 1 : 2 (mole ratio); solvent = chlorobenzene; catalyst amount = 6 wt%.

^a Substrate : oxidant = 1 : 6 (mole ratio).

^b Substrate : oxidant = 1 : 3 (mole ratio).

Table 2
Oxidation of ethylbenzene over (Cr)MCM-41 (Catalyst-2)

Catalyst	Conversion (wt%)	Selectivity (%)	TBHP efficiency (%)
Calcined (Cr)MCM-41	70.0	92.0	93.0
First recycle	43.0	94.0	82.0
Second recycle	30.2	75.0	75.0
Third recycle	30.0	75.0	73.1
Washed (Cr)MCM-41	32.0	72.3	75.0
First recycle	30.3	75.5	75.9
Second recycle	31.2	68.9	73.7
Washed (Cr)MCM-41 ^a	56.0	88.8	87.1
Calcined MCM-41	4.1	67.1	43.7
No catalyst	4.7	60.0	47.8

Note: Reaction conditions: temperature = 393 K; time = 2 h; substrate: oxidant = 1:2 (mole ratio); solvent = chlorobenzene; catalyst amount = 6 wt%.

^a Catalyst amount = 15 wt%.

to the presence of low chromium content (0.78 wt%) resulting in the formation of an intermediate product, α -methyl benzyl alcohol. However, upon increasing the catalyst amount (see figure 4 and table 2) both the conversion and selectivity were increased. On the other hand, a considerable decrease in activity was noticed when the reaction (tetralin) was carried out in polar solvents such as methanol (54% conversion with 96% selectivity) or acetonitrile (32% conversion with 95% selectivity). This may be due to the fact that methanol/acetonitrile, being more polar compared with the substrate molecules, preferentially attacks the active sites. As a consequence, the interaction of the substrate molecules with the catalytically active peroxy species is hindered and thus the low conversion.

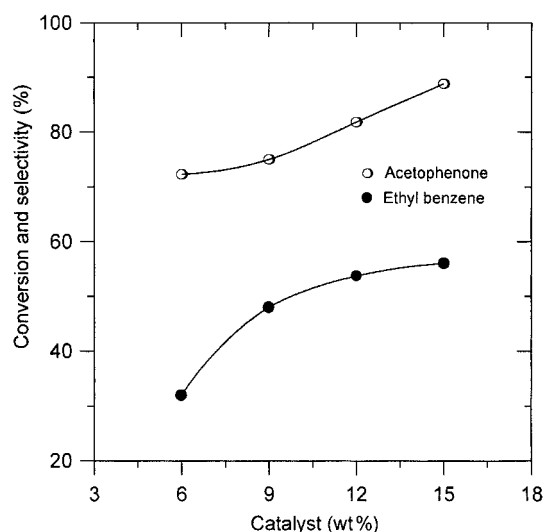


Figure 4. Effect of catalyst amount on the reaction over washed (Cr)MCM-41 (Catalyst-2).

4. Conclusions

We report here, for the first time, very high substrate conversion and product selectivity of certain alkylaromatics over mesoporous (Cr)MCM-41 molecular sieve catalyst. The excellent catalytic activity of these materials is attributed to the complete conversion of trivalent chromium ions (in the as-synthesized form) to hexavalent chromium ions (in the calcined form).

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