

Mesoporous (Cr)MCM-41 and (Cr)MCM-48 molecular sieves: promising heterogeneous catalysts for liquid phase oxidation reactions

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Chromium-containing mesoporous MCM-41 and MCM-48 silicate molecular sieves were synthesized and characterized. Unlike the chromium-containing microporous materials, the mesoporous analogues show significant activity for the chosen (ethylbenzene oxidation) reaction even after several recycling or washing treatments.

KEY WORDS: (Cr)MCM-41; (Cr)MCM-48; ethylbenzene oxidation; mesoporous materials

1. Introduction

Chromium compounds, in general, oxidize all organic functional groups in homogeneous medium [1,2]. However, they have several disadvantages owing to difficulty in separation of product from the reaction mixture, disposal of toxic effluents, *etc.* Hence, in recent years, attempts have been made to develop chromium-based heterogeneous catalysts, *e.g.*, molecular sieves, pillared clays and supported catalysts [3–14]. However, one of the major problems associated with these chromium-based catalysts is leaching of active chromium ions under the reaction conditions. Among the various molecular sieve based catalysts, the mesoporous MCM-41 and MCM-48 structures [15] are attractive as they can stabilize chromium ions in the matrix [13] in a similar way to that of functionalization of organic/inorganic molecules in the mesopores [16]. However, only few reports are available on the incorporation of chromium ions in MCM-41 and MCM-48 [8–14], and there were no attempts on the evaluation of the stability of chromium under the reaction conditions or repeated use of the catalysts. In order to unravel some of these problems, in this letter, we report a systematic study on the preparation, characterization and catalytic activity of chromium-containing MCM-41 and MCM-48. For this purpose, ethylbenzene oxidation was chosen as a test reaction.

2. Experimental

2.1. Synthesis and characterization

Tetraethyl orthosilicate (TEOS; Aldrich 98%), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Alfa 98.5%), sodium

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hydroxide (NaOH; Loba 98%) were used as sources for silicon, chromium and alkali, respectively. Tetradecyltrimethyl ammonium (TDTMA) bromide (SRL 99%), and cetyltrimethylammonium (CTA) bromide (Aldrich 99%) were used as template for the synthesis. Chromium-containing MCM-41 was synthesized hydrothermally, according to literature procedure [10,13], using a Teflon-lined autoclave at 373 K in an air oven for 24 h with a typical (molar) gel composition: $1 \text{ SiO}_2 : 0.25 (\text{TDTMA})_2\text{O} : 0.25 \text{ Na}_2\text{O} : 45 \text{ H}_2\text{O} : 0.01 \text{ Cr}_2\text{O}_3$. Likewise, chromium-containing MCM-48 was also synthesized hydrothermally, as per the procedure reported earlier for siliceous MCM-48 [17], using a Teflon-lined autoclave at 383 K for 8 days with a (molar) gel composition: $1 \text{ SiO}_2 : 0.30 (\text{CTA})_2 : 0.25 \text{ Na}_2\text{O} : 62 \text{ H}_2\text{O} : 0.01 \text{ Cr}_2\text{O}_3$.

The synthesized samples of both (Cr)MCM-41 and (Cr)MCM-48 were calcined in a tubular furnace under a flow of oxygen at 823 K for 6 h. All the samples were systematically characterized by various analytical and spectroscopic techniques, *viz.*, powder X-ray diffraction (XRD; Siemens D 500), thermogravimetry-differential thermal analysis (TG-DTA; Dupont 9900/2100), inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Labtam Plasma 8440), diffuse reflectance ultraviolet-visible (DRUV-Vis; Shimadzu UV-260); and electron paramagnetic resonance (EPR; Varian E-112) spectroscopic techniques. Various analytical and spectroscopic studies indicate the absence of framework chromium ions in both MCM-41 and MCM-48 matrix [13]. Thus, the chromium-incorporated MCM-41 and MCM-48 samples are, henceforth, referred as (Cr)MCM-41 and (Cr)MCM-48.

2.2. Washing studies

In order to remove the non-framework chromium ions present in the mesoporous matrix, the calcined samples were

Table 1
Oxidation of ethylbenzene over (Cr)MCM-41 and (Cr)MCM-48.^a

Experimental conditions	Ethylbenzene conversion (wt%)		Acetophenone selectivity (%)	
	(Cr)MCM-41	(Cr)MCM-48	(Cr)MCM-41	(Cr)MCM-48
Calcined catalyst	70.0	76.3	92.0	85.9
First recycle	43.0	54.5	94.0	69.8
Second recycle	30.2	47.4	75.0	67.5
Third recycle	30.0	45.5	75.0	68.0
Quenching	28.1	10.2	87.0	78.0
Washed catalyst	32.0	47.1	72.3	73.6
First recycle	30.3	46.0	75.0	71.0
Second recycle	31.2	45.2	69.0	68.9
Quenching	2.3	5.1	79.0	46.0

^a Reaction conditions: temperature 393 K, time 12 h, substrate : oxidant = 1 : 2, catalyst 6 wt%; no catalyst: ethylbenzene conversion 4.7 wt%, acetophenone selectivity 60.0%.

treated with ammonium acetate solution (1 M) as per the following procedure. About 100 mg of the catalyst was stirred with 30 ml of the solvent for 12 h at room temperature and then it was filtered, washed, dried at 373 K and recalcined at 723 K for 6 h in oxygen atmosphere. The resulting sample is designated as ammonium acetate washed catalyst.

2.3. Reaction procedure

The catalytic activity of the calcined as well as treated/washed catalysts was evaluated for the liquid phase oxidation reaction of ethylbenzene (Merck 99%) with 70% tertiary-butyl hydrogen peroxide (TBHP; Merck 70%) as oxidant and chlorobenzene (SRL; 99%) as solvent at 393 K for 12 h. The products, *viz.*, acetophenone and α -methylbenzyl alcohol were analyzed by gas chromatography (GC; NUCON 5700) employing an SE-30 column. This was further confirmed by combined gas chromatography–mass spectrometry (GC-MS, Hewlett G1800A) with a HP-5 capillary column.

2.4. Recycling/quenching studies

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. The recycle experiment was done as per the following procedure. After the reaction, the catalyst was separated from the reaction mixture, washed with acetone, and was dried at 353 K. Then in order to remove the adsorbed molecules, the catalyst was calcined at 823 K for 6 h in oxygen atmosphere. The reaction was then carried out on the recycled catalyst. The quenching experiment was carried out by separating the catalyst from the reaction mixture, under the reaction conditions, and the reaction was followed in the filtrate solution. The results of various sets of the reactions are summarized in table 1.

3. Results and discussion

Figure 1 shows the XRD patterns of (Cr)MCM-41 and (Cr)MCM-48. The diffraction patterns are typical of mesoporous MCM-41 and MCM-48 [15,17]. All the reflections

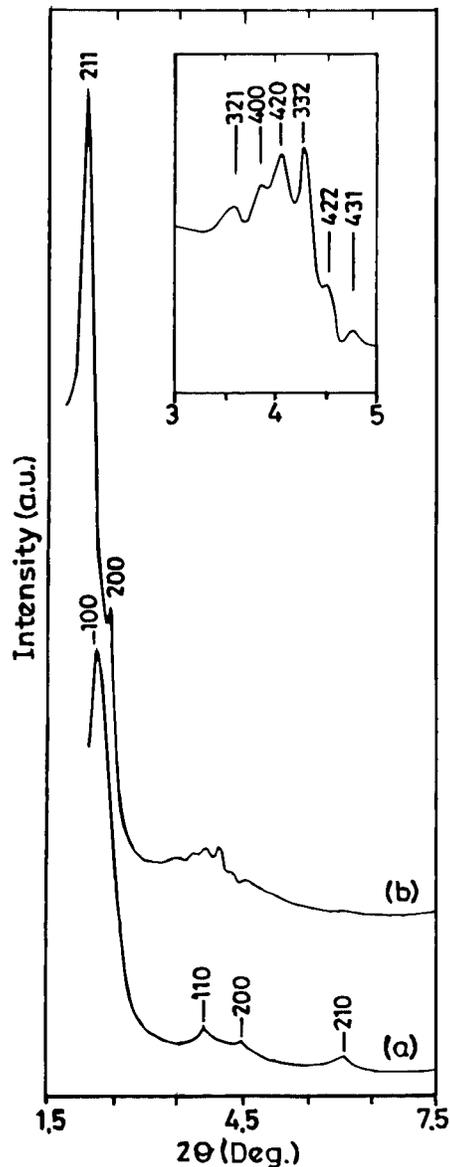


Figure 1. XRD pattern of (a) (Cr)MCM-41 and (b) (Cr)MCM-48.

are indexed based on hexagonal and cubic symmetry, respectively. TG of the calcined samples show a relatively small weight loss (10% for (Cr)MCM-41 and 5% for

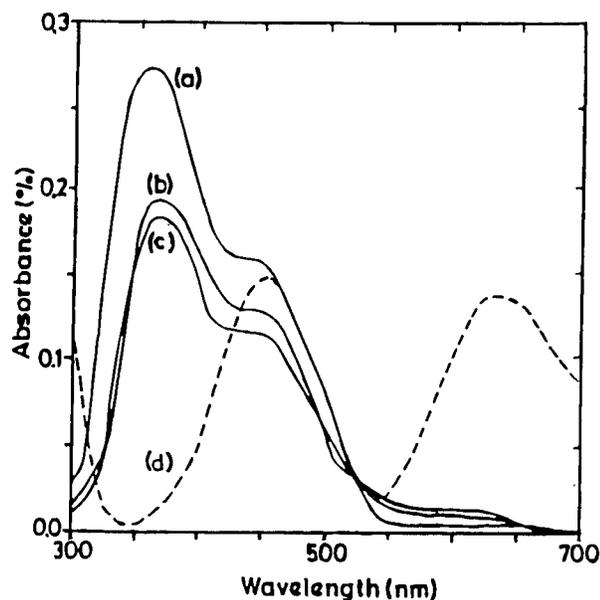


Figure 2. DRUV-Vis spectra of (a) calcined (Cr)MCM-41; (b) first recycled, (c) second recycled and (d) synthesized (Cr)MCM-41.

(Cr)MCM-48) as compared to its siliceous analogues (18% for MCM-41 and 22% for MCM-48) suggesting that part of the silanol groups are consumed for stabilization of chromium ions in the matrix in a similar manner as reported for chromium oxide supported on silica matrix [6]. DRUV-Vis spectra of synthesized samples (figure 2(d)) show absorption bands at 620, 440 and 270 nm, corresponding to trivalent chromium in octahedral coordination [10,18]. The calcined samples show a new prominent band at 367 nm with a shoulder around 440 nm (figure 2(a) and 3(a)). They are assigned to charge transfer bands associated with chromate and/or polychromate type species [10,18]. EPR spectra of synthesized samples show broad spectra ($g_{\text{eff}} = 1.98$) indicating the presence of trivalent chromium in octahedral coordination, while the sharp signal at $g_{\text{eff}} = 1.97$, for the calcined samples, is characteristic of pentavalent chromium in tetrahedral coordination [18]. This could be produced due to the partial oxidation of trivalent chromium during calcination. ICP-AES results of calcined samples show 1.23 and 1.58 wt% of chromium in MCM-41 and MCM-48, respectively, while the corresponding washed sample shows 0.78 and 0.98 wt% of chromium, respectively. The decrease in chromium amount is in good agreement with DRUV-Vis data (figure 2(b) and 3(b)), where a proportional decrease in absorption band intensities was noticed.

It is clear from table 1 that the calcined (Cr)MCM-41 and (Cr)MCM-48 catalysts show good substrate (ethylbenzene) conversion and product (acetophenone) selectivity. Further, the latter gives higher conversion than the former, which could directly be related to the higher chromium content in the matrix. On the other hand, the product selectivity was comparatively lower in case of (Cr)MCM-48 than (Cr)MCM-41 owing to the formation of some unidentified products. However, as expected, the catalytic activity was decreased upon recycling experiments on both the catalysts,

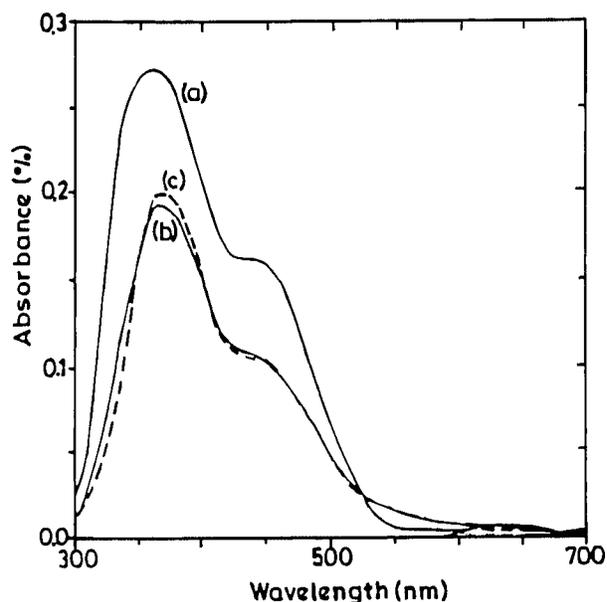


Figure 3. DRUV-Vis spectra of (a) calcined (Cr)MCM-41, (b) washed catalyst and (c) washed catalyst recycled.

owing to the leaching of non-framework chromium ions from the matrix under the reaction conditions. This was further confirmed by quenching study, where the quenched solution shows a typical conversion equivalent to that obtained from the leached chromium under the reaction condition. It is, however, interesting to note that after the second cycle the catalysts, (Cr)MCM-41, show nearly the same conversion indicating no more leaching of chromium from the matrix. Moreover, ICP-AES analysis of the quenched solution confirms the absence of chromium. In addition, the DRUV-Vis spectrum of the recycled catalyst shows very little or no change in the absorption band intensities (figure 2(c)) thus supporting the above observations.

On the other hand, the catalytic activity remains constant, for the ammonium acetate washed catalysts, even after several recycle experiments. This was well supported by DRUV-Vis studies (figure 3 (b) and (c)), *i.e.*, no appreciable change in absorption band intensities of washed catalyst during recycle experiments, thus indicating the heterogeneous nature of the catalysts. This was confirmed by quenching experiments carried out on ammonium acetate washed samples, where the quenched solution shows only 2–5 wt% conversion which corresponds to the conversion obtained without catalyst (see table 1). A similar trend was also noted for (Cr)MCM-48.

4. Conclusion

From this study, it is concluded that the mesoporous (Cr)MCM-41 and (Cr)MCM-48 molecular sieves behave as truly heterogeneous catalysts and that the active chromium ions are stabilized in the matrix. Further, the catalysts are quite promising for the liquid phase oxidation of ethylbenzene.

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