Oxidation of Phenols over Mesoporous (Cr)MCM-41 Molecular Sieves

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(Received June 28, 1999; CL-990570)

The catalytic performance of mesoporous chromium containing MCM-41 molecular sieves was investigated for the oxidation of phenols. The substrate conversion and the product selectivity are remarkably enhanced by ammonium acetate, acetylacetonate treatments of this unique catalyst. In particular, phenol shows excellent results compare to the TS-1 catalyst.

Chromium incorporated microporous as well as mesoporous molecular sieves are of particular interest because chromium compounds are widely used as stoichiometric oxidants in organic synthesis[1] and as homogeneous catalysts [2] in the presence of alkyl hydroperoxides. Moreover, Cr(VI) typically catalyzes oxidations *via* an oxometal mechanism in which chromyl (CrO_2^{2+}) species are the active oxidants. Only few of reports[3,4] are available concerning the oxidation of phenols over chromium containing microporous as well as mesoporous molecular sieves. Further, the results are not encouraging, and attempts to reproduce the results on repeated use of the catalyst (recycling) were largely unsuccessful.[3,4] Moreover, the chromium ions normally tend to leach out from the matrix under the reaction conditions.[3]

It is however, to be noted here that the titanium containing microporous molecular sieve based catalysts, e.g., TS-1,[5] TS-2[6] and TiAPO-5,[7] are also proved to be excellent catalysts for such oxidation reactions under mild conditions. In this letter, we report the selective oxidation of phenol and substituted phenols, viz., 3,5-dimethyl phenol (DMP) and 2,3,5-trimethyl phenol (TMP), to the corresponding quinones over chromium containing MCM-41 catalyst. Further, we also demonstrate that the substrate conversion as well as the product selectivity is remarkably enhanced by ammonium acetate/acetylacetonate treatment of this catalyst.

The chromium containing MCM-41 was synthesized[8] hydrothermally in teflon-lined stainless steel autoclaves, at 373 K for 24 h, using tetraethyl orthosilicate, tetradecyltrimethyl ammonium bromide (TDTMABr), sodium hydroxide, distilled water and chromium(III) nitrate nonahydrate with a typical gel (molar) composition of : $1SiO_2$: 0.5TDTMABr : 0.25NaOH : $45H_2O$: $0.02Cr_2O_3$. The as-synthesized sample was then calcined in a flow of oxygen at 823 K for 12 h. The calcined sample is designated as Catalyst-A. In order to remove the non-framework chromium ions, one part of the Catalyst-A was treated separately with ammonium acetate (1 M) and acetylacetonate, and they are referred to as Catalyst-B and Catalyst-C, respectively.

The as-synthesized sample was pale green in colour and turned to pale yellow upon calcination. Powder X-ray diffraction, thermogravimetry (53% wt. loss), differential thermal analysis, and BET surface area (1066 m^2g^{-1}) measurements confirm the mesoporous nature of the samples. Various analytical and spectroscopic studies indicate the absence of framework substitution of chromium ions in MCM-41, however, support anchoring of chromium ions on the pore wall structure via surface hydroxyl groups.[8] Thus, the chromium incorporated MCM-41, henceforth, is designated as (Cr)MCM-41.

Diffuse reflectance ultraviolet-visible (DRUV-VIS) spectrum of as-synthesized (Cr)MCM-41 shows bands at 270, 440 and 620 nm (Figure 1a). They are respectively assigned to ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transitions indicating Cr(III) in octahedral coordination.[9] On the other hand, for the calcined sample (Catalyst-A), a prominent band appears at 367 nm along with a shoulder at 440 nm (Figure 1b) typical of chromate and/or polychromate species.[9–11] However, the band intensities were reduced by ~ 30% for the Catalyst-B (Figure 1c) and ~ 52% for the Catalyst-C (Figure 1d) owing to the removal of non-framework chromium ions. Further, inductively coupled plasma-atomic emission spectroscopic results on the chromium content support the above observation.

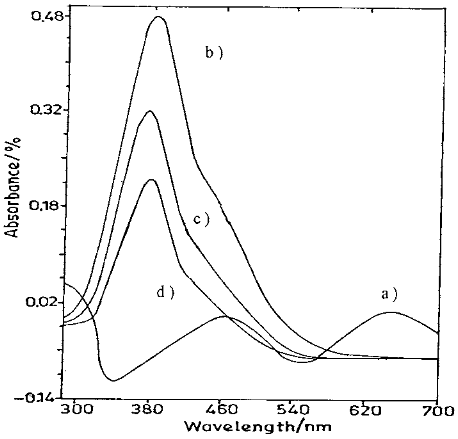
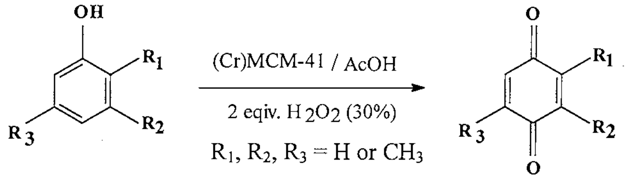


Figure 1. DRUV-VIS spectra of (Cr)MCM-41: (a) as-synthesized; (b) Catalyst-A; (c) Catalyst-B and (d) Catalyst-C.

The oxidation reaction of various phenols (Scheme 1) were performed as per the following procedure: One gram of the substrate was dissolved in 10 ml of glacial acetic acid and 50 mg of catalyst-A was added at room temperature. To this, 3.5 ml of aq. H_2O_2 (30%) was added drop wise for 10–15 min under constant stirring. The reaction was continued for 12 h and the mixture was then quenched by pouring into ice cold water (50 ml). The catalyst was filtered off and the aqueous phase was collected thrice with 25 ml of petroleum ether. The solvent petroleum ether was removed under vacuum and the residue was dissolved in chloroform for analysis. All the product analyses were carried out by gas chromotography using 2m OV–17 ChromoSorb G: AW/DMCS (100–200 mesh) column and flame ionization detector.



Scheme 1.

Figure 2 depicts the results of oxidation of phenol with H_2O_2 over (Cr)MCM-41. As can be seen from the figure that on treating the catalyst-A with ammonium acetate (Catalyst-B) and acetylacetonate (Catalyst-C), a two-fold increase in quinone selectivity was noted. However, traces of diphenol and tars were observed when the reaction was carried out for more than 16 h. At the same time, it is interesting to note that the TS-1 catalyst shows a low phenol conversion (25%) with a mixture of hydroquinone and catechol and that the selectivity to quinone varied only by modification of the catalyst.[12]

In the case of substituted phenols, the Catalyst-B and Catalyst-C not only increase the quinone selectivity but also increase the substrate conversion significantly (Table 1).

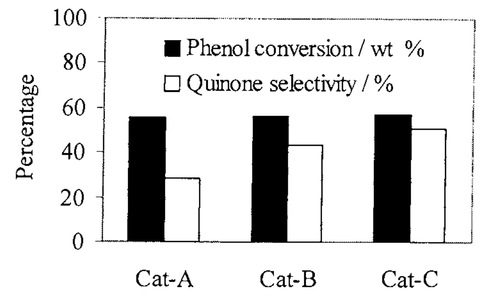


Figure 2. Oxidation of phenol over (Cr)MCM-41.

Table 1. Oxidation of substituted phenols over (Cr)MCM-41

Substrate	Catalyst	Substrate conversion / wt%	Quinone Yield / wt%	Quinone Selectivity / %
3,5-DMP	A	62.7	36.0	57.3
	B	72.0	49.3	68.5
	C	78.5	62.7	79.9
2,3,5-TMP	A	58.7	37.1	63.3
	B	63.0	45.6	72.9
	C	72.0	63.9	88.7

Table 2. Oxidation of phenols using the filtrate from Catalyst-A

Substrate	Substrate conversion / wt %	Quinone yield / wt %	Quinone selectivity / %
Phenol	4.81	1.10	23.1
3,5-DMP	7.30	2.77	38.0
2,3,5-TMP	9.80	3.92	40.1

It is noteworthy that no appreciable substrate conversion was obtained when the reaction was carried out with the filtrate obtained by treating the Catalyst-A with glacial acetic and aq. H_2O_2 (Table 2). Thus, the unique catalytic performance of (Cr)MCM-41 may possibly due to the location of active chromate species within the mesopores of MCM-41. In fact, the removal of non-framework chromium ions from the matrix enhances both the conversion and selectivity.

In conclusion, it was inferred from this study that the oxochromium species, which is probably responsible for the excellent catalytic activity, are stabilized or strongly (anchored) held within the mesoporous matrix.[8] It was also demonstrated that the non-framework chromium, which may be responsible for the by-products formation and in the reduction of the product selectivity, can be removed by ammonium acetate and acetyl acetonate treatments. Thus, the treated catalysts exhibit significant activity for the chosen reactions.

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