Supplementary Information

Experimental section

Chemicals / reagents

Tetramethylammonium hydroxide (TMAOH, 26 wt%), chromium nitrate nonahydrate (Cr(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O), phenyl acetonitrile were purchased from Wako Pure Chemical Industries Ltd. (Wako). Cetyltrimethylammonium bromide (CTAB), fumed silica (SiO\textsubscript{2}), silica gel grade 62 (pore diameter 15 nm) were purchased from Sigma-Aldrich. All chemicals were used as received.

Preparation of the catalysts

CrMCM-41 catalyst was prepared as described previously with slight modification in gel composition. Typically, 3.0 g SiO\textsubscript{2} is slowly added to a mixture of 2.63 g of aqueous TMAOH and 0.3 g NaOH dissolved in 28.0 g distilled water under vigorous stirring for 30 min. Subsequently, an aqueous suspension of CTAB (4.92 g in 14 g distilled water) is added to the above mixture. Finally, an aqueous solution of 0.4 g Cr(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O is slowly added to the above synthesis gel and stirred for another 1 h. The final molar gel composition was SiO\textsubscript{2}: 0.27 CTAB: 0.15 TMAOH: 0.15 NaOH: 60 H\textsubscript{2}O: 0.01 Cr\textsubscript{2}O\textsubscript{3}. The resulting gel is transferred into Teflon-lined stainless steel autoclaves (ca. 100 ml), which are kept in an air oven at 100 °C for 24 h. The solid product obtained, designated as as-synthesized CrMCM-41 is filtered off, washed with distilled water and dried at 80 °C for 12 h. The as-synthesized sample is then calcined to remove the surfactant at 550 °C for 8 h in air. The catalyst was characterized by various techniques, XRD (Rigaku: RINT 2200); TEM (Tecnai 20 ST, FEG 200kV); N\textsubscript{2} adsorption (BEL SORP 28SA, BEL Japan); DR-UVVIS (Perkin-Elmer, Lambda 35). The chromium content is determined by ICP-AES (SPS 7800 plasma spectrometer, Seiko Instruments, Japan) and the chromium content was 2.0 wt.%. The chromium detection level is 5 bpp.

Similarly, CoMCM-41 and MnMCM-41 were prepared according to the procedure described above with cobalt nitrate hexahydrate (Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O) and manganese nitrate hexahydrate (Mn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O) as metal precursor. The cobalt and manganese content was 1.9 wt.% and 1.8 wt.%, respectively.

The microporous catalysts, CoMFI\textsuperscript{1} and CrAPO-5\textsuperscript{2} were prepared according to the literature procedure with slight modification. The metal content in CoMFI and CrAPO-5 was 1.2 wt.% and 1.5 wt.%, respectively. The measured XRD patterns for microporous catalysts were matched with those reported in the Collection of Simulated XRD patterns for Zeolites.\textsuperscript{3}

The macroporous catalyst Cr/SiO\textsubscript{2} having 2.0 wt.% chromium was prepared by incipient wetness impregnation method described elsewhere.\textsuperscript{4} Firstly, chromium nitrate (0.02 g) is dissolved in 2 ml distilled water and then preactivated silica gel grade 62 (1g) is added. The mixture is stirred gently at room temperature for 4 h. The solid product is obtained by drying at 80 °C for 12 h. Finally, it is calcined at 550 °C for 12 h in air and designated as Cr\textsubscript{x}O\textsubscript{y}/SiO\textsubscript{2} for simplicity Cr/SiO\textsubscript{2}.

All prepared catalysts were dried in air at 150 °C for 2 h before catalytic experiments. The weight loss due to drying was determined by thermogravimetric analysis (TG-DTA 2010 SAT) and used to calculate the dry mass of the catalyst.

Characterization of the catalysts

Figure 1 shows the powder XRD patterns of various metal containing MCM-41 catalysts. It can be seen from figure that XRD patterns for Cr, Co and MnMCM-41 shows three reflections at (100), (110), and (200), respectively. This is characteristic of hexagonal mesoporous MCM-41 structure.\textsuperscript{5} Figure 2 shows N\textsubscript{2} adsorption isotherm for the CrMCM-41 catalyst before and after the reaction. It is a typical reversible type IV adsorption isotherm as defined by IUPAC for mesoporous materials.\textsuperscript{6} Specific surface area, pore volume and pore diameter as determined from nitrogen adsorption isotherms of the CrMCM-41 before reaction were, \(A_{\text{BET}} = 1150 \text{ m}^2\text{g}^{-1}\), \(d_p = 2.4 \text{ nm}\), \(V_p = 0.98 \text{ cm}^3\text{g}^{-1}\) and after reaction 1020 \(\text{ m}^2\text{g}^{-1}\), \(d_p = 2.4 \text{ nm}\), \(V_p = 0.92 \text{ cm}^3\text{g}^{-1}\), respectively. Though slight reduction of specific surface area and pore volume was noticed for the catalyst after reaction but values are in tandem with those typical for mesoporous
materials. The HR-TEM image of CrMCM-41 catalyst before reaction showed a regular hexagonal array of uniform channels of MCM-41-type material (Fig. 3). Similarly after reaction the catalyst showed the same hexagonal array pattern (not shown here).

![HR-TEM of CrMCM-41 before the reaction.](image)

**Figure 1.** XRD of transition metal containing MCM-41 catalysts. **Figure 2.** N$_2$ adsorption of CrMCM-41: (a) before reaction and (b) after the reaction.

DRUV-VIS studies of as-synthesized CrMCM-41 showed bands around 620, 440 and 270 nm, corresponding to $^4$A$_{2g}(F) \rightarrow ^4T_{2g}(F)$, $^4$A$_{2g}(F) \rightarrow ^4T_{1g}(F)$ and $^4$A$_{2g}(F) \rightarrow ^4T_{1g}(P)$ transitions, respectively, typical of trivalent chromium in octahedral coordination. The calcined and recycled CrMCM-41 catalyst showed strong charge transfer (O $\rightarrow$ Cr(VI)) bands around 375 nm and a weak shoulder at 445 nm assigned to monochromate and/or polychromate like species in tetrahedrally coordinated environments. The proposed chromium species in CrMCM-41 catalyst is discussed in detail in the previous studies.

**Product analysis**

The THP, TOne, and TOI selectivity were also determined by $^1$H-NMR on Varian Unity INOVA-500. $^1$H-NMR (CDCl$_3$) data for the tetralin oxidation were as follows.
Tetralin:
\[ \delta [7.05 \text{ (m, } 4\text{H, H-Ar}), 1.79 \text{ (m, } 4\text{H, H-2, H-3}), 2.75 \text{ (m, } 4\text{H, H-4, H-5})]. \]

1-tetralin hydroperoxide (THP):
\[ \delta [1.47–2.14 \text{ (m, } 4\text{H, H-2, H-3}), 2.74 \text{ (m, } 2\text{H, H-4}), 5.0 \text{ (d, } 1\text{H, H-1 of peroxide}), 6.96–7.28 \text{ (m, } 4\text{H, H-Ar}), 7.38 \text{ (m, } 1\text{H, H-Ar})]. \]

1-tetralone (TOne):
\[ \delta [2.119 \text{ (m, } 2\text{H, H-2}), 2.632 \text{ (dt, } 2\text{H, H-3, } J = 6.1 \text{ and } 13.1 \text{ Hz}), 2.98 \text{ (t, } 2\text{H, H-4, } J = 6.1 \text{ Hz}), 7.21 \text{ (d, } 1\text{H, H-5, } J = 7.5 \text{ Hz}), 7.33 \text{ (t, } 1\text{H, H-7, } J = 7.5 \text{ Hz}), 7.46 \text{ (ddd, } 1\text{H, H-6, } J = 1.3, 7.5 \text{ and } 7.5 \text{ Hz}), 8.012 \text{ (dd, } 1\text{H, H-8, } J = 1.3 \text{ and } 7.5 \text{ Hz})]. \]

1-tetralol (TOl):
\[ \delta [2.02 \text{ (s-broad, } 1\text{H, OH}), 1.47–2.14 \text{ (m, } 4\text{H, H-2, H-3}), 2.74 \text{ (m, } 2\text{H, H-4}), 4.72 \text{ (d, } 1\text{H, H-1, } J = 3.6 \text{ Hz}), 6.96–7.28 \text{ (m, } 3\text{H, H-Ar}), 7.38 \text{ (m, } 1\text{H, H-Ar})]. \]

References