Supplementary Information

Experimental section

Chemicals / reagents

Tetramethylammonium hydroxide (TMAOH, 26 wt%), chromium nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$), phenyl acetonitrile were purchased from Wako Pure Chemical Industries Ltd. (Wako). Cetyltrimethylammonium bromide (CTAB), fumed silica (SiO_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_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 $Cr(NO_3)_3{\cdot}9H_2O$ is slowly added to the above synthesis gel and stirred for another 1 h. The final molar gel composition was SiO_2: 0.27 CTAB: 0.15 TMAOH: 0.15 NaOH: 60 H_2O: 0.01 Cr_2O_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_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 ($Co(NO_3)_2{\cdot}6H_2O$) and manganese nitrate hexahydrate ($Mn(NO_3)_2{\cdot}6H_2O$) as metal precursor. The cobalt and manganese content was 1.9 wt.% and 1.8 wt.%, respectively.

The microporous catalysts, CoMFI[1] and CrAPO-5[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.[3]

The macroporous catalyst Cr/SiO_2 having 2.0 wt.% chromium was prepared by incipient wetness impregnation method described elsewhere.[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_xO_y/SiO_2 for simplicity Cr/SiO_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.[5] Figure 2 shows N_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.[6] Specific surface area, pore volume and pore diameter as determined from nitrogen adsorption isotherms of the CrMCM-41 before reaction were, A_{BET} = 1150 $m^2\ g^{-1,}$ d_p = 2.4 nm, V_p = 0.98 cm^3g^{-1} and after reaction 1020 $m^2\ g^{-1,}$ d_p = 2.4 nm, V_p = 0.92 cm^3g^{-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.[5] HR-TEM image of CrMCM-41 catalyst before reaction showed a regular hexagonal array of uniform channels of MCM-41-type material (Fig. 3).[5] Similarly after reaction the catalyst showed the same hexagonal array pattern (not shown here).

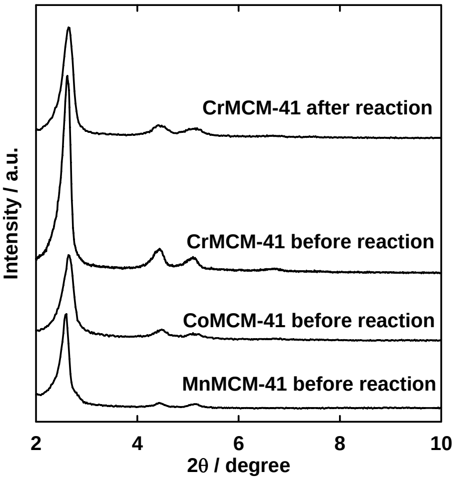

Figure 1. XRD of transition metal containing MCM-41 catalysts.

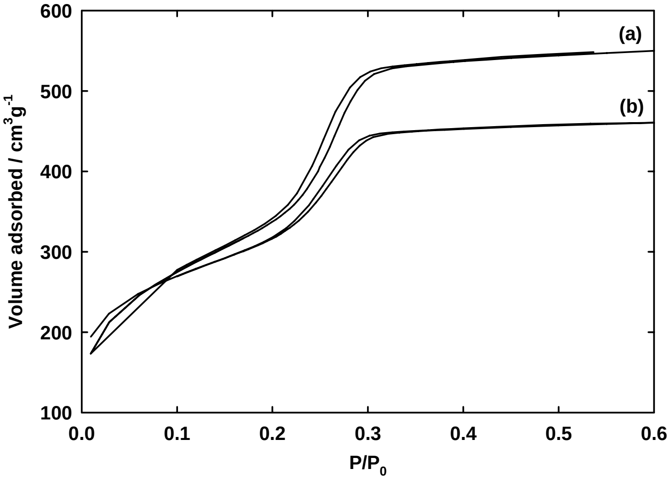

Figure 2. N_2 adsorption of CrMCM-41: (a) before reaction and (b) after the reaction.

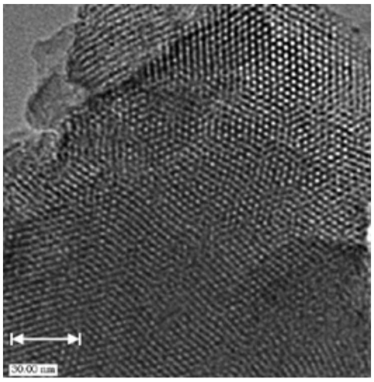

Figure 3. HR-TEM of CrMCM-41 before the reaction.

DRUV-VIS studies of as-synthesized CrMCM-41 showed bands around 620, 440 and 270 nm, 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, typical of trivalent chromium in octahedral coordination.[7] The calcined and recycled CrMCM-41 catalyst showed strong charge transfer (O → 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.[8,9] The proposed chromium species in CrMCM-41 catalyst is discussed in detail in the previous studies.[9]

Product analysis

The THP, TOne, and TOl 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:

δ [7.05 (m, 4H, H-Ar), 1.79 (m, 4H, H-2, H-3), 2.75 (m, 4H, H-4, H-5).

1-tetralin hydroperoxide (THP):

δ [1.47–2.14 (m, 4H, H-2, H-3), 2.74 (m, 2H, H-4), 5.0 (d, 1H, H-1 of peroxide), 6.96–7.28 (m, 4H, H-Ar), 7.38 (m, 1H, H-Ar).

1-tetralone (TOne):

δ [2.119 (m, 2H, H-2), 2.632 (dt, 2H, H-3, J = 6.1 and 13.1 Hz), 2.98 (t, 2H, H-4, J = 6.1 Hz), 7.21 (d, 1H, H-5, J = 7.5 Hz), 7.33 (t, 1H, H-7, J = 7.5 Hz), 7.46 (ddd, 1H, H-6, J = 1.3, 7.5 and 7.5 Hz), 8.012 (dd, 1H, H-8, J =1.3 and 7.5 Hz).

1-tetralol (TOl):

δ [2.02 (s-broad, 1H, OH), 1.47–2.14 (m, 4H, H-2, H-3), 2.74 (m, 2H, H-4), 4.72 (d, 1H, H-1, J = 3.6 Hz), 6.96–7.28 (m, 3H, H-Ar), 7.38 (m, 1H, H-Ar).

Referenecs

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