Synthesis of highly active tungsten-containing MCM-41 mesoporous molecular sieve catalyst

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A tungsten-containing MCM-41 mesoporous molecular sieve is synthesized by the hydrolysis of tetraethylorthosilicate and ammonium tungstate in the presence of cetylpyridinium bromide as template in acidic medium and found to be more active than the conventional WO_3 catalyst in the hydroxylation of cyclohexene using H_2O_2 as oxidant.

WO_3-based catalysts are important not only in hydrodesulfurization and alkene metathesis[1] but also in hydroxylation of unsaturated compounds.[2] Recently, the breakthrough discovery of silica-based mesoporous molecular sieves M41S, including the hexagonal MCM-41,[3,4] offered new opportunities for creating highly dispersed and more accessible catalytic sites by incorporating transition-metal ions into their silica-based frameworks.[5–9] Many of the mesoporous molecular sieve catalysts thus obtained therefore showed quite good catalytic properties in different reactions.[10,11] Here, we report the synthesis, characterization and catalytic performance of the tungsten-containing MCM-41 mesoporous molecular sieve catalyst (W-MCM-41) in the hydroxylation of cyclohexene with 30 mass% H_2O_2.

In a typical synthesis of the W-MCM-41, 5.67 g (20 mmol) of ammonium tungstate [Aldrich, 99.99% $(NH_4)_2WO_4$] was dissolved in 100 ml of water to prepare solution A; 6.2 g (15 mmol) of cetylpyridinium bromide (Aldrich, 98% $C_{16}H_{33}NC_5H_5Br{\cdot}H_2O$, CPBr) was combined with 60 ml of HCl (5 mol dm^{-3}) to form solution B. Then 11.4 g (50 mmol) of tetraethylorthosilicate [Aldrich, 98% $Si(OEt)_4$, TEOS] and a determined amount of solution A were simultaneously introduced into solution B under vigorous stirring to give the following composition: 1 TEOS : 0.3 CPBr : 0.02 W : 6 HCl : 60 H_2O. After allowing the resulting gel to age at 323 K under gentle stirring for 22 h, the solid product was centrifuged, washed with distilled water and air-dried. The calcination of the W-MCM-41 sample was carried out in air at *ca.* 533 K for 1.5 h, then at 873 K for 4 h.

The calcined W-MCM-41 sample was colorless, indicating the absence of colored crystalline WO_3 species outside the framework. This result was verified by Raman and UV–VIS spectroscopy.

An X-ray powder diffraction pattern (Rigaku, D/Max-2400, with Cu-Kα radiation; λ = 0.154 18 nm) of the calcined sample is depicted and indexed in Fig. 1 and corresponds to MCM-41 mesoporous silicas reported previously.[4,5]

Fig. 2 shows the Raman spectra (Nicolet, Raman 910) of W-MCM-41 and crystalline WO_3. Crystalline WO_3 is a very strong Raman scatterer, so the absence of intense peaks at *ca.* 804, 714, 327, 267 and 137 cm^{-1} (in WO_3) corresponding to octahedral WO_6 groups[13] in the spectrum of W-MCM-41 indicated that the W was highly dispersed in the silica-based framework structure. This result was also supported by the diffuse reflectance (DR) spectra of W-MCM-41 and WO_3 crystals in the UV–VIS region. In the DR UV–VIS spectrum of the calcined W-MCM-41 sample, there is no absorption band corresponding to crystalline WO_3.

The chemical analysis using ICP atomic emission spectroscopy (ARL 3520) showed the WO_3 content in the W-MCM-41 to be 7.1 mass% ($SiO_2 : WO_3$ *ca.* 50). The HK mean pore size and BET surface area of the as-synthesized W-MCM-41 calculated on the basis of nitrogen adsorption–desorption isotherms (Coulter, Omnisorp 360CX) were *ca.* 2.9 nm and 1059 m^2 g^{-1}, respectively.

As mentioned above, different physicochemical characterizations confirmed that in the W-MCM-41 sample prepared, the W was highly dispersed in the silica-based framework structure, and it was found to be active for carrying out catalytic oxidations of unsaturated hydrocarbons using H_2O_2 as oxidant. Here the H_2O_2 hydroxylation of cyclohexene was carried out over W-MCM-41, Si-MCM-41 and conventional WO_3 catalysts suspended in acetic acid (HAc) media; where Si-MCM-41 was a pure silica sample synthesized by the method described above but leaving out the tungsten ion precursor. Since H_2O_2 in HAc alone is a hydroxylating agent,[2] a comparative experiment was also made in the absence of any catalyst. The results summarized in Table 1 clearly show that W-MCM-41 is a good catalyst for the test reaction, on which the hydroxylation rate of

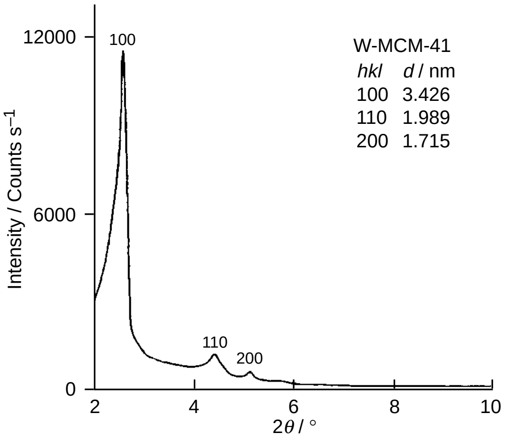

Fig. 1 PXRD pattern of the calcined W-MCM-41

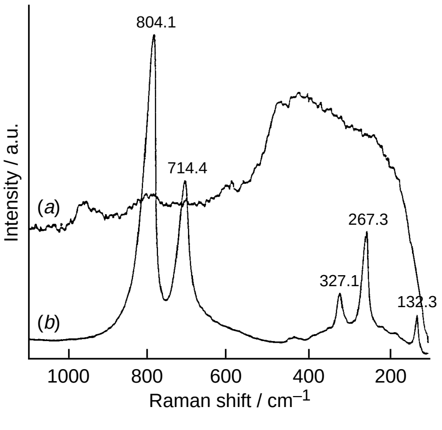

Fig. 2 Raman spectra of (*a*) W-MCM-41 and (*b*) crystalline WO_3

Table 1 Activity of W-MCM-41 and related materials for hydroxylation of cyclohexene with hydrogen peroxide[a]

					Conversion (%)		Selectivity (%)[b]	
Expt.	Catalyst	C_6H_{10}/mmol	H_2O_2/mmol	*t*/min	H_2O_2	C_6H_{10}	Glycol	Ester
1	W-MCM-41	50	50	80	*ca.* 100	84.6	80.3	12.0
2	W-MCM-41	50	65	60	97.1	*ca.* 100	78.1	10.4
3	WO_3	50	65	160	97.8	*ca.* 100	78.6	10.0
4	Si-MCM-41	50	65	240	94.5	*ca.* 100	72.4	7.4
5	None	50	65	240	94.1	*ca.* 100	74.0	6.7

[a] *Reaction conditions*: substrate/solvent: 1 : 20 (v/v), catalyst: 0.2 g, *T*: 353 K, H_2O_2: 30 mass% aqueous solution; C_6H_{10}: cyclohexene; *t*: time required for completing the reaction. [b] Calculated on alkene consumed; glycol: *trans*-cyclohexane-1,2-diol; ester: *trans*-cyclohexane-1,2-diol monoacetate.

cyclohexene could be increased significantly without decreasing the yields of *trans*-cyclohexane-1,2-diol. However, the Si-MCM-41 catalyst is equivalent to the blank H_2O_2–HAc system and inferior to the conventional WO_3 catalyst in activity. These data indicated that the highly dispersed W in silica-based molecular sieve might play a critical role in promoting the reaction. Systematic investigations toward understanding the mechanism for this catalytic reaction are still in progress.

Footnote and References

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