

Catalytic hydroxylation of benzene over transition-metal substituted hexagonal mesoporous silicas

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Ti-, V-, Cr-, Mo-, and Mn-substituted hexagonal mesoporous silicas prepared at ambient temperature by electrostatic (S^+X-I^+) and neutral (S^0I^0) surfactant templating pathways are catalytically active for the peroxide hydroxylation of benzene to phenol in the absence of a solvent.

The newly discovered hexagonal mesoporous molecular sieves MCM-41¹ and HMS² offer new opportunities for transition-metal incorporation into silica frameworks. Two surfactant templating mechanisms for MCM-41 preparation have been reported.³ One pathway involves electrostatic interactions between cationic quaternary ammonium ion surfactants (S^+) and anionic silicate precursors (I^-) under hydrothermal conditions. The other pathway involves counter-ion mediated S^+X-I^+ assembly, where $X^- = Cl^-$, or Br^- . In contrast, HMS silicates^{2,4} are prepared *via* neutral S^0I^0 assembly between a primary amine template (S^0) and a silicon alkoxide precursor (I^0).

Although Ti-,⁵ V-⁶ and Mn-substituted⁷ MCM-41 silicas have been prepared by the electrostatic S^+I^- pathway under hydrothermal conditions, very few transition-metal substituted analogues have been prepared by the counter-ion mediated S^+X-I^+ pathway.⁴ Also, relatively few metal substituted HMS derivatives have been reported *via* the S^0I^0 pathway.

Here we report the ambient temperature preparation of V-, Cr-, Mo-, and Mn-substituted MCM-41 and HMS silicas by the electrostatic S^+X-I^+ and neutral S^0I^0 templating pathways, respectively. We show that these mesoporous metallosilicates are capable of catalysing the peroxide hydroxylation of benzene at low conversions in the absence of solvent.

MCM-41 and HMS metallosilicates were prepared from tetraethylorthosilicate (TEOS) as the silicon source. Aqueous solutions of Na_3VO_4 , CrO_3 , K_2MoO_4 and $MnCl_2 \cdot 4H_2O$, as well as $Ti(OPr)_4$ in isopropyl alcohol served as the transition-metal ion precursors. For the preparation of MCM-41 derivatives by

the S^+X-I^+ templating pathway, the TEOS (1.0 mol) and the transition-metal ion precursor (0.010 mol) were mixed with a solution containing cetyltrimethylammonium bromide (0.20 mol) and HCl (1.00 mol) in H_2O (150 mol). For the S^0I^0 templated synthesis of HMS derivatives, the TEOS (1.0 mol) and the transition-metal ion precursor (0.010 mol) were allowed to react in the presence of dodecylamine (0.20 mol) in a mixture of H_2O (150 mol) and ethanol (6.0 mol) as a co-solvent. Each reaction mixture was stirred vigorously at ambient temperature for 24 h. The crystalline metallosilicates were filtered, washed with deionized water, air-dried, and calcined in air at 923 K for 4 h to remove the template.

The X-ray diffraction patterns for all the metal-substituted MCM-41 and HMS derivatives were similar to those reported previously for unsubstituted MCM-41 and HMS silicas.^{2,4,6} However, the relative intensity of the $d(100)$ reflection for our metal-substituted materials was higher than that of the pure silica analogues. Table 1 summarizes the $d(100)$ spacings, lattice parameters (a_0), Horvath-Kawazoe (HK) pore sizes, framework wall thicknesses (FWT), N_2 BET surface areas (S_{BET}) and metal loadings determined by chemical analysis for the calcined metallosilicates.

Several conclusions may be drawn from the data presented in Table 1. (i) The unit-cell parameter a_0 increases by 1 to 8 Å upon incorporation of transition metal into the framework of MCM-41 and HMS at the 1 mol% level. An increase in unit-cell size also occurs upon the incorporation of metal ions larger than silicon in the framework of silicalite.⁸ (ii) The FWT values for the transition-metal substituted analogues of MCM-41 and HMS are larger in general than those of the corresponding pure silicas. In accord with our previous observations for the pure silica analogues,² the FWTs are consistently larger for the metal-substituted HMS materials than for the MCM-41 analogues. (iii) The BET surface areas are smaller for HMS than MCM-41 silicates, which is consistent with the thicker pore walls of HMS. (iv) The S^0I^0 pathway incorporates more

Table 1 Properties of calcined MCM-41 and HMS metallosilicates

Silicate phase	Metal ion (mol%)	$d(100)/\text{\AA}$	$a_0/\text{\AA}$	HK pore size/ \AA	FWT ^b / \AA	$S_{BET}/\text{m}^2 \text{g}^{-1}$
MCM-41 (S^+X-I^+) ^c	none	31.2	36.0	26	10	1345
	Ti(0.36)	33.7	38.9	25	14	1312
	V(0.23)	33.0	38.1	23	15	1227
	Cr(0.61)	37.4	43.2	25	18	1342
	Mn(0.03)	37.4	43.2	27	15	1358
	Mo(1.04)	32.0	37.0	16	21	854
HMS (S^0I^0) ^c	none	36.0	41.5	24	17	1108
	Ti(1.3)	39.8	45.9	29	17	1287
	V(0.76)	38.7	44.7	24	21	1209
	Cr(1.4)	42.5	49.1	26	22	1080
	Mn(0.84)	43.0	49.6	32	18	1010
	Mo(0.50)	43.3	50.0	21	29	565

^a The hexagonal unit-cell parameter (a_0) was calculated using the formula $a_0 = 2d(100)/\sqrt{3}$. ^b The framework wall thickness (FWT) was calculated by subtracting the Horvath-Kawazoe (HK) pore size obtained from N_2 adsorption from the hexagonal unit-cell parameters (a_0). ^c Cetyltrimethylammonium bromide, and dodecylamine were used as surfactants for mesostructure synthesis *via* S^+X-I^+ and S^0I^0 templating pathways, respectively.

transition metal into the silica framework than the $S^+ X^- I^+$ pathway, with the exception of molybdenum. Preliminary ^{29}Si MAS NMR studies in the case of Ti-MCM-41 indicate that the degree of framework crosslinking in the as-synthesized products is substantially enhanced in the presence of the metal ion, the fraction of Q^4 sites increasing from 44 to 57% upon 1% Ti substitution. Accordingly, we attribute the increase in unit-cell parameter upon transition-metal substitution to an increase in wall thickness caused by enhanced crosslinking in the presence of the metal.

In a test of catalytic reactivity for benzene hydroxylation, 25 mg of catalyst, 100 mmol of benzene and 30 mmol of H_2O_2 (30% aqueous solution) were charged into a glass flask and vigorously stirred at 345 K for 24 h. As shown by the results in Table 2, all of the metal-containing mesoporous materials are active for benzene hydroxylation to phenol, whereas the pure silica analogues are completely inactive. This result indicates that isolated metal sites exist in these mesoporous catalysts because isolated sites are required for benzene hydroxylation over TS-1. In all cases the solution of the hydroxylation product was colourless except for Ti-HMS, which afforded a slightly yellow solution. No benzoquinone or other products were detected by gas chromatographic methods. Therefore, the selectivity to phenol is approximately 100%, at least at low conversions. At higher conversions (*ca.* 10%) further oxidation of phenol occurs to afford tar-like products. The titanium and vanadium derivatives of MCM-41 are more active for benzene hydroxylation than the HMS analogues, but the reverse is true

for the chromium forms. The dependence of reactivity on wall thickness and the method of framework synthesis may arise from differences in the siting of the transition-metal ions. Regardless of the method used for framework synthesis, however, molybdenum-substituted derivatives of MCM-41 and HMS exhibit relatively low activities for benzene hydroxylation.

We have previously reported⁴ the hydroxylation of benzene to phenol over Ti-HMS and Ti-MCM-41 in acetone, the solvent normally used for benzene hydroxylation with TS-1 and related silicalite catalysts.⁸ We now find that Ti-HMS and Ti-MCM-41, unlike TS-1, catalyse the oxidation of acetone at rates that are competitive with benzene oxidation. One of the acetone oxidation products, namely, 3,3,6,6-tetramethyl-1,2,4,5-tetraoxacyclohexane, has a GC retention time very near that for phenol. Consequently, our previous analysis of the product distribution for benzene oxidation⁴ greatly overestimated the phenol yields. Interestingly, the peroxide oxidation of the sterically bulky 2,6-di-*tert*-butylphenol to quinones proceeds at a rate that is much larger than that for acetone oxidation, yet it is evident that benzene hydroxylation is competitive with acetone oxidation. Nevertheless, benzene in the absence of a solvent can be oxidized primarily to phenol by transition-metal substituted MCM-41 and HMS catalysts, provided that the conversions are kept sufficiently low to avoid over-oxidation to complex mixtures.

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Table 2 Turnover numbers for benzene hydroxylation over transition-metal substituted MCM-41 and HMS catalysts^a

Metal substituent	MCM-41	HMS
none	0	0
Ti	189	15
V	148	101
Mn	> 200 ^b	7.1
Cr	30	54
Mo	14	28

^a The turnover number is the moles of phenol formed per mole of transition-metal after a 24 h reaction time at 345 K. The selectivity to phenol is approximately 100% for all catalysts. The reactions were carried out in the absence of solvent using 100 mmol of benzene, 30 mmol of H_2O_2 (30 mass% aqueous solution) and 25 mg of catalyst. ^b Owing to the low manganese content (*ca.* 0.03 mol%), the turnover number may not be accurate, but the result may be an indicative of benzene hydroxylation requiring highly isolated transition-metal sites.

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