FTIR Studies on Selected Mesoporous Metallosilicate Molecular Sieves

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Different M–MCM-41 materials (M = Ti, V, Cr, Mn, Co, Ni, Zr, Cu, Nb, Ce, Sn, and Mo) were synthesised and characterized and the incorporation of metal ions on the silica surface also confirmed by FTIR analysis based on their ionic sizes.

Since the discovery of MCM-41 in 1992 by Mobil scientists,[1] numerous studies have been reported concerning synthesis mechanisms, preparation conditions, characterization, and application of these materials as catalysts and catalyst supports in various reactions.[2–5] Pure siliceous hexagonal MCM-41 cannot be directly used as catalysts because the materials suffer from limited thermal stability and negligible catalytic activity because of the neutral framework and the lack of sufficient acidity. Mesoporous metallosilicates, developed by isomorphous substitution of Si with a metal ion in a silicate structure, are used for catalysts in fine chemical industries to improve product yield.[5] In recent years, increasing attention has been directed towards the study of metal-containing mesoporous molecular sieves. These M41S-type mesoporous materials with large pores (20–100 Å) are suitable for the transformation of bulky organic compounds.[6–13] Many researchers have reported the oxidation properties of metal ions such as Ti,[14] V,[15] Cr,[16] Mn,[17] Fe,[17] Co,[17] Ni,[18] Zr,[19] Cu,[20] Nb,[21] Ce,[22] Sn,[23] and Mo,[24] incorporated into the MCM-41 framework. In those studies, the incorporated metal ions were identified using DR/UV–vis and ESR results. Kosslick et al.[25] reported only incorporated trivalent metals such as Al, Fe, and Ga by FTIR results. No other metal ions incorporated into silica have been reported to be identified by FTIR analysis based on their ionic sizes. This technique may be valuable to most researchers since, unlike XRD, ESR, and DR/UV–vis, FTIR is relatively inexpensive and readily available in most research laboratories. In this study, the synthesis of metal ion-containing MCM-41 with suitable Si/M ratios and the confirmation of metal ion incorporation on silica surface by FTIR are investigated.

Mesoporous metallosilicates, M–MCM-41 (M = Ti, V, Cr, Mn, Co, Ni, Zr, Cu, Nb, Ce, Sn, and Mo), were synthesized according to the published procedure.[26] The metallosilicates were characterized by XRD, TG/DTA, N_2-adsorption, DR/UV–vis and ESR according to published procedures.[5,6,14–24] Particularly, IR spectra were recorded in the range of framework vibrations on an IRF 180 spectrometer (ZWG) at a resolution of better than 2 cm^{-1} using the KBr technique. The pellets contained ca. 0.5 mg of sample per 800 mg of KBr.

The *d*-spacing value and unit cell parameter of different metal ion-containing Si–MCM-41 structures are likely increased because the size of metal ions (M^+) is larger than that of Si^{4+}. Similar observations were also reported by earlier workers with different metal ions incorporated into MCM-41.[11] The decrease in surface area, pore diameter, pore volume, and increase in wall thickness are probably determined by the synthesis conditions and metal ion content. The oxidation state of the metal ions on the silica surface was confirmed[6,14–24] as previously reported and is shown in Table 1. Infrared spectroscopy has been used extensively for the characterization of transition-metal cation-modified zeolites. The as-synthesized M–MCM-41 samples exhibit absorption bands around 2921 and 2851 cm^{-1}, corresponding to *n*-C–H and *d*-C–H vibrations of the surfactant molecules. The broad bands around 3500 cm^{-1} may be attributed to surface silanols and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the absorption bands[11] at 1623–1640 cm^{-1}. The substitution of silicon by metal ions shifts the lattice vibration band to a lower wave number. Compared to the Si–MCM-41, the wavenumber of the anti-symmetric Si–O–Si vibration band of M–MCM-41 sample probably increases from 1066 to 1096 cm^{-1} (Figure 1). These shifts should be due to the increase of the mean Si–O length in the walls caused by the substitution of the silicon (radius 40 pm) by the metal ions of larger size.[27] The observed shifts, which also depend on the change in the ionic radii as on the degree of substitution, are comparatively small. Therefore, only a low degree of substitution is suggested. Interestingly, the wavenumber shifts decrease in the series Cr- > V- > Mo- > Ti- > Fe- > Sn- > Co- > Mn- > Zr- > Nb- > Ni- > Cu- > Ce–MCM-41, although the ionic radius of the metal ions, from Cr to Ce ions is linearly decreased. At the same time, the wavenumber of the antisymmetric Si–O–M (M-metal ions) vibration bands of M–MCM-41 samples increase from 954 to 990 cm^{-1} (Figure 1). The absorption band at 1057 and 1223 cm^{-1} are

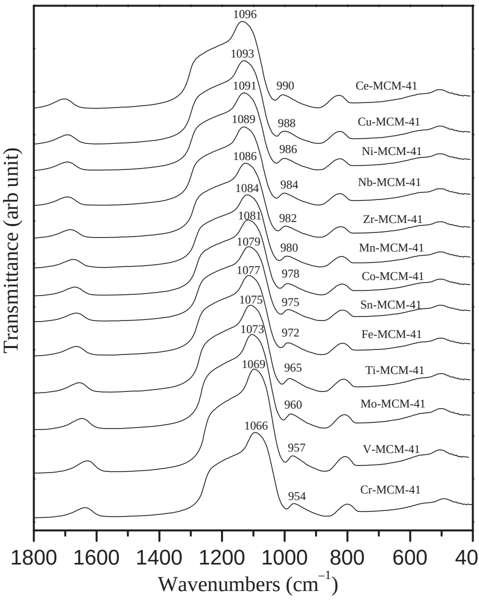

Figure 1. FTIR spectra of different metal ion-containing MCM-41.

Table 1. Confirmation of metal ion incorporation and environments on Si–MCM-41

M–MCM-41	Surface area (m^2/g)	Pore size /Å	Ionic radius /Å	FTIR		UV–vis		ESR	
				Vibration band /cm^{-1}	M–O–Si bond	Wavelength /nm	Oxidation state and environment	g-value	Oxidation state and environment
Ti–MCM-41	1081	30.9	0.42	965	Ti–O–Si	210–220	Ti^{4+}(tetrahedral)	—	—
V–MCM-41	869	27.7	0.36	957	V–O–Si	264–274	V^{5+}(tetrahedral)	—	—
Cr–MCM-41	883	26.9	0.26	954	Cr–O–Si	280 and 370	Cr^{6+}(tetrahedral)	—	—
Mn–MCM-41	906	26.9	0.58	980	Mn–O–Si	270	Mn^{3+}(tetrahedral)	—	—
Fe–MCM-41	908	29.4	0.49	972	Fe–O–Si	265	Fe^{3+}(tetrahedral)	—	—
Co–MCM-41	903	26.9	0.56	978	Co–O–Si	580, 650 and 684	Co^{2+}(tetrahedral)	—	—
Ni–MCM-41	913	28.4	0.69	986	Ni–O–Si	—	—	2.10–2.33	Ni^{2+}(octahedral)
Cu–MCM-41	854	31.8	0.73	988	Cu–O–Si	—	—	2.39	Cu^{2+}(octahedral with a tetragonal elongation)
Zr–MCM-41	888	31.0	0.59	982	Zr–O–Si	210	Zr^{4+}(tetrahedral)	—	—
Nb–MCM-41	949	24.1	0.64	984	Nb–O–Si	235	Nb^{5+}(octahedral)	—	—
Mo–MCM-41	866	30.9	0.41	960	Mo–O–Si	242 and 277	Mo^{6+}(tetrahedral)	—	—
Sn–MCM-41	1080	30.4	0.55	975	Sn–O–Si	213	Sn^{4+}(tetrahedral)	—	—
Ce–MCM-41	996	30.7	0.77	990	Ce–O–Si	300	Ce^{4+}(tetrahedral)	—	—

due to asymmetric stretching vibrations of Si–O–Si bridges, while the 954 to 990 cm^{-1} bands are due to Si–O$^-$M$^+$ (M = metal ions) vibrations in metal-incorporated silanols. By the disappearing peaks at 2851 and 2921 cm^{-1}, one could conclude that calcination of the original framework was complete, while the identity of the organic molecule completely disappeared from the calcined M–MCM-41.[13] Additionally, an absorption band in the range 954–990 cm^{-1} assigned to a stretching vibration of Si–O$^-$M$^+$ linkage was observed. This is generally considered to be evidence of the incorporation of the heteroatom into the framework. Cambler et al.[28] have reported similar stretching vibrations of Si–OH groups present at defect sites.

We have discussed the synthesis and characteristics of the different metal-incorporated MCM-41 structures while the metal ion incorporation on the silica surface are confirmed and discussed by FTIR analysis.

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26 a) M. Selvaraj, P. K. Sinha, K. Lee, I.-S. Ahn, A. Pandurangan, and T. G. Lee, *Microporous Mesoporous Mater.*, **78**, 139 (2005). b) Mesoporous metallosilicates were synthesized using a hydrothermal method. For example, in the synthesis of the Mn–MCM-41 (Si/Mn = 40), 21.2 g (1 mol) of sodium metasilicate (44–47% SiO$_2$) solution was mixed with 0.43 g (0.025 mol) of manganese(II) acetate solution. Next, the mixture was stirred for 30 min at about 250 rpm. The pH of the solution was reduced to 10.8 by adding 0.5 M sulfuric acid while continuously stirring for another 30 min when a gel is formed. Then, 9.1 g (0.25 mol) of cetyltrimethylammonium bromide was added dropwise (30 mL h^{-1}, dual syringe pump) until the gel began to change into a suspension. After further stirring for one more hour, the resulting gel of 1SiO$_2$/0.025MnO/0.25CTMABr/100H$_2$O was transferred into a teflon-lined steel autoclave and heated at 165 °C for 48 h. After cooling to room temperature, the materials were recovered by filtration, washed with de-ionized water and ethanol, and calcined at 540 °C for 6 h in air. Other M–MCM-41 (M-metal) catalysts (Si/M = 40) were synthesized in a similar manner wherein only the ratios of sodium metasilicate to metal source were varied resulting in the gel molar composition of 1SiO$_2$/0.25MO$_2$/0.25CTMABr/100H$_2$O.

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