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 (200–100 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, N2-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 (ZGW) 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 Si⁴⁺. 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 confirmed6,14–24 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 bands31 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.

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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\(^{-1}\) vibrations in metal-incorporated silanols. while the 954 to 990 cm\(^{-1}\) due to asymmetric stretching vibrations of Si–O–Si bridges, discussed by FTIR analysis.

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 reported similar stretching vibrations of Si–OH groups present at different metal-incorporated MCM-41 structures.

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**References and Notes**