

Generalised route to the preparation of mesoporous metallosilicates via post-synthetic metal implantation

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A post-synthesis route, through which various metal elements can be grafted onto siliceous frameworks using non-aqueous solutions of AlCl_3 , $\text{Al}(\text{NO}_3)_3$, SnCl_2 , $\text{Zn}(\text{O}_2\text{CMe})_2$, $\text{Mn}(\text{O}_2\text{CMe})_2$, etc., is developed as a generalised means to obtain mesoporous metallosilicates molecular sieves with various structures such as MCM-41 (hexagonal), MCM-48 (cubic *Ia3d*), SBA-1 (cubic *Pm3n*), KIT-1 (disordered) and MSU-1 (disordered) with superior structural integrity, acidity and catalytic activity to those of materials having metals incorporated during synthesis.

During the past five years, various kinds of mesoporous silica so-called MCM-41,^{1,2} MCM-48,^{1,2} SBA-1,³ MSU-1,⁴ KIT-1,^{5,6} FSM-16,⁷ etc. have been synthesized using surfactant micelles as the structure-directing agent. A large number of papers have reported the incorporation of aluminium and other metal elements within the siliceous frameworks of the mesoporous materials by adding metal precursors prior to hydrothermal synthesis reaction in order to improve ion exchange capacity, acidity and catalytic activity.⁸ However, the method incorporating Al precursors into the surfactant-silicate gel requires specialised synthesis conditions depending on the respective structures of the materials being synthesised, incorporating metals, and silica sources. Besides, the synthesis method is often hindered by a severe decrease in the structural order as the metal content increases.

Here we report a generalised route through which various metal elements such as Al, Sn, Zn and Mn can be incorporated within various mesoporous materials such as MCM-41 (hexagonal), MCM-48 (cubic *Ia3d*), MSU-1 (disordered), SBA-1 (cubic *Pm3n*) and KIT-1 (disordered), after the synthesis of pure silica forms. We show that the resultant mesoporous aluminosilicates can have not only high ion exchange capacity due to tetrahedral Al, but also superior structural integrity, acidity and catalytic activity to those obtained by the mixed-gel approach.

The silica forms of MCM-41, MCM-48, MSU-1, SBA-1 and KIT-1 were obtained by hydrothermal synthesis following methods reported in the literature.¹⁻⁶ The as-synthesized materials except SBA-1 were washed with slurring in EtOH-HCl at room temp.; less than 1 g of sample was washed with a mixture of 0.5 ml of 37% HCl and 20 ml of 95% EtOH. The sample was immediately dried in an oven at 393 K. The washing resulted in the removal of more than 95% of the surfactant, which was confirmed by IR absorption spectroscopy. The surfactant in SBA-1 was removed by calcination in O_2 flow at 823 K since the structure collapsed upon washing with EtOH-HCl. The mesoporous materials after the removal of surfactant, either by solvent extraction or calcination, were slurred in absolute EtOH solutions containing the anhydrous form of various metal compounds such as AlCl_3 , $\text{Al}(\text{NO}_3)_3$, SnCl_2 , $\text{Zn}(\text{O}_2\text{CMe})_2$ and $\text{Mn}(\text{O}_2\text{CMe})_2$, with magnetic stirring for 1 h at 298–333 K. The mesoporous materials were then washed with absolute EtOH, dried and calcined in air using a muffle furnace. The calcination temperature was increased to 823 K over 10 h and maintained there for 5 h.

The obtained materials were characterised by X-ray powder diffraction (XRD), BET surface area measurement, ^{27}Al MAS NMR, temperature programmed desorption (TPD) of NH_3 , and K^+ ion exchange. XRD patterns and NMR spectra were obtained in the same manner reported in our recent papers.^{9,10} Ammonia TPD and K^+ ion exchange capacity were measured following refs. 11 and 12, respectively.

All mesoporous metallosilicates obtained by the present metal-implantation route gave the same XRD patterns as those for their pure-silica analogues, as shown in Fig. 1. There were no significant changes in the XRD peak intensities and linewidths resulting from the implantation of Al, Sn, Zn and Mn throughout the investigated range of $\text{Si}/\text{Al} \geq 8$, $\text{Si}/\text{Sn} \geq 20$, $\text{Si}/\text{Zn} \geq 10$ and $\text{Si}/\text{Mn} \geq 20$. No additional XRD peaks appeared beyond the 2θ region shown in Fig. 1, indicating that the implanted metal elements were well dispersed. The BET areas of the various samples ranged from 900 to 1200 $\text{m}^2 \text{g}^{-1}$, and showed no more decreases than those attributable to increases in the sample mass due to the addition of the metal elements.

Recently, aluminosilicate forms of MCM-41 have been clarified to exhibit ion exchange capacity comparable to that for aluminosilicate zeolites whereas little ion exchange occurs with pure-silica MCM-41.¹² The ion exchange capacity can then be used as a means to probe the incorporation of metal elements with oxidation states less than +4. We have therefore measured the K^+ -ion exchange capacity of our various metal-containing samples, and summarised results in Table 1. Note that the present Al-implanted samples showed a K^+ -ion exchange capacity comparable to a result of 0.4 K^+/Al which was reported previously¹² with an AlMCM-41 ($\text{Si}/\text{Al} = 39$) sample prepared by the addition of sodium aluminate into the surfactant-silicate gel. The ion exchange capacity of the present Al-implanted samples depended more or less on structures and Si/Al ratios. The K^+/Al ratios decreased, in general, as the Si/Al ratios decreased. Sn-, Zn- and Mn-implanted samples also showed remarkable K^+ ion exchange capacity. It is thus evident that the

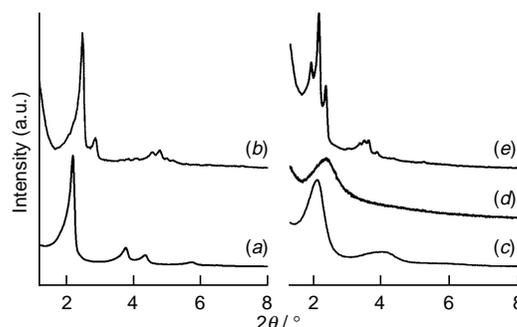


Fig. 1 X-Ray diffraction patterns for various mesoporous molecular sieves obtained after calcination with metal implantation: (a) AlMCM-41 ($\text{Si}/\text{Al} = 32$), (b) AlMCM-48 ($\text{Si}/\text{Al} = 8$), (c) AlKIT-1 ($\text{Si}/\text{Al} = 33$), (d) AlMSU-1 ($\text{Si}/\text{Al} = 53$) and (e) AlSBA-1 ($\text{Si}/\text{Al} = 11$). The XRD patterns of the calcined samples with and without the metals were indistinguishable from each other.

Table 1 Potassium ion exchange on mesoporous metallosilicates prepared by the metal-implantation method

Samples	Al implanted		Sn implanted	Zn implanted	Mn implanted
	Si/Al (K/Al) ^a	Si/Al (K/Al)	Si/Sn (K/Sn)	Si/Zn (K/Zn)	Si/Mn
KIT-1	47.7 ^b (0.15)	10.3 ^c (0.07)	71.7 (0.12)	20.4 (0.09)	68.5
MCM-41	48.9 ^b (0.20)	8.3 ^c (0.18)	218 (0.39)	21.1 (0.13)	56.1
MCM-48	37.1 ^b (0.24)	6.9 ^c (0.10)	56.7 (0.23)	18.7 (0.26)	
SBA-1	56.3 ^b (0.49)	10.8 ^c (0.27)	79.2 (0.13)	23.6 (0.29)	
MSU-1	53.4 ^b (0.52)	27.1 ^c (0.33)	230 (0.34)		

^a Numbers in parentheses denote the atomic ratio between the ion exchanged K⁺ and the implanted metal, determined by ICP emission spectroscopy. Metal leaching during ion exchange treatment occurred much less than K⁺ exchange. Release of H⁺ was also confirmed, indicating that the K⁺ was exchanged with H⁺. The pure-silica sample gave a K/Si ratio of 0.0004. ^b For Al incorporation, siliceous material was slurred in ethanol containing AlCl₃ at 298 K. ^c Slurry and filtration repeated three times using an excess of AlCl₃.

ion exchange capacity of the metal implanted samples arises from the incorporation of the metal elements within the silica framework, or at least in the form closely associated with it.

The incorporation of Al within the silica framework is consistent with a remarkable increase in the ²⁷Al MAS NMR peak intensity for Al with tetrahedral coordination, upon calcination as shown in Fig. 2. The NMR spectrum before calcination shows a much lower peak intensity for the tetrahedral Al (δ 52) than that for octahedral aluminium (δ 0). The intensity order was reversed after calcination, throughout the range of Si/Al = 10 to infinity for the various mesoporous materials after calcination. This result indicates that a considerable proportion of the Al achieves tetrahedral coordination after calcination and probably becomes implanted within the silica framework.

Fig. 3 shows NH₃ TPD for the resulting Al-implanted samples. The other aluminosilicate samples also gave two TPD peaks which were centered around 430 and 830 K, respectively. The relative peak intensities and positions depended more or less on the structures and Si/Al ratios. The low temperature peak is similar to the TPD results reported previously for AlMCM-41. However, the high temperature peak was not reported previously.^{9,13} The high temperature peak may be due to strong Lewis acidity of the extraframework Al species. The Al-

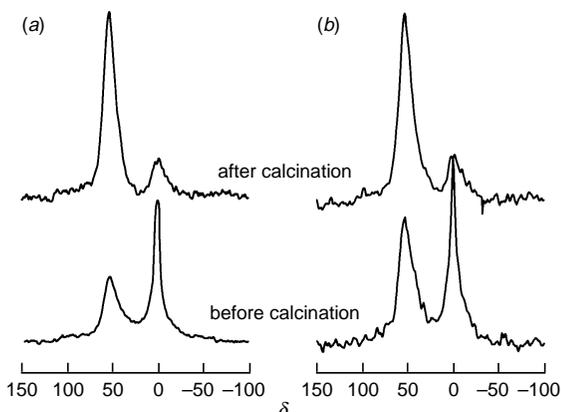


Fig. 2 ²⁷Al MAS NMR spectra for Al-implanted samples: (a) AIMCM-41 (Si/Al = 32) and (b) AlKIT-1 (Si/Al = 33). The NMR spectra show transition from octahedral to tetrahedral Al upon calcination.

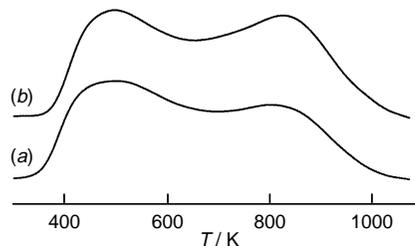


Fig. 3 NH₃TPD spectra for Al-implanted samples: (a) AlKIT-1 (Si/Al = 33) and (b) AlMCM-41 (Si/Al = 32)

implanted samples exhibited 2–3 times higher catalytic activity for *n*-butane cracking under 0.5 kPa butane and 110 kPa He at 801 K. This can be due to the presence of a relatively large amount of Al on the framework surface of the implanted samples, while much Al is imbedded within the pore wall of the samples which were synthesized with the addition of Al sources into the surfactant–silicate gel. Upon extrapolation to zero conversion, the turnover frequency for freshly calcined KIT-1 (Si/Al = 33) catalyst after Al implantation was 0.13 s⁻¹. This result is comparable to 0.30 s⁻¹, which was obtained for HZSM-5 (Si/Al = 25) based on the total number of Al sites under the same measurement conditions. Further details of the catalytic activity measurements will be reported in a full paper.

We have confirmed that it is important to use moisture-free EtOH or MeOH and anhydrous metal compounds since the presence of water inhibited metal implantation. It is believed that the metal species in the moisture-free solution was grafted onto silanol groups on the silica framework. The metal became probably incorporated within the siliceous framework *via* thermal activation during calcination. The resulting metallosilicate samples showed superior structural integrity, acidity and catalytic activity, compared to the materials obtained by the addition of a metal source into the surfactant-silicate gel. Thus, our metal implantation method can be useful for the preparation of various existing and new mesoporous metallosilicates.

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Footnote and References

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