Transition metal substituted derivatives of cubic MCM-48 mesoporous molecular sieves

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Mesoporous Ti-, Cr- and V-substituted derivatives of the cubic silica molecular sieve MCM-48 have been hydrothermally synthesized at 373 K by an electrostatic assembly pathway using cetyltrimethylammonium cation as the templating agent. The transition metal substituted products all exhibit improved crystallinity and a narrower pore size distribution relative to the pristine molecular sieve. Transition metal substitution caused an enlargement of the cubic unit cell as well as an increase in the degree of crosslinking in the mesopore walls. The coordination of V-sites in the meso-structure is exclusively tetrahedral, as judged by NMR spectroscopy. These sites as well as those of Ti and Cr sites are active and selective for the peroxide oxidation of styrene and methyl methacrylate to benzaldehyde and methyl pyruvate, respectively.

Keywords: Ti-, Cr-, V-substituted MCM-48; mesoporous molecular sieve; peroxide oxidation

1. Introduction

MCM-41 and MCM-48 are hexagonal and cubic forms of mesoporous silica molecular sieves discovered by Mobil scientists [1]. The surfactant to silicon ratio has a dramatic effect on the formation of the mesoporous phases, with MCM-41 and MCM-48 [2] formed at surfactant to silicon ratios of ~ 0.6 and ≥ 1.0, respectively. The incorporation of Ti and V into hexagonal MCM-41 has been reported [3,4]. However, there are, to date, no reports of Ti, Cr and V substituted into the cubic MCM-48 phase. We report here a hydrothermal synthesis of MCM-48 and its metal substituted derivatives using tetraorthosilicate (TEOS) as the silicon source and cetyltrimethylammonium bromide as the surfactant at a surfactant to silicon ratio of 0.5. This procedure affords Ti-, Cr-, and V-substituted cubic MCM-48 (M-MCM-48) with relatively high crystallinity and very narrow Horvath–Kawazoe pore size distribution. All three M-MCM-48 derivatives are active catalysts for oxidative double bond cleavage of methyl methacrylate and styrene with hydrogen peroxide to form methyl pyruvate and benzaldehyde as the dominant respective products.

2. Experimental

2.1. Synthesis

MCM-48 and Ti-, Cr-, and V-substituted MCM-48 materials were prepared according to the following procedure. First, a gel with a molar composition of $0.020M : 1.0Si : 0.50surf : 0.50OH^- : 170H_2O$ was pre-

pared. TEOS was used as the silicon source, cetyltrimethylammonium bromide was the surfactant, NaOH was the OH^- source. Tetra-isopropyl titanate (Ti-i-$(OPr)_4$), $CrCl_3 \cdot 6H_2O$ and $VOSO_4 \cdot 3H_2O$ served as the transition metal precursors. The gel was charged into a Teflon-lined autoclave and heated at 373 K for 10 days. The product was filtered and washed thoroughly with water and then with 0.2 M NH_4Cl aqueous solution to remove residual sodium ions. TS-1 with an analytically determined titanium loading of 2 mol% was synthesized following the method described by Notari et al. [5] by using tetra-propyl ammonium hydroxide as template (TPAOH) and TEOS as the silicon source at 443 K for 48 h. The gel composition used was $0.022Ti : 1.0Si : 0.35TPAOH : 35H_2O$. The as-synthesized product was dried at ambient temperature in air, calcined at 813 K in air for 6 h and sealed in a vial for use as a catalyst and for further characterization. Chemical analysis by means of ICP atomic emission spectroscopy verified essentially quantitative incorporation of the transition metal into the final product for all three derivatives.

2.2. Characterization

Powder X-ray diffraction patterns were measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode and Cu Kα radiation. N_2 adsorption and desorption isotherms were obtained at 77 K on a Coulter Omnisorp 360CX sorptometer using a continuous adsorption procedure. ^{29}Si and ^{51}V MAS NMR spectra were measured on a Varian VXR-400S spectrometer at frequencies of 59.6 and 78.9 MHz, respectively. The magic angle spin speed used for ^{51}V and ^{29}Si spectra recording were 6.0 and 4.2 kHz, respectively. The ^{29}Si NMR spectra were fitted by using a Gaussian function

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in order to obtain the Q^3 and Q^4 connectivities of the silicon sites.

2.3. Peroxide oxidation of olefins

Peroxide oxidation of methyl methacrylate (MMA) and styrene were carried out in a round-bottom flask. For each run, the flask was charged with the following components: 30 mg of catalyst, 10.0 mmol of substrate, 10 ml of acetonitrile. For MMA oxidation, 40.0 mmol of 30% H_2O_2 was used, and the reaction was run at 321 K for 6 h. For styrene oxidation, 20.0 mmol of 30% H_2O_2 was used, and the reaction was run at 321 K for 3 h. The reaction products were analyzed using a HP 5890 GC with a SPB-20 capillary column. The conversion was calculated by normalization of all detectable hydrocarbon derivatives using pre-measured corresponding response factors.

3. Results and discussion

Representative powder X-ray diffraction patterns of calcined V-MCM-48 and its pure silica analog are shown in fig. 1. The pattern for V-MCM-48 consists of six distinguishable Bragg peaks which can be indexed to different (hkl) reflections. These reflections verify the presence of cubic phases with unit cell dimensions of 83.2 and 79.5 Å for the V-substituted and pure silica derivatives, respectively. The unit cell expansion signifies V-substitution of Si in the MCM-48 structure. Similar unit cell enlargement is known to occur upon heteroatom substitution in silicalite [6].

The unit cell parameters for transition metal substituted MCM-48 and the pristine MCM-48 are compared in table 1. Obviously, the unit cell has been enlarged for all three M-MCM-48 samples. In general, unit cell expansion can be caused by insertion of the heteroatom into the framework of silica as in the case of TS-1 [6], or by an increase in the framework wall thickness [7]. Variations in the size of surfactant micelles would also cause
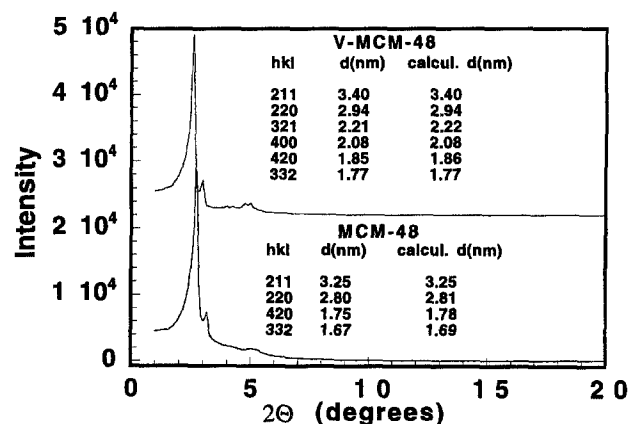
Table 1
X-ray diffraction parameters of transition metal substituted calcined MCM-48 derivatives

M-MCM-48	$d(hkl)$ (Å)				Unit cell[a] (Å)	Δ[b] (Å)
	(211)	(220)	(420)	(332)		
none	32.5	28.0	17.5	16.7	79.5	18.9
Ti-	32.6	28.3	17.7	16.9	79.8	16.8
V-	34.0	29.4	18.5	17.7	83.2	17.0
Cr-	34.5	29.8	18.9	18.0	84.5	12.1

[a] The cubic phase unit cell parameter, a, was calculated according to $a = d(hkl)\sqrt{(h^2 + k^2 + l^2)}$.
[b] Δ is the unit cell contraction upon calcination at 813 K.

a change in unit cell size [1], but this seems to be unreasonable, because all our MCM-48 samples were synthesized using cetyltrimethylammonium bromide as the templating surfactant under very similar reaction conditions. To attribute the unit cell expansion completely to heteroatom insertion into the framework of silica also seems to be unreasonable because 2% metal substitution should not cause such a large change of unit cell (~ 5 Å in the case of Cr-MCM-48). Thus, we favor an increase in wall thickness as the reason for the increase in unit cell parameter upon transition metal substitution.

It is apparent from the contraction in unit cell parameter (Δ) upon calcination at 831 K that transition metal substituted MCM-48 derivatives exhibit improved mesostructure thermal stability. This may occur via transition metal promoted crosslinking of the amorphous [8] mesopore walls, hence, resulting in a thicker wall structure and enlarged unit cell. This interpretation is further supported by pore size measurements and ^{29}Si MAS NMR spectra of V-MCM-48 and MCM-48 (see below).

The N_2 adsorption–desorption isotherm and the Horvath–Kawazoe (HK) pore size distribution for V-MCM-48 are presented in fig 2. A well defined step occurs in the adsorption curve between $P/P_0 = 0.2$ and 0.3, which is indicative of the filling of framework-confined mesopores with an average pore of 23 Å. The sharp HK pore size distribution peak with a ~ 0.5 nm width at half-height indicates that the framework-confined mesopores in V-MCM-48 are exceptionally uniform. Approximately the same HK pore size (± 1 Å) and N_2 adsorption–desorption isotherms were obtained for Cr-MCM-48 and Ti-MCM-48. This result is consistent with the increase in lattice parameters being due to an increase in wall thickness.

The strongest evidence for vanadium isomorphous substitution of Si in mesoporous MCM-48 was found by ^{51}V MAS NMR spectroscopy (see fig. 3). The ^{51}V NMR spectrum of calcined V-MCM-48 recorded under magic angle spinning (6000 Hz) conditions shows only one signal at ~ 530 ppm relative to $VOCl_3$ as a reference. The isotropic chemical shift of ca. ~ 500 ppm is diagnostic of tetrahedral vanadium [9]. The spectrum for V-

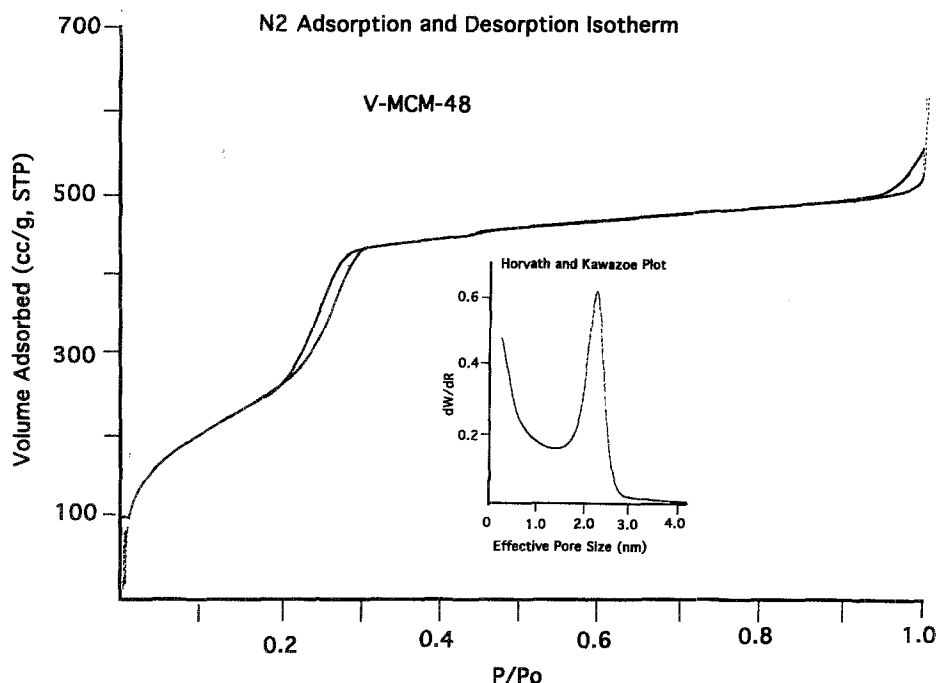Fig. 1. X-ray diffraction patterns of MCM-48 and V-MCM-48.

Fig. 2. N_2 adsorption and desorption isotherm of V-MCM-48. Insert: Horvath–Kawazoe pore size distribution.

MCM-48 is different from that of V-MCM-41, which exhibits two tetrahedral [51]V signals, as reported by Sayari et al. [4]. So, the tetrahedral V-sites in our V-MCM-48 sample are uniquely homogeneous.

The ^{29}Si MAS NMR spectra of as-synthesized MCM-48 and V-MCM-48 are presented in fig. 4. It is apparent that V-substitution causes a dramatic increase of Q^4-Si ($Si(OSi)_4$) sites. A similar increase was also observed for Ti-MCM-48 and Cr-MCM-48. The full width at half-height of NMR lines and relative Q^2, Q^3 and Q^4 percentages obtained from fitted spectra are summarized in table 2. Metal substitution caused Q^4 peak broadening was observed for all of the M-MCM-48

derivatives. This is another indication that isomorphous transition metal substitution has occurred. The decrease of Q^2- and Q^3-Si sites along with the increase of Q^4, strongly supports metal promoted crosslinking of the mesopore walls. Approximately, $\sim$ 25% more Q^4-Si was formed for V-MCM-48 and Ti-MCM-48. Unlike titanium and vanadium which isomorphously substitute for Si in silicalite, Cr only partially substitutes and partially grafts to the surface of silicalite [10]. This may also occur for Cr-MCM-48 because washing the sample with dilute acetic acid (the same approach used in ref. [10]) results in the depletion of approximately half the amount of Cr from the sample. Therefore, it is reasonable to attribute
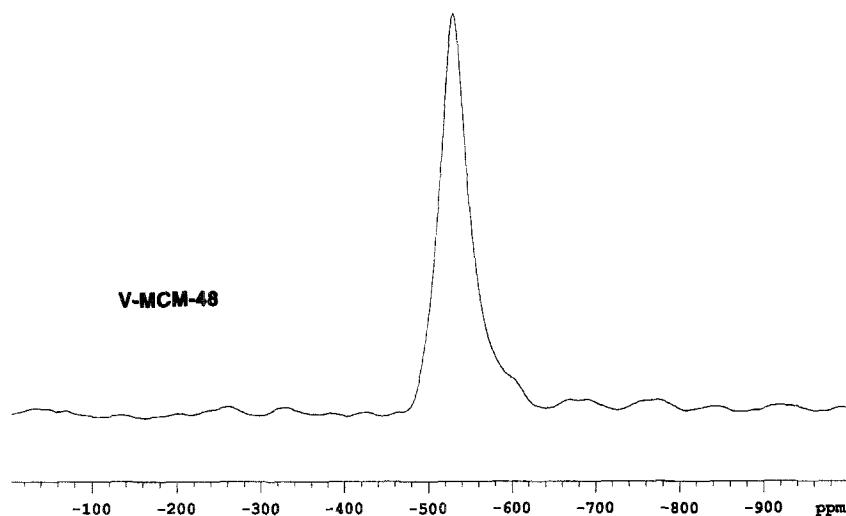

Fig. 3. [51]V MAS NMR spectrum of V-MCM-48 calcined at 813 K. MAS speed was 6000 Hz. Chemical shift was measured using $VOCl_3$ as a reference.
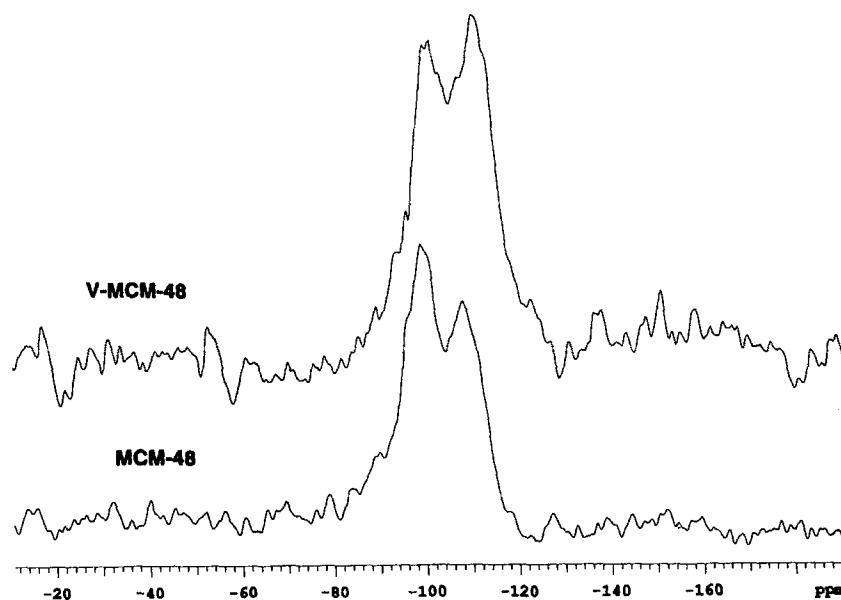
Fig. 4. ^{29}Si MAS NMR of as-synthesized MCM-48 and V-MCM-48. MAS speed was 4200 Hz. Chemical shift was measured using talc (-98.1 ppm) as a reference.

the differences in ^{29}Si NMR parameters for Cr-MCM-48 and the Ti- and V-MCM-48 (table 2) derivative to be a result of a lower degree of Cr substitution in the structure.

In general, isolated tetrahedral Ti-, Cr- and V-sites in molecular sieve frameworks are active for peroxide oxidation reactions. In order to further confirm the existence of isolated metal sites in our M-MCM-48 samples, they were used as catalyst for the peroxide oxidation of styrene and methyl methacrylate (MMA). The results are compared in table 3 with those for 2 mol% Ti-containing TS-1. All three M-MCM-48 samples show activity for the catalytic peroxide oxidation of both substrates. For methyl methacrylate oxidation, conversion was low under the mild reaction temperature employed (321 K), but methyl pyruvate was formed with 100% selectivity. For styrene oxidation, higher conversion was achieved with good selectivity ($>$ 80%). In addition to benzaldehyde, a small amount of epoxide and diol also were formed. This may indicate that the diol might be an intermediate for double bond cleavage. The mechanism for oxidative cleavage of olefins is compli-

cated. For TS-1 [11] and Tiβ [12], a diol is proposed as an intermediate, which binds to the isolated Ti-site and undergoes further oxidation to produce ketones or aldehydes. The difference in activity between TS-1 and Ti-MCM-48 may be due to differences in the bond angles of tetrahedrally coordinated titanium, or to differences in framework accessibility.

4. Conclusion

In summary, the following conclusions have emerged from the above experiments:

(1) Transition metal substituted derivatives of the cubic mesoporous molecular sieve MCM-48 can be prepared with good crystallinity and a very narrow HK pore size distribution.

(2) V is located in a tetrahedral environment in V-MCM-48, as is strongly indicated by ^{51}V MAS NMR spectroscopy.

(3) Incorporation of V, Cr, and Ti most likely promotes the further crosslinking of the mesopore walls, which results in a larger unit cell parameter and a smaller unit cell contraction upon calcination. In addition, V, Cr, and Ti substitution causes an increase in Q^4-Si content along with a broadening of the Q^4-Si NMR peak which verifies that some isomorphous substitution takes place during synthesis.

(5) All three calcined M-MCM-48 derivatives are catalytically active for the selective peroxide oxidation of styrene and methyl methacrylate to benzaldehyde and methyl pyruvate, respectively, which indicates they possess isolated active metal sites.

Table 2
^{29}Si MAS NMR parameters for as-synthesized MCM-48 and transition metal substituted derivatives [a]

M-MCM-48	Q^4 peak width (Hz)	Q^2 (mol%)	Q^3 (mol%)	Q^4 (mol%)
none	581	8	60	32
Ti-	845	2	40	58
V-	839	3	40	57
Cr-	618	1	64	35

[a] The transition metal loading is approximately 2 mol%.

Table 3
Peroxide oxidation of olefins over transition metal substituted MCM-48 derivatives and TS-1 [a]

Activity (mol%)	M-MCM-48				2% Ti-TS-1	No catalyst
	none	V-	Cr-	Ti-		
MMA conv.	0	1.8	39	6.8	2.5	0
MPV select.	0	100	100	100	78	0
styrene conv.	1.6	4.6	27	26	8.4	1.6
PhCHO select.	71	80	84	85	71	70

[a] MMA, MPV and PhCHO are methyl methacrylate, methyl pyruvate and benzaldehyde, respectively.

Acknowledgement

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