

Hydroxylation of Phenol over M-MCM-48

Ch. Subrahmanyam¹, B. Louis², B. Viswanathan^{1*}, A. Renken² and T.K. Varadarajan¹

¹Department of Chemistry, Indian Institute of Technology Madras, Chennai-600 036, India

²Institute of Chemical Engineering, Swiss Federal Institute of Technology,
CH-1015 Lausanne, Switzerland

Abstract

The synthesis and characterization of M-MCM-48 (M= Si, Ti, V, Cr and Mn) materials have been carried out. These systems promote hydroxylation of phenol with 30 % H₂O₂ and the hydroxylation activity is highest for Ti-MCM-48. Water appears to be a better solvent than acetone and acetonitrile.

Introduction

Catalytic oxidation of aromatics has been widely used in the manufacture of fine chemicals [1]. Phenol hydroxylation has been studied over various catalysts, which include homogeneous catalysts such as Cu⁺, Au⁺, Co⁺ [2], Fe⁺ [3-4] and Fe⁺ [5-7]. Though these metal ions in homogeneous phase are active for diphenol production, the reaction rate and selectivity to diphenols are not favorable. Metal complexes, such as metal phthalocyanine [M= V, Mo, Sn, Co, Fe] [8], Fe (III) bipyridine [9] and Co(II)-schiffs base complexes have also been used [10]. Though these metal complexes exhibit better catalytic activity and selectivity than metal ions, these complexes are not desirable for industrial applications due to shortcomings of homogeneous catalysts such as difficulties in handling and recovery of the catalyst.

Homogeneous catalysts have also been immobilized in the cavities of well-defined microporous zeolites and used as catalysts for phenol hydroxylation [11]. However, the results are disappointing due to narrow pores of the host species. Zeolites containing transition metal ions in their framework exhibit unique redox properties in oxidizing organic substrates with peroxides as oxidizing agents. The success of TS-1, a microporous titanosilicate, as selective oxidation catalyst with 30% H₂O₂ under milder conditions, has led to synthesize molecular sieves containing transition metal ions other than titanium [12]. However, applications of the microporous catalysts are limited

due to their narrow pore sizes. With the discovery of silica based mesoporous molecular sieves MCM-41 and MCM-48 by Vartuli et al. it has been possible to overcome the existing problems with zeolites [13]. Various transition elements [Ti, V, Cr and Mo] have been incorporated in hexagonal MCM-41 and the resulting catalysts have potential activity for various catalytic reactions [14-17]. However, cubic MCM-48 is a better choice as a catalyst due to its high surface area and three-dimensional network of pores, which can resist pore blockages [18]. In this communication we report the synthesis of M-MCM-48 [M= Ti, V, Cr and Mn] and their catalytic activity for phenol hydroxylation with 30 % H₂O₂.

Experimental

Synthesis

M-MCM-48 materials [M= Si, Ti, V, Cr and Mn] were synthesised under hydrothermal conditions at 423 K in a static stainless-steel autoclave. In a typical synthesis of M-MCM-48, to a 25% aqueous solution of cetyltrimethylammoniumbromide (CTAB) (S.D. Fine Chem.) tetraethylorthosilicate (TEOS, 98%, Merck-Schuchardt) was added along with the required amount of transition metal precursor. The pH of the gel was adjusted to 10.0-10.5. The typical molar gel composition was SiO₂: M_xO_y: CTAB: Na₂O: EtOH: H₂O = 2.0: 0.015: 0.24: 0.5: 5.0: 195. The gel was stirred for 3h at room temperature and autoclaved at 423 K for 10 h. The solid product was filtered, washed several times with deionised water, dried over night in air at 373 K, calcined for 1h in N₂ atmo-

*corresponding authors. E-mail: bviswanathan@hotmail.com

sphere followed by air at 823 K for 10 h. Pure silica materials were also prepared by the same procedure.

Characterisation

Various techniques have been used for the characterisation of the materials synthesised. The low angle X-ray diffraction pattern of the sample was recorded on a Siemens D 500 ($\theta/2\theta$) using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of $1^\circ/\text{min}$ over the range $2 < 2\theta < 10^\circ$. Thermal analysis of the samples were made with thermal analyser (Perkin Elmer model TGA 7) at a heating rate of 20 K/min . Diffuse reflectance UV-VIS spectroscopy was carried out on a Cary 5 E UV-VISNIR spectrophotometer. ESR spectra were recorded with Varian E-112 spectrometer at room temperature. N_2 adsorption-desorption measurements at 77 K were made using a CE instruments, Sorptomatic 1990. The sample was out gassed at 473 K for 12 h. X-ray photoelectron spectroscopic measurements (XPS) were performed on a PHI-550 ESCA-System (Perkin-Elmer GmbH).

Catalytic activity

Phenol hydroxylation was carried out in liquid phase in a three-necked round bottom flask equipped with reflux condenser. The reactions were performed at 333 K in water, acetone and acetonitrile as solvents. The temperature of the reaction was maintained by a thermostated oil bath. After each experiment the catalyst was filtered and dried. The dried catalysts were then calcined in air at 673 K for 6 h and reused. It was observed that the performance of the catalyst has not decreased after second run of the experiment. After each experiment, XRD was recorded to examine the morphological changes. The catalyst maintained the same morphology after the completion of the reaction. The reaction products were identified by GC-MS (Hewlett-Packard, HPG 1800A GCD system, HP-5) and analysed by gas chromatography (Shimadzu GC-14A, 30m HP-5. FID).

Results and Discussion

XRD

The powder X-ray diffractograms of the calcined M-MCM-48 samples are shown in Fig. 1. It can be seen that highly ordered MCM-48 mesoporous materials consistent with an Ia3d cubic symmetry were obtained. In the procedure adopted in the present study

the synthesis of the MCM-48 at low surfactant to silicon ratio was achieved, unlike the synthesis reported by Mobil researchers where higher ratios are mandatory to obtain the cubic structure [12]. In this approach, MCM-48 materials have been prepared at lower concentrations of the template. The Si-MCM-48 materials exhibit a maximum intense peak with d_{211} value of $34.50 \text{ \AA}$, which on calcination decreased to $33.0 \text{ \AA}$. All catalysts, in addition to reflection due to (211), show less intense peaks corresponding to (220), (321), (400) and (322) reflections. After the calcination at 823 K in air, the cell parameter calculated was found to be $80.6 \text{ \AA}$. After the catalytic experiments, the material showed similar XRD pattern indicating that the material maintains the same morphology even after the reaction.

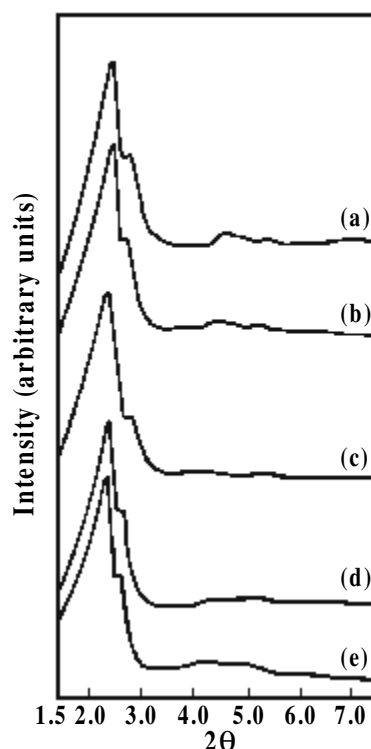


Fig. 1. XRD patterns of M-MCM-48 (Calcined): (a) Si-MCM-48; (b) Ti-MCM-48; (c) V-MCM-48; (d) Cr-MCM-48 and (e). Mn-MCM-48

N_2 adsorption-desorption

The N_2 adsorption-desorption isotherms for MCM-48 materials are shown in Fig. 2. All M-MCM-48 [where M = Si, Ti, V, Cr and Mn] catalysts showed typical type IV adsorption-desorption isotherms with a hysteresis characteristic of mesoporous materials. The isotherms have an inflection around $p/p_0 = 0.2$ - 0.3 indicative of mesoporous nature. The BET sur-

face areas of the materials and pore size of the various catalysts are given in Table 1. The BET surface area of the catalysts ranges from 1000 m²/g for Si-MCM-48 to 640 m²/g for Cr-MCM-48.

Thermal Analysis

Thermogram of the Si-MCM-48 is given in Fig. 3 which shows mainly three weight loss regions, the first one corresponds to loss of physisorbed water below 373 K and the second and main weight loss in the temperature range 473 K – 523 K corresponds to removal of the template. The final weight loss above 550 K corresponds to loss of water from the condensation of silanol groups. It was observed that these catalysts are stable up to 1073 K.

UV-VIS DRS spectra

The presence of various transition elements in the mesoporous network has been confirmed with UV-

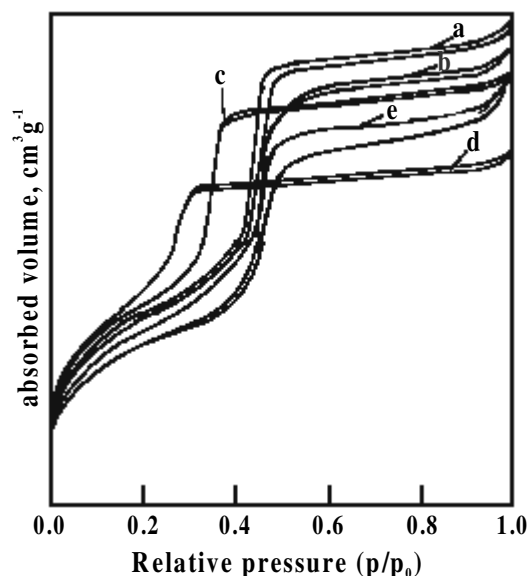


Fig. 2. N₂ adsorption-desorption isotherms of M-MCM-48: (a) Si-MCM-48; (b) Ti-MCM-48; (c) V-MCM-48; (d) Cr-MCM-48 and (e) Mn-MCM-48

Table 1
Physico-Chemical properties of M-MCM-48 catalysts

Catalyst	d ₂₁₁ [uncal]	d ₂₁₁ [cal]	a = d × (h ² + k ² + l ²) ^{1/2} , Å	BET surface area m ² /g	Pore size Å	Pore volume cm ³ /g
Si-MCM-48	33.7	32.9	80.5	1020	28	1.01
Ti-MCM-48	34.5	32.9	80.5	953	28	0.85
V-MCM-48	35.3	33.4	81.9	745	28	0.77
Cr-MCM-48	35.9	33.6	82.4	640	29	0.70
Mn-MCM-48	36.4	34.1	83.5	850	29	0.87

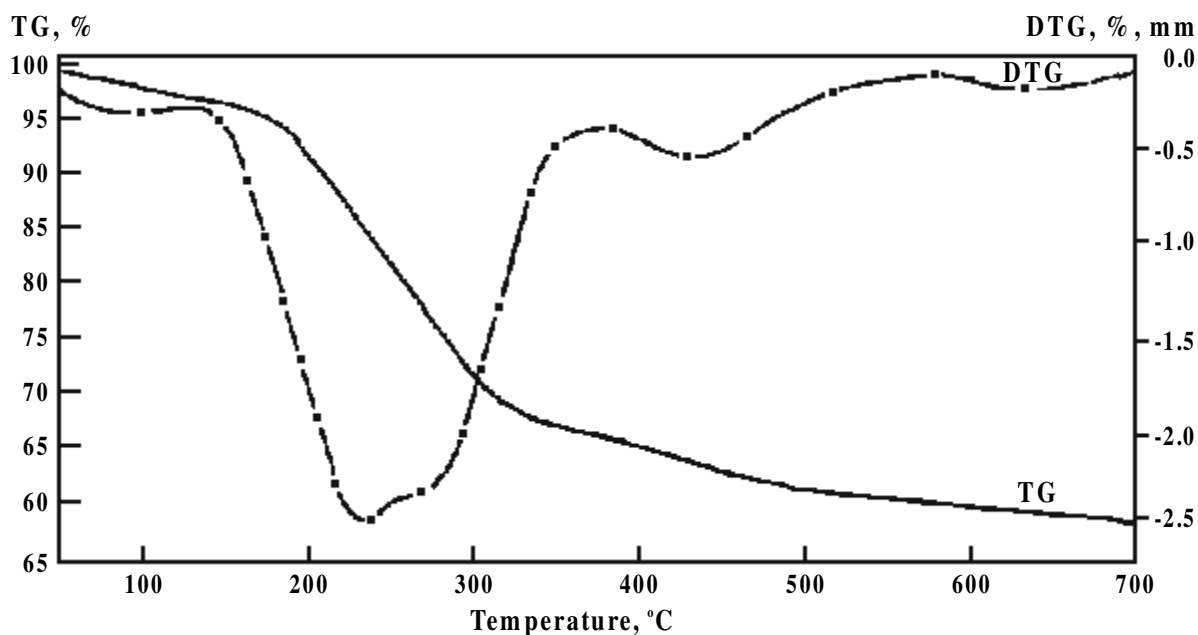


Fig. 3. TGA of Si-MCM-48

VIS spectroscopy. The presence of a CT band at 230 nm confirms the incorporation of Ti^{+4} in mesoporous network for Ti-MCM-48. V-MCM-48 as synthesised material shows a band characteristic of V^{+4} species in the region 250-285 nm, which upon calcination an additional band between 285-340 nm was observed confirming the presence of V^{+5} species in T_d environment. For unclacined Cr-MCM-48, a band at 440 nm characteristics of Cr^{+3} was observed. Upon calcination, the presence of an additional charge transfer band at 370 nm confirms the higher oxidation states (+5 and/or +6) of chromium. The presence of chromium in both oxidation states has been further confirmed by ESR spectroscopy.

Catalytic activity

Phenol hydroxylation has been carried out at 333 K in water, acetone and acetonitrile as solvents and the results are given in Tables 2, 3 and 4. It has been observed that all the catalysts are active for phenol hydroxylation and in all the cases, a mixture of

catechol, hydroquinone and benzoquinone are formed. The formation of catechol and hydroquinone could be more likely due to electrophilic substitution of ($\bullet OH$) on the benzene ring of phenol at *ortho* and *para* positions [19]. Further oxidation of hydroquinone leads to benzoquinone. When the reaction was performed in the absence of solvent, conversion of phenol was low [$< 2\%$] which indicates solvent participation is required. Among the solvents for phenol hydroxylation, water is a better solvent compared to acetone and acetonitrile. The reason may be that phenol and H_2O_2 can reach the active sites more easily in water than in the organic solvents. It has been observed that Ti-MCM-48 shows higher conversion compared to the other members. This could be due to optimized hydrophobic/hydrophilic environment of the pore walls of Ti-MCM-48. It has been observed that next to Ti, Mn substituted systems show better conversion, which may due to high dispersion of Mn species in Mn-MCM-48, which is necessary for oxidation of phenol.

Table 2
Hydroxylation of phenol over various catalysts in water

Catalyst	Conv. of phenol (%)	Product selectivity (%)		
		Catechol	Hydroquinone	Para benzoquinone
Ti-MCM-48	12.65	51.4	43.3	5.3
V-MCM-48	10.50	50.5	41.7	7.8
Cr-MCM-48	10.60	50.7	40.7	8.6
Mn-MCM-48	10.65	51.5	40.4	8.1

Reaction conditions: weight of the catalyst = 100 mg
Temperature = 333 K, Duration = 4 h,
Mole ratio of the reactants = phenol: H_2O_2 : Solvent = 1:1:10

Table 3
Hydroxylation of phenol over various catalysts in acetone

Catalyst	Conv. of phenol (%)	Product selectivity (%)		
		Catechol	Hydroquinone	Para benzoquinone
Ti-MCM-48	10.25	52.6	31.3	16.1
V-MCM-48	4.46	50.7	22.7	26.6
Cr-MCM-48	4.96	59.1	20.0	20.9
Mn-MCM-48	7.86	51.5	18.7	29.8

Reaction conditions: weight of the catalyst = 100 mg,
Temperature = 333 K, Duration = 4h,
Mole ratio of the reactants = phenol: H_2O_2 : Solvent = 1:1:10

Table 4
Hydroxylation of phenol over various catalysts in acetonitrile

Catalyst	Conv. of phenol (%)	Product selectivity (%)		
		Catechol	Hydroquinone	Para benzoquinone
Ti-MCM-48	10.70	58.9	24.6	16.5
V-MCM-48	3.57	50.1	17.9	32.0
Cr-MCM-48	7.53	51.8	20.5	27.7
Mn-MCM-48	8.12	61.1	23.5	15.4

Reaction conditions: weight of the catalyst = 100 mg

Temperature = 333 K, Duration = 4 h,

Mole ratio of the reactants = phenol: H₂O₂: Solvent = 1:1:10

Conclusions

Transition metal substituted derivatives of the cubic mesoporous MCM-48 have been prepared at lower concentrations of the template with good crystallinity. All the four M-MCM-48 [M = Ti, V, Cr and Mn] catalysts are active for the selective hydroxylation of phenol to a mixture of catechol and hydroquinone/para benzoquinone. Ti substituted systems shows higher catalytic activity compared to rest of the systems.

Acknowledgements

The authors are grateful to Dr. Kiwi-Minsker for fruitful discussions and Dr. P. Rastogi for providing fellowship to Ch. Subrahmanyam under the IIT-EPFL collaboration scheme.

References

1. R.A. Sheldon, I.W.C.E. Arends, H.E.B. Lempers, *Catal. Today* 41 387 (1998)
2. P. Maggioni, *German Offenlegunschrift*. 2, 341, 743 (1974)
3. A.V. Eliseev, *React. Kine. Catal. Lett.* 43, 419 (1991)
4. M.B. Hocking, *J. Chem. Tech. Biotech. Chem. Technol.* 35A, 365 (1985)
5. P. Maggioni, *Chem. Ind. (Milan)* 59, 239 (1977)
6. A.I. Brodskii, *Zh. Obshch. Khim.* 32, 2273 (1962)
7. A.P. Ereemeev, *Zh. Prikl. Khim.* 53, 386 (1980)
8. Z. Masari, M. Hronec, in "Dioxygen Activation and Homogeneous Catalytic Oxidation" (L. I. Simandico, Ed) Elsevier, Amsterdam (1991)
9. B.V. Rao, *Indian J. Chem. Sect. A.* 19, 257 (1980)
10. D.R.C. Huybrechts, *Catal. Lett.* 8, 273 (1991)
11. C. Bowers, P.K. Dutta, *J. Catal.* 122, 271 (1990)
12. M.G. Cleric, *Appl. Catal.* 68. 249 (1991)
13. J.C. Vartuli, K.D. Schmitt, C.T. Kresge, W.J. Roth, M.E. Leonowicz, S.B. McCullen, S.D. Hellring, J.S. Beck, J.L. Schlenker, D.H. Olson, E.W. Sheppard, *Chem.Mater.* 6, 2317 (1994). 13.
14. P.T. Tanev and T.J. Pinnavaia, *Science* 267 (1995) 865
15. K.M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc. Chem. Commun.*(1994) 1059
16. N. Ulagappan, C.N.R. Rao, *J. Chem. Soc. Chem. Commun.*, (1995) 875.
17. Rohit Kumar Rana, B. Viswanathan, *Catal. Lett.* 52, 25, 1998.
18. Ch. Subrahmanyam, B. Viswanathan, T.K. Varadarajan, *Bull. Catal. Soc. India.* 10 (6) 2000.
19. Chibiao Liu, Yongkui Shan, Xiangguang Yang, Xingakai, Yue Wu, *J. Catal.* 168, (1997) 35

Received 7 March 2001.