Effect of Si/Ti Molar Ratio on the Thermal Stability of Ordered Mesoporous TiO_2/MCM-41 Materials

GINA-DUMITRITA MIHAI[1,2*], VERA MEYNEN[1], NICOLAE BILBA[2], PEGIE COOL[1]
[1] Laboratory of Adsorption and Catalysis, University of Antwerpen, Universiteitsplein 1, B-2610 Wilrijk, Belgium
[2] Laboratory of Materials Chemistry, "Al.I. Cuza" University of Iasi, B-dul Carol, nr.11, 700506, Iasi, Romania

TiO_2/MCM-41 materials are prepared by an in-situ synthesis method. A clear influence of the calcination temperature and the TiO_2 content of these materials on their stability and structural properties can be observed using N_2 adsorption-desorption measurements. UV-VIS diffuse reflectance and Raman spectra show that, the increase of the calcination temperature leads to an enhancement of TiO_2 crystallization in MCM-41 materials causing a partial structural collapse at high temperatures and TiO_2 contents.

Keywords: MCM-41, one-pot synthesis, titanium dioxide catalyst, characterization

In the last decade, new ordered mesoporous materials with adjustable pore size and extremely high surface area of up to about 1000m²/g have stimulated great interest in the fields of catalysis, adsorption, separation and others. One of the most widely studied materials is MCM-41 that can be used as host for incorporation of different metals, ions and oxides thereby creating and enlarging the activity inside the porous frameworks. Various processes have been utilised for the introduction of active sites in mesoporous materials, such as: one-pot synthesis [1-5], template-ion exchange [6] and several post-synthesis modification methods [7-9]. A wide variety of catalytic reactions can be applied with supported catalysts. Photocatalysis is one of these growing fields. Here, TiO_2 is used as the active element and is preferably present as anatase or a mixture of anatase and rutile [10]. Therefore, it is of utmost importance that as much titania as possible is present in the correct crystal phase. However, also high surface area and large pores are preferred in order to allow good mass transfers and high activity. High calcination temperatures are necessary to transfer the amorphous titania phase into the optimal crystal phases. Because of the necessity for higher calcination temperatures, the thermal stability of these silica-titania composite materials is crucial.

In this work, we investigate the thermal stability of the TiO_2/MCM-41 materials prepared by an in-situ method [11]. Moreover, the improvement of anatase formation in the MCM-41 host material by changes in the heat treatment is discussed. Two samples with Si/Ti ratio 3 and 15 were prepared and calcined at two different temperatures: 550°C and 650°C.

Experimental part

For TiO_2/ MCM-41 materials the molar composition: xSi/1Ti/0.24CTMABr/0.19TEAOH/36 H_2O, with x = 3 and 15 was realised using tetraethylorthosilicate (TEOS), cetyltrimethylammonium bromide (CTMABr from Acros Organics), titanium tetraisopropoxide (Ti-ISOP) and tetraethylammonium hydroxide (TEAOH from Sigma Aldrich). CTMABr was dissolved in water under stirring at room temperature for 30 min. The solution was heated at 40°C in a reflux setup. Then 9.6 mL TEAOH was added to provide an alkaline reaction medium. After 15 min, TEOS and Ti-ISOP were added and the mixture was stirred during 24h at 40°C. The resulting gel was then transferred into an autoclave and maintained at 140°C for 48h. The final product was filtered, washed, dried at room temperature and calcined at 550 °C for 6h (using a temperature ramp of 1°C/min). The samples are denoted TiOM (x)-y, where x is the Si/Ti ratio and y is the calcination temperature. For comparison, a pure siliceous MCM-41 was prepared using the same synthesis procedure.

FT-Raman spectra were recorded on a Nicolet Nexus 670 FT-Raman spectrometer with a Ge detector and a 1064 nm Nd:YAG laser.

UV-Vis diffuse reflectance spectra were recorded on a Thermo-electron evolution 500 UV-Vis spectrometer equipped with a Thermo-electron RSA-UC40 Diffuse Reflectance cell.

Nitrogen adsorption/desorption isotherms were collected at -196° C on a Quantachrome Autosorb-1-MP.

Results and discussions

Nitrogen adsorption-desorption isotherms of TiOM(x)-y samples along with their BJH pore size distributions (inset) are shown in figure 1a and 1b.

All samples exhibit isotherms of type IV, characteristic for mesoporous materials. At high Ti loadings (Si/Ti = 3), the capillary condensation becomes less steep, smaller and a broader pore size distribution can be observed (fig. 1a) to the Si-MCM-41. However, the structure still possesses a high surface area and pore volume (table 1). A similar effect can be observed when a lower amount of Ti is used (Si/Ti=15) (fig. 1b). However, it is clear that the effect is more significant at high loading (Si/Ti=3).

Larger differences in isotherms can be observed when the calcination temperature is changed from 550°C to 650°C (fig. 1a and 1b). After calcination at 650°C, the pore structure of the TiOM (3) sample only shows a very small condensation and broad pore size distribution. However, the sample with a Si/Ti ratio of 15 still shows a clear and sharp capillary condensation and pore size distribution. These results indicate a partial collapse of the TiOM (3) structure at these temperatures in contrast to the TiOM (15) structure. Furthermore, the increase in calcination temperature leads to a deterioration of the textural characteristics that is more significant at high Ti contents (table 1).

The reason for this structural instability at temperatures above 550°C should be found in the crystallization of titania.

---

* email: pgdgina@yahoo.com; Tel: +32 (0)3 820 23 80

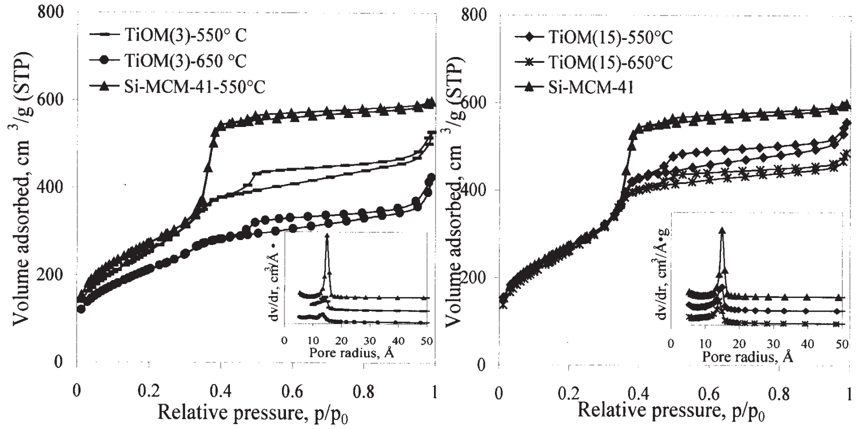

Fig. 1 N_2 adsorption-desorption isotherms of (a) TiOM(3)-y samples and (b) TiOM(15)-y samples calcined at 550°C and 650°C. Inset of figures is BJH pore size distribution of TiOM(x)-y samples

Sample	Si/Ti (molar ratio)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
TiOM(3)-550°C	3	955	0.75	2.82
TiOM(3)-650°C	3	783	0.55	2.69
TiOM(15)-550°C	15	1000	0.80	2.98
TiOM(15)-650°C	15	955	0.7	2.81
Si-MCM-41-550°C	∞	1001	0.9	2.97

Table 1
PHYSICOCHEMICAL CHARACTERISTICS OF THE TiOM(x)-y SAMPLES

Crystalline titania could be identified using FT-Raman Spectroscopy. The Raman spectra of TiOM(3)-550°C sample show broad bands at 638, 453, 399 and 283 superimposed on a broad signal of amorphous silica (fig. 2).

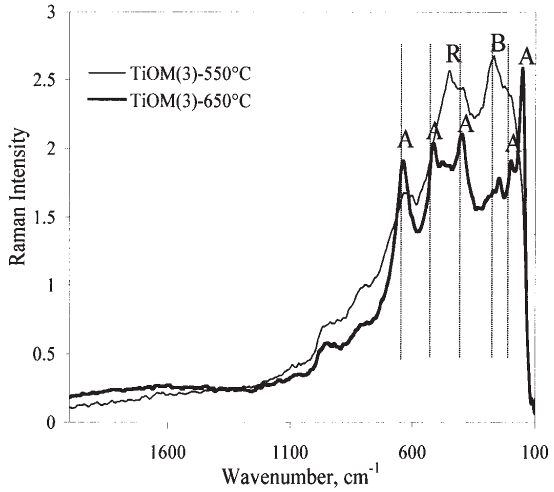

Fig. 2 Raman scattering result of TiOM (3) calcined at 550°C and 650°C

These bands could be attributed to anatase, rutile and brookite crystalline phases. Once that calcination temperature increases from 550°C to 650°C, the anatase peaks became more visible, indicating crystal growth. At the same time, some other anatase peaks develop which evidences the improvement of the crystalline anatase phase. Only weak contributions from crystalline titania can be observed (figure not shown) when a lower amount of Ti is present. Here, the high amount of silica will prevent fast crystalline growth of the titania phase.

For further evidence, UV-VIS diffuse reflectance spectra are recorded. As previously reported [12, 13], the absorption band at ~ 270 nm observed in TiOM(3)-550°C can be assigned to the presence of TiO_2 octahedral polymeric species. The existence of a weak absorption band at ~ 325 nm [14] corresponds to the crystalline anatase (fig. 3a).

This absorption band becomes more intense with increasing calcination temperature, due to an enhancement of the titania crystallization. This is in agreement with Raman measurements. At lower titania contents, only a very small absorption edge above 330nm can be observed (fig. 3b).

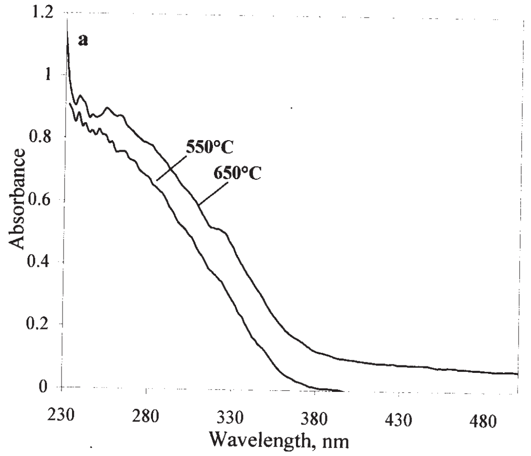

Fig. 3a UV-Vis Diffuse Reflectance Spectra of TiOM (3) calcined at 550°C and 650°C

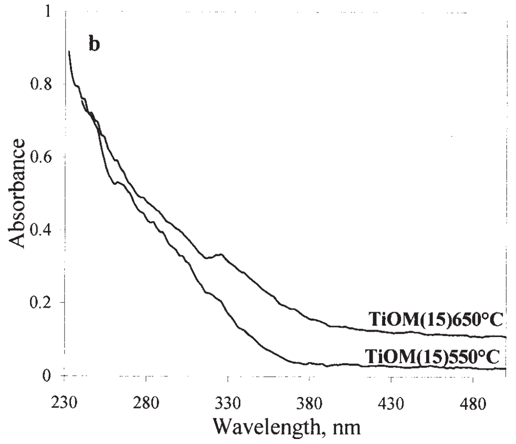

Fig. 3b UV-Vis Diffuse Reflectance Spectra of TiOM (15) calcined at 550°C and 650°C

Only at temperatures over 650°C, a clear appearance of an absorption edge over 330nm is observed for TiOM (15) indicating the formation of crystalline phases at these temperatures.

Conclusions

The thermal stability of TiO_2-MCM-41 materials was found to be dependent of the Si/Ti molar ratios used in the synthesis. The structural ordering of materials is more affected by the calcination temperatures (550°C and 650°C) when higher amounts of titania are used (TiOM(3)-y). The partial collapse of the structure upon heating (thermal stability) can be attributed to the uncontrolled growth of the crystalline titania phase (anatase). This was found to strongly depend on the titania content. A higher crystallinity of anatase phase could be observed in the samples calcined at 650°C.

Acknowledgements. This work is part of the NoE project "Inside Pores" and the GOA project funded by the Special Fund for Research of the University of Antwerp. V. Meynen acknowledges the FWO-Flanders (Fund for Scientific Research) for financial support.

References

1. MOREY, M.S., STUCKY, G.D., SCHWARZ, S., FRÖBA, M., J. Phys. Chem. B, **103**, 1999, p. 2037
2. DE WITTE, K., BUSUIOC, A.M., MEYNEN, V., MERTENS,M., BILBA, N., VAN TENDELOO,G., COOL, P., VANSANT, E.F., Micropor. Mesopor. Mater., **110**, 2008, p. 100
3. CHEN, Y., HUANG, Y., XIU, J., HAN, X., BAO,X., Appl. Catal. A: Gen. , **273,** 2004, p. 185
4. MESSINA, P.V:, SCHULZ, P.C., J. Colloid Interf. Sci. **299**, 2006, p. 305
5. HOSHIKAWA, T., IKEBE,T., YAMADA, M., KIKUCHI, R., EGUCHI,K., J. Photochem. Photobiol. A: Chem., **184**, 2006, p. 78
6. BOURLINOS, A.B., KARAKASSIDES, M.A.., PETRIDIS, D., J. Phys. Chem. B, **104**, 2000, p. 4375
7. HANU, A. M., LIU, S., MEYEN,V., COOL, P., POPOVICI, E., VANSANT,E.F., Micropor. Mesopor. Mat. , **95**, 2006, p. 31
8. DE WITTE, K., COOL,P., DE WITTE,I., RUYS,L., RAO, J., VAN, TENDELOO, G., VANSANT,E.F., J. Nanosci. Nanotechnol. , **7**, 2007, p. 2511
9. MEYNEN, V., SEGURA, Y., MERTENS, M., COOL,P., VANSANT, E.F., Micropor. Mesopor. Mat. , **85**, 2005, p. 119
10. CARP, O., HUISMAN,C.L., RELLER, A., Progr. Solid State Chem. , **32**, 2004, p. 33
11. MIHAI, G.D., MEYNEN, V., BEYERS, E., MERTENS,M., BILBA, N. COOL, P., VANSANT, E.F., J. Porous. Mater., In Press: DOI 10.1007/s 10934-007-9174-7
12. PETRINI, G., CESANA,A., DE ALBERTI, G., GENONI,F., LEOFANTI, G., PADOVAN, M., PAPARATTO, G., ROFFIA, P., Stud. Surf. Sci. Catal. , **68**, 1991, p. 761
13. PRASAD, M.R., MADHAVI, G., RAO, A.R., KULKARNI, S.J., RAGHAVAN, K.V., J. Porous Mater. , **13**, 2006, p. 81
14. LUAN, Z., KEVAN, L., J. Phys. Chem. B, **101**, 1997, p. 2020

Manuscript received: 10.06.2008