DALTON
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Mesoporous titania nanostructures thermally stabilized by doping with “sodium oxide”†

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Received 24th July 2001, Accepted 23rd August 2001
First published as an Advance Article on the web 6th September 2001

The thermal stabilization effect of doping “sodium oxide” on mesoporous titania nanostructures has been demonstrated.

Since Mobil researchers first demonstrated the synthesis of hexagonally packed mesoporous silicate and aluminosilicate materials (MCM-41) in 1992,[1] there have been many attempts to synthesize transition metal oxide analogues.[2–5] The mesoporous transition metal oxides are expected to have applications in a wide variety of catalytic processes. However, their applications are much more limited compared to MCM-41 due to low thermal stability. In 1995 Antonelli and Ying first reported the synthesis of a hexagonally packed mesoporous TiO_2 by a modified sol–gel method.[3] This material is only thermally stable to 350 °C and contains a significant amount of phosphorus. A phosphorus-free mesoporous titania prepared by a modified ligand-assisted templating method was recently reported by Antonelli.[3] This material has a high surface area of over 700 $m^2 g^{-1}$, however, the pore structure collapses above 300 °C. Some efforts have been made to enhance the thermal stability of mesoporous titania. Schüth and co-workers demonstrated that post-synthesis treatment with phosphoric acid could stabilize the mesoporous titanium oxo-phosphate framework to 550 °C.[2] Herein we report an example of phosphorus-free mesoporous titania whose thermal stability is dramatically enhanced by doping with “sodium oxide”.

Since previous research has demonstrated that high-quality mesoporous transition metal oxides can be obtained by a long chain amine ligand-assisted templating method due to the formation of a strong nitrogen–metal bond between the surfactant head group and metal centers,[3] a similar ligand-assisted templating route was adopted in this work. Although mixing titanium isopropoxide (17 g, 60 mmol) and 1-dodecylamine (11 g, 60 mmol) at room temperature did not result in a significant reaction, distilling off the generated isopropanol led to the formation of complex $Ti(O^iPr)_3[NH(CH_2)_{11}CH_3]$.‡ Hydrolysis of the complex in an isopropanol–water co-solvent, and subsequently aging at room temperature for 1 d and at 80 °C for 5 d gave the as-synthesized material. The surfactants were partially removed by treatment with phosphoric acid at pH = 0.5. The introduced phosphate group was removed by treatment with aqueous NaOH solution (10%) and exhaustively washing with water, in the mean time some surfactants were also removed, as confirmed by TGA and IR spectroscopy. As evidenced by elemental analysis, sodium was introduced into the material even after exhaustively washing with water. Calcination at 350 °C burnt off remaining surfactants completely, and a “sodium oxide” doped mesoporous titania was obtained. The Na content in the material can be tuned by controlling the pH of the water filtrate.§

A single reflection at low angle is observed in the XRD patterns of the “Na_2O” doped mesoporous titanias and the synthetic intermediates. This reflection can be indexed as (100) assuming a hexagonal unit cell. Although this phenomenon has been attributed to either disordered packing of individual tubes in mesostructures or very small crystallite size,[3] materials with only one distinct XRD reflection have also been found to contain a substantial MCM-41 structure.[2] The enhanced scattering intensity and sharpness of the (100) peak compared to the as-synthesized and phosphoric acid treated materials suggest that NaOH treatment tends to preserve the crystallinity of the material.[6] The much higher *d*-spacing (5.7 nm) of the “Na_2O” doped materials, compared to that of the as-synthesized material (d = 3.4 nm) and the phosphoric acid treated sample (d = 3.6 nm), is presumably due to a better condensation of the wall.

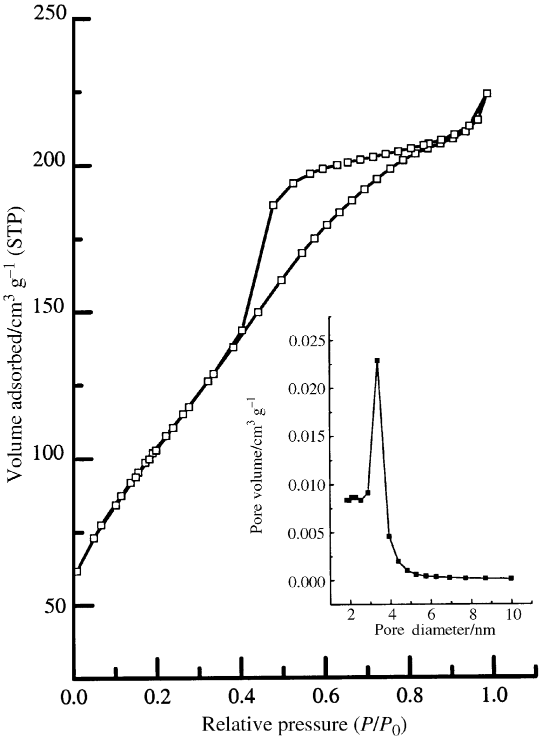

Fig. 1 Nitrogen adsorption–desorption isotherm and the pore size distribution (insert) of the calcined (350 °C) mesoporous titania doped with “Na_2O” (Na = 5.5 wt%).

Taking the “Na_2O” doped mesoporous titania containing 5.5 wt% of Na as an example, the N_2 adsorption–desorption isotherm is shown in Fig. 1, which can be classified as type IV. This type of hysteresis loop is in principal due to cylindrical pores open at both ends. The sharp decline in the desorption curve indicates the mesoporosity of the material. The BET surface area is *ca.* 390 $m^2 g^{-1}$. The pore size distribution is narrow and the average pore diameter, determined from the BJH desorption branch, is 3.0 nm.

The “Na_2O” doped mesoporous titania has a distinct advantage over the pure mesoporous titania¶ in terms of thermal

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† Electronic supplementary information (ESI) available: complete synthetic details; powder X-ray diffraction patterns and DSC curves for mesoporous titanias. See http://www.rsc.org/suppdata/dt/b1/b106649h/

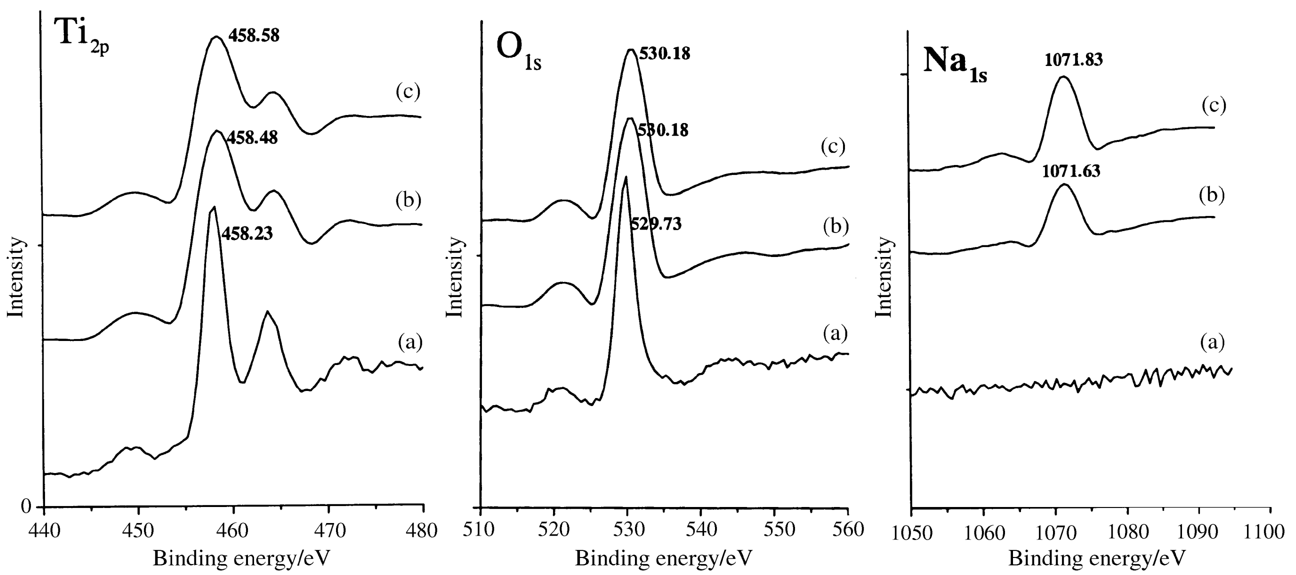

Fig. 2 Ti_{2p}, O_{1s} and Na_{1s} XPS spectra of the pure mesoporous titania (a) and "Na_2O" doped mesoporous titania containing 4.8 wt% (b) and 8.7 wt% (c) of Na.

stability. Additionally, the thermal stability increases with increasing sodium content. An exothermic peak at 490 °C in the DSC of the pure mesoporous titania originates from the structure collapsing, which has been confirmed by N_2 adsorption and XRD. The corresponding structural collapse exothermic peaks of "Na_2O" doped mesoporous titanias appear at higher temperatures, being 530 °C for 4.9 wt%, 550 °C for 5.5 wt% and 575 °C for 7.1 wt% of Na. We assume that sodium titanate formed on the surface of the mesoporous structure contributes to the enhanced thermal stability. This is based on the observation of the characteristic XRD reflections of a sodium titanate $Na_2Ti_6O_{13}$ ($2\theta = 11.84, 24.50, 48.46°$).[7] Fig. 2 compares the Ti_{2p}, O_{1s} and Na_{1s} XPS spectra between the "Na_2O" doped mesoporous titanias and the pure mesoporous titania. The bonding energies for Ti $2p_{3/2}$ (458.23 eV) of pure mesoporous titania are lower than the reference value (458.70 eV) for titania (anatase). The fact that the binding energies of Ti_{2p} and O_{1s} in the "Na_2O" doped samples shift to higher energies compared to that in the pure mesoporous titania, together with the Na_{1s} value of the "Na_2O" doped samples, provide further evidence for the existence of sodium titanate on the surface of titanium oxide.[8]

In summary, we have demonstrated a convenient method to effectively enhance the thermal stability of mesoporous titania by doping with "sodium oxide". The high thermal stability is certainly one of the most important features with respect to possible catalytic applications.

Acknowledgements

We thank Mr Barth and his staff for their excellent analytical service. We also thank the Bayerische Forschungstiftung (FORKAT) and the Fonds der Chemischen Industrie for their financial support.

Notes and references

‡ Calc. for $C_{21}H_{47}NO_3Ti$ (408.9): C, 61.60; H, 11.57; N, 3.42; Ti, 11.69. Found: C, 61.59; H, 12.29; N, 3.10; Ti, 10.27%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, 3H); 0.98 (s, 1H); 1.22 (t, 37H); 1.39 (m, 2H); 2.63 (t, 2H); 4.45 (m, 3H).

§ Elemental analysis data for: pure mesoporous titania (a): C, 0.27; H, 0.86; N, 0.05; Na, 4.9; P, 0.06; Ti, 47.0%. "Na_2O" doped mesoporous titania containing 4.8 wt% Na (b): C, 0.24; H, 0.23; N, 0.06; Na, 5.52; P, 0.08; Ti, 52.24% and 8.7 wt% Na (c): C, 0.43; H, 0.73; N, 0.00; Na, 7.1; P, 0.02; Ti, 48.8%.

¶ See Q. Li, Ph.D. thesis, Technische Universität München, Germany, 2001. Found: C, 0.15; H, 0.66; Cl < 0.1; N, 0.00; Na, 0.1; P, 0.02; Ti, 51.42%. The XRD shows a single reflection centered at $d = 5.7$ nm. The BET surface area is 461 $m^2 g^{-1}$, the pore volume is 0.459 $cm^3 g^{-1}$ and the pore diameter is 3.45 nm, obtained from the BJH desorption branch.

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