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Novel non-hydrolytic synthesis of a V_2O_5–TiO_2 xerogel for the selective catalytic reduction of NO_x by ammonia†

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A vanadia–titania mesoporous xerogel (10.5 wt% V_2O_5) was prepared from chloride precursors using a one-step non-hydrolytic sol–gel route and subsequent drying at ambient pressure; after calcination at 773 K for 5 h no crystalline V_2O_5 was detected and the resulting mixed oxide exhibited remarkable activity in the selective reduction of NO with NH_3.

Vanadia-based catalysts are known for their high efficiency in the selective catalytic reduction (SCR) of NO by NH_3 which is a widely used process for de-NO_x-ing waste gases from stationary sources (eqn. (1)).

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad (1)$$

The best support is TiO_2-anatase, which ensures high activity and resistance against poisoning by SO_2. As a consequence, the preparation of V_2O_5–TiO_2 catalysts has been intensively studied during the last two decades.[1] Elaborated procedures have been used to increase the activity of vanadia–titania catalysts, such as multiple grafting, sol–gel synthesis using chemically modified precursors and 2-step procedures to improve the dispersion of vanadia species, or supercritical drying to increase the specific surface area of the catalyst.[2,3]

The non-hydrolytic sol–gel process[4] offers a simple and efficient way to prepare mixed oxides.[5] This process is based on the condensation between chloride and alkoxide groups at moderate temperature (around 100 °C). The alkoxide groups can also be formed *in situ*, for instance by reaction of chlorides with an organic ether, thus avoiding the use of expensive alkoxide precursors.

In this work we present the first non-hydrolytic sol–gel synthesis of a vanadia–titania xerogel (atomic ratio Ti/V $\approx$ 10), hereafter named 10 Ti/V and its performance in the SCR of NO by NH_3. The overall synthesis process can be represented by eqn. (2).

$$VOCl_3 + 10TiCl_4 + 21.5{}^iPr_2O = (V_2O_5)_{0.5}(TiO_2)_{10} + 43{}^iPrCl \qquad (2)$$

The preparation was carried out under argon in oven-dried glassware. First, 0.310 g (1.77 mmol) of $VOCl_3$ (Aldrich, 99%) was introduced by syringe in a glass tube; after addition of 3.233 g (17.0 mmol) of $TiCl_4$ (Acros Organics, 99.9%) and 3.926 g (38.04 mmol) of ${}^iPr_2O$ (Acros Organics, 99%), the tube was frozen in liquid nitrogen, sealed under vacuum and heated under autogeneous pressure at 383 K for 3 days. The tube was opened under argon and the dark-brown gel was first dried under vacuum at room temperature and then at 393 K for 12 h. Finally, the sample was calcined at 773 K (heating rate 10 K min^{-1}, air flow 50 cm^3 min^{-1}) for 5 h, turning into a beige powder.

The texture of the calcined mixed oxide was analysed by nitrogen physisorption at 77 K on a Micromeritics ASAP 2000 instrument; before measurement, the sample was degassed at 573 K to about 2 Pa. The pore size distribution was calculated from the desorption branch of the isotherm, using the BJH method. The type IV isotherm (Fig. 1) indicated that the material was mesoporous, with a total pore volume of 0.24 cm^3 g^{-1} and a BET surface area of 78 m^2 g^{-1}; the average pore diameter (4 V/S_{BET}) was 12 nm. According to *t*-plot analysis, microporosity was negligible. This texture is attractive compared to that of conventional xerogel samples of similar composition, which exhibited either much lower surface areas[6] or significant microporosity.[7] Catalysts derived from two-step aerogels calcined at 573 K showed higher surface areas (*ca.* 180 m^2 g^{-1}) but they still contained a considerable amount of organic species;[3] furthermore, these solids appeared less thermally stable than mesoporous titania or vanadia–titania prepared by other methods:[8] upon calcination at 723 K their surface area dropped to *ca.* 42 m^2 g^{-1} and crystallisation of rutile and V_2O_5 was observed.[3]

The X-ray diffraction pattern (performed on a Seifert θ–θ powder diffractometer, 2θ range 19–90°, using Cu K_α radiation) of our sample revealed the presence of TiO_2-anatase only. Despite the high calcination temperature neither TiO_2-rutile nor crystalline V_2O_5 could be detected, thus indicating a high thermal stability of the anatase phase and a good dispersion of vanadia species.

The static solid state ${}^{51}V$ NMR spectrum of our vanadia–titania sample (acquired on a Bruker AM400 spectrometer) displayed two broad resonances centred at −225 ppm and −570 ppm, indicating the presence of octahedral and tetrahedral vanadium species.[9] More precise information on the nature of vanadium species was obtained by micro FT-Raman spectroscopy (Labram 1B Confocal Jobin-Yvon instrument, excitation by He–Ne laser at 632.8 nm) (Fig. 2).

Beside the peaks at 202, 390, 506, and 628 cm^{-1} assigned to anatase, three peaks were detected: two broad ones centred at about 810 and 935 cm^{-1} and a narrower, stronger one at 1028 cm^{-1}. The peak at 1028 cm^{-1} is attributed to VO stretching in monomeric vanadyl species directly bound to the surface by three V–O–Ti

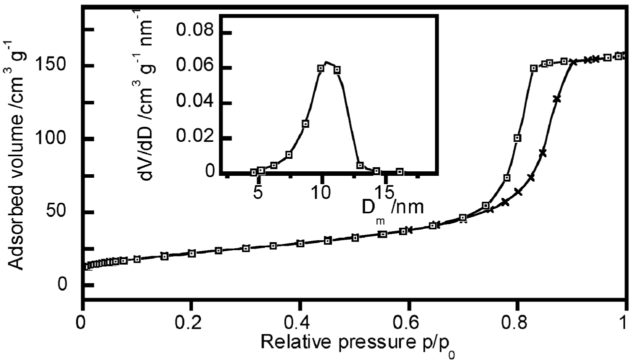

Fig. 1 Nitrogen isotherm (×-adsorption, ⊡-desorption) and pore size distribution (insert) for 10 Ti/V, after 5 h calcination at 773 K.

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† Electronic supplementary information (ESI) available: Temperature Programmed Desorption of NH_3 and isothermal catalytic tests. See http://www.rsc.org/suppdata/cc/b4/b408073d/

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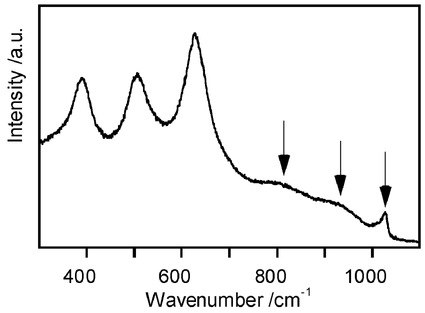

Fig. 2 RAMAN spectrum of calcined 10 Ti/V.

bonds; the broad peaks at 935 and 810 cm^{-1} are ascribed to VO stretching and V–O–V stretching in polymeric metavanadates, respectively.[10] The absence of a sharp and strong line at about 995 cm^{-1} proved once more that the presence of crystalline vanadia can be ruled out.

Accordingly, the tetrahedral species detected by NMR are most likely monomeric vanadyls while the octahedral species would correspond to vanadium atoms either in polymeric metavanadate species or to vanadium atoms participating in the mixed oxide network.

Temperature programmed desorption (TPD) of NH_3 (Micromeritics AutoChem 2910) showed that the maximum amount of adsorbed NH_3† was about 1.3 mmol g^{-1} of catalyst.

The SCR catalytic activity was evaluated in a continuous flow quartz glass reactor; an aliquot of 20 mg (about 0.04 cm^3) of catalyst was used. The feed mixture consisted of 0.2% NO, 0.2% NH_3 and 3% O_2 (in volume), with He as balance gas; the total gas flow was 138 cm^3 min^{-1}, thus resulting in a very high gas hourly space velocity (GHSV) of 207 000 h^{-1}. The temperature was raised up to *ca.* 650 K at a constant rate of 6 K min^{-1}; the effluent concentration in NO, NH_3, O_2, N_2, H_2O and N_2O was continuously monitored by on-line sampling to a quadrupole mass spectrometer (Balzers QMS 421) equipped with Faraday and channeltron detectors. Prior to the tests, *in situ* activation was done by heating the aliquot up to 770 K for 30 min under O_2–He flow.

The catalytic data indicated that our V_2O_5–TiO_2 catalyst (Fig. 3) was highly active: NO conversion reached 50% at 500 K, with negligible N_2O formation (about 8 ppm). At 423 K (7% NO conversion) the turnover frequency (TOF), expressed as mol NO converted per mol V per hour was 2.2 (on the basis of the nominal vanadium content). This value is about 8 times higher than the TOF values reported by Schneider *et al.*[3] for a sample with a similar vanadium content prepared from a 2-step aerogel or by Pearson *et al.*[6] for mixed sol–gel samples. It is even higher than the TOF values reported for a catalyst prepared by multiple grafting of vanadyl trichloride on titania aerogel[2] or for a 2-step aerogel with 30 wt% V_2O_5.[3]

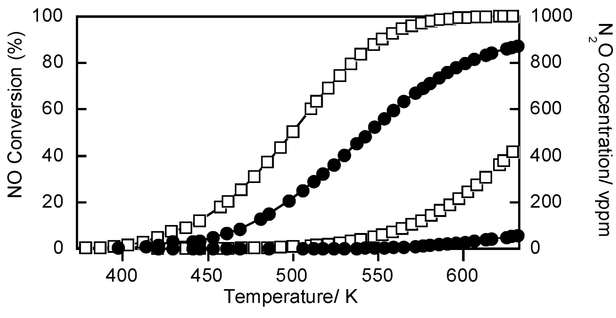

Fig. 3 NO conversion and N_2O production for: calcined 10 Ti/V (□) and the EUROCAT catalyst (●).

However, at higher temperature, significant formation of N_2O occured. This lack of selectivity, and at the same time the high activity, could be explained by a high amount of surface polyvanadate species which are believed to be up to 10 times more active than monovanadyl species but at the same time less selective.[11]

Constant temperature catalytic tests were performed at 573 ± 2 K. Under steady state conditions, the conversion was only marginally lower (93 ± 1%) than under dynamic conditions. No deactivation was observed during 100 h,† indicating promising stability of our catalyst. In addition, the effect of SO_2 and water on the activity of our catalyst was investigated. Despite the high vanadia content of the catalyst, these tests† indicated no influence of SO_2 (25 vppm for 3.5 h) and only a small (*ca.* 4%) and reversible decrease of the activity in the presence of water (1.1 vol% for 3.5 h).

Finally, in order to facilitate comparison, we have performed a test under the same experimental conditions on the V_2O_5–WO_3/TiO_2 EUROCAT catalyst, which was chosen as a reference catalyst in a joint European project on de-NO_x.[12] EUROCAT is a more complex system than 10 Ti/V, containing about 3 wt% V_2O_5, 9 wt% WO_3, 6.5 wt% SiO_2 and 78 wt% TiO_2.[13]

The EUROCAT catalyst, which contains 3.5 times less vanadia, appeared significantly less active but more selective than 10 Ti/V (Fig. 3). However, at equal conversion, selectivity of EUROCAT was only marginally better; for instance, at 75% conversion we found 20 ppm N_2O for EUROCAT and 25 ppm for our 10 Ti/V catalyst.

The non-hydrolytic sol–gel method presented here is a simple and attractive method to prepare vanadia–titania catalyst starting from low-cost (albeit moisture sensitive) chloride precursors and using ambient pressure drying. After calcination at 773 K, the catalyst presented excellent textural properties as well as high dispersion of the active vanadia phase. As a consequence, this material was very efficient in the SCR of NO by ammonia at moderate temperature.

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