Ultra stable ordered mesoporous phenol/formaldehyde polymers as a heterogeneous support for vanadium oxide†

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Ordered mesoporous phenol/formaldehyde polymers are presented as an ultra stable heterogeneous support for vanadium oxide.

In modern heterogeneous catalysis, supported vanadium catalysts are widely used in the manufacture of important chemicals and in the reduction of environmental pollution such as toxic NO_x.[1] In recent years, ordered mesoporous materials as a support for vanadium oxides have attracted extensive research, due to their unique properties such as high specific surface areas and large pore volumes. However, the common mesoporous silica materials (MCM-48, SBA-15,...) exhibit low mechanical and hydrothermal stability attributed to hydrolysis of the siloxane bridges.[2] Furthermore, the active catalytic sites grafted on the surface are the subject of leaching phenomena due to the well-known weak silica–vanadium interaction.[3] The question about the true nature of the catalytic reaction—heterogeneous or homogeneous—is therefore a relevant one. In recent years, many studies have already been inspired by the improvement of the catalytic stability,[4] strongly driven by increasing environmental concerns and economic perspectives.

In this study, ordered mesoporous *FDU*-type phenol/formaldehyde polymers are presented as a novel support for vanadium oxides with straightforward prospects in heterogeneous catalysis. The high stability of these materials, mechanical, thermal and hydrothermal, is proven. Furthermore, a controlled deposition of tetrahedral vanadium species on the surface is reported and a strong interaction between the support and the inorganic catalyst is established by leaching experiments.

Ordered mesoporous phenol/formaldehyde resins (P/F) are synthesized in basic media according to a modified procedure previously described by Zhao *et al.*[5,6] Hereby, the organic–organic self-assembly of the triblock copolymer F127 and the low-molecular weight P/F resin, namely resol, is induced by evaporation of the ethanol solvent. The final reactant molar composition was phenol : formaldehyde : NaOH : F127 : EtOH = 1 : 2.2 : 0.09 : 0.0135 : 64.5. After thermopolymerization of the phenolic precursor, surfactant removal is carried out by calcination in a tubular furnace at 350 °C under nitrogen atmosphere. Subsequently, the vanadium precursor was grafted on the surface by two methods. First, in the gas phase modification by a chemical vapour deposition with $VOCl_3$ as a vanadium source at 350 °C under dynamic vacuum conditions. The samples are degassed for 2 additional hours to ensure the removal of all physically adsorbed vanadium excess. Additionally, a liquid phase deposition is also applied by a single impregnation step, stirring the support in a 10% $VOCl_3$ solution in dried toluene at 80 °C for 2 h. Afterwards the samples were washed with fresh toluene. Finally, all the samples are exposed to air to induce hydrolysis of the unreacted V–Cl groups of the vanadium precursor.

Fig. 1 shows the nitrogen adsorption/desorption isotherms and the pore size distributions of the mesoporous P/F resin before and after vanadium deposition. Notably, the desorption branches of these isotherms are not closed at the low relative pressures, which is typical for polymers.[7] According to the IUPAC classification, the isotherms have both a type IV curve and a relative steep capillary condensation step—suggesting uniform mesopores—is observed before and after vanadium deposition. The BET-surface area and pore volume decrease from 536 to 334 $m^2\ g^{-1}$ and from 0.54 to 0.35 $cm^3\ g^{-1}$ after vanadium deposition.

Diffuse reflection infrared spectra of the initial support and of the support after liquid phase deposition with $VOCl_3$ are presented in Fig. 2. The characteristic absorption bands for phenol/formaldehyde polymers are marked in both spectra. In comparison with the original sample, a new absorption peak appears at 1010 cm^{-1} after vanadium deposition. This band

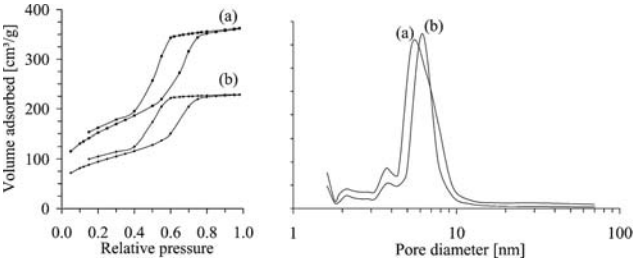

Fig. 1 Nitrogen adsorption/desorption isotherms and pore size distributions (a) before and (b) after vanadium deposition in the gas phase. The pore size distribution is obtained using the BJH model for the adsorption branch isotherm.

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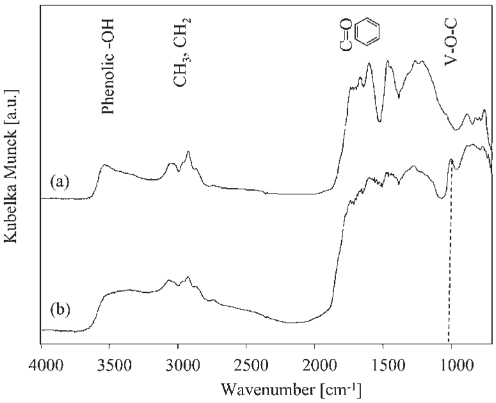

Fig. 2 DRIFT-spectra of phenol/formaldehyde resin (a) before and (b) after liquid phase deposition of $VOCl_3$.

can be assigned to a V–O–C bond vibration,[8] which signifies the vanadium species are covalently bonded on the organic support.

To verify the oxidation state and the geometric structure of the vanadium species grafted on the surface, XPS measurements were recorded on a X-ray photoelectron spectroscopy spectrometer with monochromated Al (1486 eV) exciting radiation. Fig. 3 shows the $V2p_{3/2}$ region in the XPS spectra of the phenol/formaldehyde resin after $VOCl_3$ deposition and of the reference samples V_2O_5, NH_4VO_3 and $VO(acac)_2$. At least two different $V2p_{3/2}$ peaks at 514.1 and 511.8 eV can be distinguished for the P/F resin after $VOCl_3$ treatment. Comparison of the binding energies of the V2p core levels for the P/F supported sample to those for bulk polymeric V_2O_5 suggests the absence of crystalline clusters on the surface. The absence of crystalline V_2O_5 was also confirmed by means of wide-angle powder X-ray diffraction measurements (see ESI†). The $V2p_{3/2}$ peak at 514.1 eV of the P/F resin accords with the $V2p_{3/2}$ peak of the reference sample NH_4VO_3 (513.9 eV), which indicates a tetrahedral geometry of the species with the vanadium center in the 5+ oxidation state. Surprisingly, a second peak at the lower binding energy of 511.8 eV is observed. This peak position corresponds with binding energy of the reference sample $VO(acac)_2$ and can be attributed to a lower 4+ oxidation state, although the vanadium center in the initial vanadium precursor $VOCl_3$ exhibits the 5+ oxidation state. Vanadium species are, however, very sensitive for reduction and the reduction of vanadium during XPS measurement under hard vacuum conditions is reported in the literature.[1] Indeed, the ratio of the 4+ : 5+ increased from 1 : 2 to 1 : 1 after sputtering the samples with argon bombardment under ultra-high vacuum conditions (see ESI†).

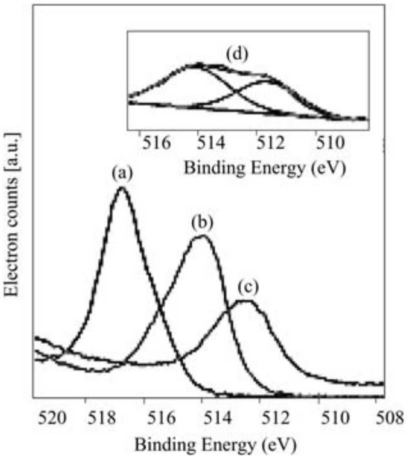

Fig. 3 $V2p_{3/2}$ region in the XPS spectra of (a) V_2O_5, (b) NH_4VO_3, (c) $VO(acac)_2$ and (d) phenol/formaldehyde resin after gas phase deposition of $VOCl_3$.

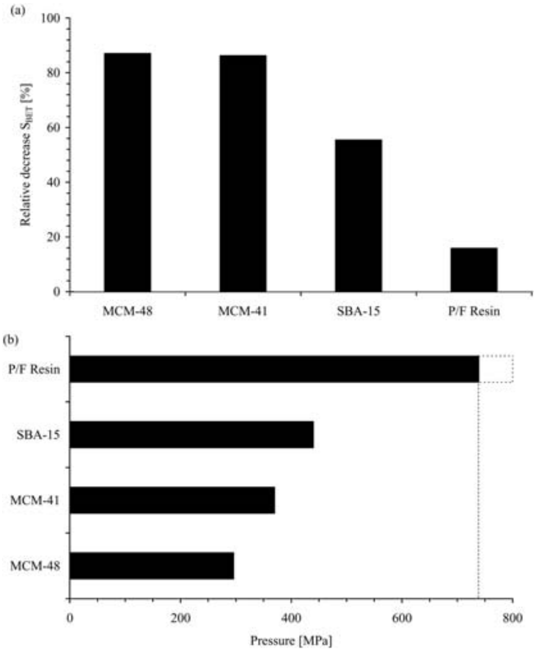

Fig. 4 (a) Relative decrease of specific surface area of the mesoporous material after hydrothermal treatment with steam at 100 °C for 24 h at autogeneous pressure with a relative humidity of 100% and (b) maximal lateral pressure at which the porous structure collapses. The dotted line indicates the maximal obtainable pressure in the lab.

Hydrothermal stability tests of the mesoporous P/F support were performed by exposing the sample to steam at 100 °C for 24 h with a relative humidity of 100% at autogeneous pressure. Fig. 4(a) presents the relative decrease in specific surface area of the P/F resin after hydrothermal treatment compared to different silica samples (MCM-41, MCM-48 and SBA-15). As can be seen from Fig. 4, the specific surface area of the silica materials decreases by more than 50 and 80% for the SBA and the MCM materials, respectively. In contrast, only a relatively small decrease of 15% was observed in case of the P/F resin after hydrothermal treatment. Furthermore, a comparative mechanical stability study between the P/F resin and the different silica materials was conducted by keeping the pelletized samples under constant lateral pressure for 2 min. Fig. 4(b) shows the minimal pressure at which the structure loses its porosity. All the silica samples collapse at a pressure of 444 MPa or lower. In contrast, no collapse and even no decrease in surface area or pore volume was observed in case of the P/F resin at 739 MPa, the highest pressure experimentally obtainable in our lab. The high stability of these mesoporous organic membranes, both mechanical and hydrothermal, can be explained by the three-dimensional

Table 1 Comparative leaching study results (V nm^{-2}) between P/F resin and Kieselgel 60

	Washing	Water treatment 1[a]	Water treatment 2[a]	Water treatment 3[a]	H_2SO_4 destruction[b]	Residual	Total V-loading
Kieselgel 60 (G)	1.01	0.15	0.05	0.04	0.00	—	1.25
P/F Resin (G)	0.10	0.07	0.06	0.02	0.02	0.16	0.43
Kieselgel 60 (L)	0.64	0.15	0.12	0.06	0.11	—	1.08
P/F Resin (L)	0.34	0.16	0.03	0.03	0.08	0.41	1.05

[a] Catalyst was stirred at 80 °C for 30 min in water, [b] Catalyst was stirred at 80 °C for 30 min in 2.5 M sulfuric acid solution.

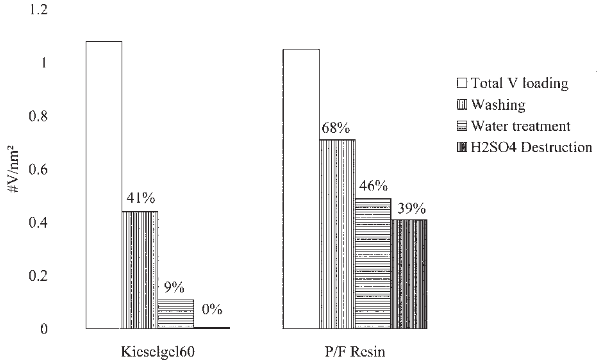

Fig. 5 Comparative leaching study between Kieselgel60 and P/F resin after vanadium deposition in the liquid phase—Absolute number of vanadium species found on the surface after different treatments.

connected covalently C–C bonded framework and its resistance towards hydrolysis. Further, TGA measurements show the materials are stable up to 350 °C under air (see ESI†).

In order to evaluate the degree of the leaching resistance of the new catalyst, a comparative study between the P/F resin and a commercial mesoporous silica (Kieselgel 60) is made. Additionally, a comparison was made between deposition in the gas (G) and in the liquid (L) phase. The vanadium loading is determined colorimetrically by means of UV/Vis spectroscopy.[9] The washing procedure and the consecutive leaching experiments are performed by stirring the catalyst for a period of 30 min in ice-cold water and in water at 80 °C, respectively. Subsequently, the catalyst is stirred in a hot sulfuric acid solution for an additional 30 min and in case of the P/F resin the residual organic support was combusted. An overview of the results are given in Fig. 5 and Table 1. From these data, a strongly reduced leaching behaviour for the P/F resin can be established compared to the silica support. For the silica support, the amount of vanadium that leached out during the washing procedure amounted to 60–80% and after three consecutive leaching experiments more than 90% was leached out. In contrast, in the case of P/F resins only 20–30% of the vanadium could be found in the washing solution. Moreover, a decreasing leaching trend line after three leaching experiments is observed and even stirring the catalyst in a hot 2.5 M sulfuric acid solution led to a leaching of only 4–7%. After combustion of the organic support, a high residual amount of 0.41 V nm^{-2} is found in case of the liquid phase deposition. These observations of strongly reduced leaching behaviour can be explained by the highly hydrophobic nature of the polymer surface which prevents attack of water molecules to the active sites and the more basic character of the phenol group (phenol $pK_a = 10$ *vs.* silanol $pK_a = 2.2$) which shows stronger affinity to the acidic $VOCl_3$.

In conclusion, mesoporous phenol/formaldehyde resins with high specific surface areas and large pore volumes are presented as a new ultra stable support material for heterogeneous inorganic catalysts. In particular, vanadium oxide species are grafted by a controlled deposition method on the surface and a high vanadium content of 1.05 V nm^{-2} is achieved. Evidence for a covalent support–vanadium bonding is presented by means of DRIFT-spectroscopy and the tetrahedral structure of the VO_x species is established by XPS. Moreover, a strongly reduced leaching behaviour is reported and the high mechanical, thermal and hydrothermal stability of these materials is shown. We believe that these interesting results open up new and straightforward opportunities for versatile heterogeneous liquid phase catalysis.

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