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MIL-100(V) – A mesoporous vanadium metal organic framework with accessible metal sites

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ABSTRACT

The large pore vanadium(III) trimesate MIL-100(V), i.e. $V_3O(H_2O)_2X[C_9H_3O_6]_2 \cdot yH_2O$ with $X = (Cl^-)_{1-z}(C_9H_5O_6)_z^-$, $y \approx 3$ and $z \approx 0.3$, has been synthesized under hydrothermal conditions (MIL stands for Materials from Institute Lavoisier). Its structure, which crystallizes in the space group *Fd*-3*m* (No. 227) with $a = 73.0286(2)$ Å, $V = 389474.4(2)$ Å^3, exhibits a zeotype architecture with mesoporous cages of approx. 25 and 29 Å diameter, accessible through microporous windows of 5.5 and 8.9 Å diameter. Synchrotron X-ray powder diffraction analysis confirms its isostructural character with previously reported MIL-100(Cr, Fe, Al) solids. Its thermal stability under O_2 and N_2, up to 523 K (250 °C), is comparable to that of MIL-100(Fe). Preliminary gas adsorption experiments and *in situ* IR-spectroscopy after NO exposure reveal that MIL-100(V) combines high sorption capacities and co-ordinatively unsaturated vanadium sites in different oxidation states (+III and +IV). With these properties this material could be a promising candidate for specific sorption or redox catalytic applications.

1. Introduction

The recent interest in the synthesis of crystalline porous hybrid inorganic–organic materials gives a new dimension to the domain of porous solids [1–6]. These compounds are typically built up from polytopic organic linkers bearing phosphonate, carboxylate, imidazolate or sulfonate groups, associated with metallic cations from almost all elements of the periodic table. Like that a wide range of three-dimensional frameworks with various pore sizes, morphologies and compositions is produced. The unique combination of both inorganic and organic moieties generates significant new scientific and technological opportunities [7,8], leading to many potential applications in gas storage and separation [9–11], catalysis [12–14], or controlled drug release [15]. Interestingly, the introduction of 3d transition metals within the skeleton provides new electronic properties and therein vanadium was assumed to be a prominent candidate for catalytic applications [16,17]. So far, vanadium has already been successfully used to built up porous hybrid compounds [18,19] such as the vanadium terephthalate denoted by MIL-47, which holds a permanent porosity [20] resulting in a BET surface area over 1400 m^2 g^{-1}. The role of the V^{III}/V^{IV} oxidation upon thermal activation (in air) in this solid was also highlighted [21]. Up to now, several examples with MIL-100 structure, mesoporous MOFs built up from oxocentered trimers of $M^{III}O_6$ octahedra (M=Cr, Fe, Al) and trimesate moieties, have been reported. These solids exhibit very large pores, high surface areas around 2000 m^2 g^{-1} [22] and a significant number of accessible Lewis metal sites [23,24]. Therefore, the present study focused on the synthesis and characterization of the vanadium analog MIL-100(V).

2. Experimental

2.1. Syntheses

The vanadium trimesate $V_3O(H_2O)_2X[C_9H_3O_6]_2 \cdot yH_2O$ with $X = (Cl^-)_{1-z}(C_9H_5O_6)_z^-$, $y \approx 3$ and $z \approx 0.3$ named MIL-100(V) was hydrothermally synthesized under autogenous pressure from a mixture of VCl_3 (4 mmol, 628 mg) and triethyl-1,3,5-benzenetricarboxylate (2 mmol, 588 mg) in 5 ml of H_2O (molar ratio 2:1:140). The synthesis was carried out in a *Parr* autoclave (23 ml volume) at 493 K (220 °C) for 72 h. The product was

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retained by filtration as a greenish powder and washed with hot ethanol in order to remove the unreacted ligand (either in its esterified or hydrolyzed form). Finally it was washed with deionizer water and dried at 373 K (100 °C) under air.

The triethyl ester has been synthesized from the trimesic acid (5 g) via acid catalyzed reaction (2 ml of concentrated H_2SO_4) in pure ethanol (100 ml, reflux for approximately 24 h). While cooling down the solution after the reaction the product precipitated and was then filtered off. It was washed with cold deionized water and dried overnight at ambient conditions.

2.2. Characterization

2.2.1. Synchrotron powder diffraction

Diffraction data of MIL-100(V) has been collected at 80 K (−193 °C) at the beamline ID31, ESRF, Grenoble, France, using a wavelength of λ = 1.29175(2) Å (data range 1.5–40° 2Θ, step size 0.004°). The pattern was fully indexed and a *LeBail* profile fit was performed using the FULLPROF suite software [25] in order to determine accurate unit cell parameters.

2.2.2. Permanent porosity and gas adsorption properties

The BET surface area measurements were performed with N_2 adsorption–desorption isotherms at liquid nitrogen temperature 77 K (−196 °C) after dehydration under vacuum at 423 K (150 °C) for 12 h using a Micromeritics Tristar 3000 instrument. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the P/P_0 range 0.05–0.2.

The volumetric high pressure experiments using CO_2 and CH_4 gas at 303 K (30 °C) were conducted using a volumetric sorption analyzer HPVA-100 (VTI Corporation, USA) equipped with a rotary vane pump and a turbomolecular drag pump. The sample holder consists of a sample cell and tube equipped with a diaphragm valve. The two assemblies are connected via a filter gasket. The complete sample environment is manufactured from 316 stainless steel. The used volumetric technique implies the dosing of a known amount of gas (adsorbate) into the sample cell, and the recording of the initial and final equilibrium pressures. This data is then used to calculate the volume of gas adsorbed by the sample. This process is repeated at given pressure intervals until the maximum pre-selected pressure is reached. Each of the resulting equilibrium points (volume adsorbed and equilibrium pressure) is then plotted to provide an isotherm. In a typical experiment, around 1 g of sample was transferred into the sample cell and outgassing was performed overnight at 423 K (150 °C) under high vacuum (approximately 10^{-5} Torr). After the outgassing, the sample cell was refilled with He (99.999%) to measure the loading amount of the dehydrated sample, which is calculated from the weight difference between the empty and the loaded sample cell. The above described activation procedure was then repeated, and the sorption measurement of the respective adsorbate was performed. High purity CH_4 (99.999%) and CO_2 (99.999%) were obtained from Korea Gas Co. The sample cell was immersed in a thermostatic circulating bath at 303 K (30 °C).

2.2.3. IR-spectroscopy

The sample was pressed (10^9 Pa) into self-supported disks (2 cm^2 area, 7-10 mg cm^{-2}). These were placed in a quartz cell equipped with CaF_2 windows. A moveable quartz sample holder allowed the adjustment of the pellet in the infrared beam for spectra acquisition and also the displacement of the sample in a furnace located at the top of the cell. With that furnace heat treatments of the sample could be performed. Additionally, the cell was connected to a vacuum line for evacuation and calcination ($P_{\text{residual}} = 10^{-3}$–$10^{-4}$ Pa) and the introduction of NO gas. Transmission IR spectra were recorded in the 500–5600 cm^{-1} range, at 4 cm^{-1} resolution, on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitter and a mercury cadmium telluride (MCT) cryodetector.

2.2.4. Thermal analysis

The thermal analyses were performed with a TGA2050 TA apparatus using either a pure O_2 flow or a pure N_2 flow and a heating rate of 3 K min^{-1} in both cases.

2.2.5. Chemical analysis

The chemical analyses were performed at the analysis center of the LMU Munich, Germany. As the amount of water in the compound is very sensitive to the temperature and humidity of the lab atmosphere and the amount of trimesic acid in the pores can vary depending on slight changes in synthesis conditions, the deduction of the formula sum resulted in a carefully balanced compromise between the chemical analysis, IR and thermal analysis data. It was also taken into account that classical combustion analysis of compounds containing vanadium and chloride at the same time may give decreased values of chlorine content due to the formation of vanadium oxide chloride species. The presence of chlorine was furthermore confirmed by qualitative EDX analysis using a FEI XL30 FEG ESEM electron microscope at the OvGU Magdeburg.

3. Results and discussion

3.1. Crystal structure, chemical analysis and thermal stability

MIL-100(V) crystallizes in the cubic space group *Fd*-3*m* (No. 227) and shows a zeotype architecture. The synchrotron powder pattern was fully indexed and a *LeBail* profile fit was performed using the FULLPROF suite software (R_p = 3.0%, wR_p = 3.8%, χ^2 = 1.75, GoF = 1.3) resulting in a = 73.0286(2) Å, V = 389474.4(2) Å^3 (Fig. 1). The pattern matches very well with the diffraction pattern of MIL-100(Cr [26], Fe [27], Al [28]), confirming that the three compounds are isotypic. MIL-100(V) is a vanadium(III) tricarboxylate built up from oxocentered trimers of VO_6 octahedra sharing a common vertex μ_3-O. These trimers are linked by the benzene-1,3,5-tricarboxylate moieties forming so-called supertetrahedra, representing hybrid assemblies of four trimers and four organic ligands. Further connection of such supertetrahedra with each other leads to a MTN type zeolite like architecture (Fig. 2). This delimits two types of mesoporous cages with free apertures of approx. 25 and 29 Å, accessible through microporous windows of approx. 5.5 and 8.6 Å.

Chemical analyses have been performed on a sample of MIL-100(V), which was used as synthesized. The analyses resulted in the following wt.% values: 20.27% V, 30.17% C, 2.41% H and 2.30% Cl. From these values the formula sum $V_3O(H_2O)_2X[C_9H_3O_6]_2{\cdot}yH_2O$ with $X = (Cl^-)_{1-z}(C_9H_5O_6)_z^-$, $y \approx 3$ and $z \approx 0.3$ was deduced (calculated values: 20.09% V, 32.69% C, 2.32% H and 3.26% Cl), in agreement with TG analyses (see below). From these considerations, we thus assume chloride as predominant counter ion within the V trimers.

In order to evaluate the effect of the oxidation on the thermal stability of MIL-100(V) thermogravimetric analyses (Fig. 3) under oxygen and under nitrogen were performed. Both thermograms show two typical weight losses between 298 K (25 °C) and 873 K (600 °C). The first, rather smooth, weight loss up to about 473 K (200 °C) amounted to approx. 5% for the sample tested under nitrogen and approx. 11% for the sample tested under oxygen. Note that it is common for highly porous MOFs to observe such a discrepancy from one batch to another. This first mass loss is attributed to the loss of water (free H_2O molecules within the pores as well as those co-ordinated to the V trimers) and the removal of some free