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Quantitative solid-state NMR investigation of V^{5+} species in VPO catalysts upon sequential selective oxidation of *n*-butane

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ABSTRACT

Bulk VPO catalysts (VPO/bulk) and VPO catalysts supported on mesoporous SBA-15 material (VPO/SBA-15) were treated sequentially in a flow of nitrogen loaded with *n*-butane and of synthetic air loaded with *n*-butane in order to reach a complete reduction and reoxidation, respectively, of the catalyst surface. The V^{5+} species on these VPO catalysts were quantitatively investigated by solid-state NMR spectroscopy and correlated with the catalytic activities of the corresponding materials in the selective oxidation of *n*-butane to maleic anhydride. By $^{31}P\{^1H\}$ cross-polarization MAS NMR experiments on the *n*-butane-loaded VPO/SBA-15 catalyst was evidenced that *n*-butane is preferentially adsorbed at surface sites of δ-$VOPO_4$-like phases. Based on the number of P/V^{5+} species in δ-$VOPO_4$-like phases as determined by MAS NMR spectroscopy, the turnover frequency of the surface sites on the VPO/SBA-15 catalyst was estimated to be about 0.2 s^{-1}.

1. Introduction

Vanadium phosphate (VPO) materials belong to the most complex catalysts in heterogeneous catalysis. VPO catalysts are industrially applied in the selective oxidation of *n*-butane to maleic anhydride (MA) comprising the stepwise abstraction of eight hydrogen atoms leading to the formation of four water molecules and the insertion of three oxygen atoms. Until now, there is a controversy discussion on the composition of the highly active VPO catalysts and the nature of their active surface sites [1]. It is widely assumed that vanadyl pyrophosphate $(VO)_2P_2O_7$ is the main component of the bulk VPO catalysts, which are covered with defect sites or other amorphous and crystalline vanadyl phosphate phases [2–6]. Recent studies focusing on the investigation of the surface structure and composition of VPO materials indicated that the surface regions of the catalyst particles are very different from the bulk phase [7–11]. Applying Raman spectroscopy, XPS, and EXAFS techniques, various orthophosphates, such as members of the δ-$VOPO_4$ family, could be indentified on vanadyl pyrophosphate particles, which are involved in redox and oxidation cycles [7,11]. In contrast to the vanadyl pyrophosphate built by vanadium atoms in the oxidation state +4 (V^{4+}), vanadyl orthophosphates consist of vanadium atoms in the oxidation state +5 (V^{5+}).

Generally, VPO catalysts are prepared *via* an *in situ* activation of vanadyl hydrogenphosphate hemihydrate $VOHPO_4{\cdot}0.5H_2O$ in a flow of air loaded with *n*-butane [1]. This procedure leads to VPO catalysts composed of vanadyl pyrophosphate and vanadyl orthophosphate phases, such as α_I-, α_{II}-, β-, γ-, δ-$VOPO_4$ [1,12–15]. Furthermore, a reversible transformation of orthophosphate phases into the vanadyl pyrophosphate is discussed, which corresponds to a change of the oxidation state of vanadium atoms from the V^{5+} to the V^{4+} state and, possibly, to the V^{3+} state and *vice versa* [15]. The change, e.g., between the V^{5+} and V^{4+} states is accompanied by a release of oxygen atoms from the catalyst framework and their transfer to reactant molecules. The formed framework vacancies are filled by oxygen from the gas phase changing the oxidation state of the framework vanadium back from V^{4+} to V^{5+}. This catalytic cycle corresponds to the Mars–van-Krevelen mechanism [16].

Since V^{4+} and V^{3+} species are paramagnetic, they are not accessible for solid-state NMR spectroscopy in a direct manner. However, static ^{31}P spin-echo NMR spectroscopy allows the separation of signals due to phosphorus atoms in the proximity of V^{5+} (−40 to 10 ppm), V^{4+} (very broad signal at *ca.* 2500 ppm), and V^{3+} species (very broad signal at *ca.* 4650 ppm) in VPO compounds [17–19]. Magnetic susceptibility measurements of vanadyl pyrophosphate confirmed the presence of paramagnetic V^{4+} species in this material. Li et al. [17] found that the observed ^{31}P NMR shifts of up to 2500 ppm for phosphorus atoms in the proximity of paramagnetic V^{4+} species are due to electron-nuclear

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dipolar-plus-contact interactions, which also cause the strong line broadenings of the ^{31}P NMR signals of up to 1000 ppm. In contrast, phosphorus atoms in the proximity of diamagnetic V^{5+} species (P/V^{5+}) and V^{5+} species themselves have been successfully investigated by high-resolution ^{31}P and ^{51}V MAS NMR spectroscopy (MAS: magic angle spinning), respectively [20–24]. In these cases, the residual line width of the ^{31}P and ^{51}V MAS NMR signals mainly depends on the distribution of bond distances and angles in the local structure of the resonating nuclei.

In the present study, the sensitivity of solid-state NMR spectroscopy for local structures and the quantitative character of this method were utilized for, to the best of our knowledge, first quantitative investigation of P/V^{5+} species in differently treated VPO catalysts. For these studies, VPO catalysts were treated under reaction conditions in such a manner that the number of catalytically active V^{5+} atoms was decreased by reduction in a flow of nitrogen loaded with *n*-butane and increased in a flow of synthetic air loaded with *n*-butane. The MAS NMR experiments focused on the separation and quantification of P/V^{5+} species and the assignment of the corresponding vanadyl orthophosphate phases after transfer of the spent catalysts into MAS NMR rotors. To enhance the sensitivity of the MAS NMR spectroscopy for the catalytically interesting P/V^{5+} sites, the VPO compounds were dispersed on mesoporous SBA-15 material acting as a catalyst support. For the obtained VPO/SBA-15 material, a significantly higher specific surface area of the VPO compounds in comparison with VPO/bulk catalysts could be expected [25,26].

2. Experimental

2.1. Materials

The bulk VPO catalyst (VPO/bulk) used as reference material was prepared *via* vanadyl hydrogenphosphate hemihydrate ($VOHPO_4 \cdot 0.5H_2O$). This precursor was obtained according to the following standard procedure [27,28]: 1.46 g V_2O_5 and 2.21 g 85% H_3PO_4 were given in 29-ml isobutanol and 2.9-ml benzyl alcohol. The synthesis was carried out at 373 K for 6 h in a 250-ml round bottom flask equipped with a stirrer and reflux condenser. After completion of the reaction, the precipitate was recovered by filtration, thoroughly washed in acetone and demineralised water, and dried in synthetic air at 393 K for 12 h leading to the blue vanadyl hydrogenphosphate hemihydrate precursor. By ICP-AES, the phosphorus to vanadium ratio of the precursor was determined to 1.01.

The synthesis of the SBA-15 material used as catalyst support was performed as described by Zhao et al. [29]: 6.0 g of the triblock copolymer P123 (Aldrich) was added to 29.4 g of HCl (37%) and 192 g deionised water until all the P123 was dissolved. Subsequently, this mixture was dropwise added to 13.2 g tetraethylorthosilicate (Aldrich, 98%) and vigorously stirred for 10 min. At first, the mixture was heated at 313 K for 24 h and, upon transfer into a Teflon-lined 200-ml autoclave, at 373 K for another 24 h. After cooling to room temperature, the solid product was washed with deionised water and dried in air at 353 K overnight. For decomposing the templates, the as-synthesized material was heated with a rate of 2 K min^{-1} up to 823 K and calcined at this temperature in synthetic air for 5 h.

For the preparation of the SBA-15-supported VPO catalyst (VPO/SBA-15 with 60 wt.% VPO), the synthesis of the vanadyl hydrogenphosphate hemihydrate precursor $VOHPO_4 \cdot 0.5H_2O$ was performed according to Li et al. [25,26]: 0.54 g of V_2O_5 was refluxed at 413 K for 5 h in a mixture of isobutanol and benzyl alcohol (10 ml each). Then, 0.524 g of polyethyleneglycol 6000 (PEG 6000 by Fluka) and 0.90 g of the calcined SBA-15 material were added accordingly. After 1 h, 0.274 g of 85% H_3PO_4 was added dropwise to the mixture. This mixture was allowed to reflux for 6 h before the suspension was filtered, and the solid was washed with isobutanol and acetone. The solid was dried in synthetic air at 393 K for 12 h. By ICP-AES, the phosphorus to vanadium ratio of the VPO/SBA-15 material was determined to 1.04.

The activation of the VPO/bulk and VPO/SBA-15 catalysts under study was carried out under a gas flow of 98.5 ml synthetic air and 1.5 ml *n*-butane per minute by heating with a rate of 2 K min^{-1} from room temperature to 678 K. This temperature was kept for 24 h under the above-mentioned gas flow.

2.2. Characterization techniques

The activated catalysts were characterized by chemical analysis (ICP-AES, Varian Vista-MPX) and X-ray diffraction (Bruker D8 ADVANCE, Cu Kα radiation). Nitrogen adsorption was carried out at a Quantachrom Autosorb 1C upon degassing the samples at 573 K for 3 h. Then, the adsorption was conducted at 77 K. SEM pictures were recorded at a Cambridge CamScan 44 scanning electron microscope for studying the morphology of the materials.

The selective oxidation of *n*-butane on the catalysts under study was investigated using a fixed-bed laboratory reactor with a bed diameter and bed height of each 10 mm, the feed rate of 100 ml min^{-1} with compositions of 98.5 vol.% synthetic air and 1.5 vol.% *n*-butane under atmospheric pressure, and at the reaction temperature of 678 K. The reactor was charged with 500 mg of the catalyst precursor crushed and sieved to particles of 200–315 μm. The reaction products were analyzed by an *on-line* gas chromatograph HP 6890 equipped with a column HP-5 (length 30 m). Before the catalytic experiments, the catalysts were activated at 678 K for 24 h as described in Section 2.1. The end of this activation procedure defined the starting point of the sequential catalytic experiments. In these sequential experiments, an oxidizing feed consisting of synthetic air loaded with *n*-butane (1.5 vol.%) was introduced into the reactor for 20 min before the feed was switched to a reducing gas mixture consisting of nitrogen loaded with *n*-butane (1.5 vol.%) for 40 min and so on.

For the *on-line* study of the oxidation state of the vanadium in the VPO catalysts, the fixed-bed laboratory reactor was equipped with a high-temperature glass-fiber reflection probe HPSUV1000A by Oxford-Electronics connected with a fiber-optic spectrometer AvaSpec-2048 and an AvaLight-DH-S light source by Avantes. The window of the reflection probe was fixed *ca.* 1 mm over the catalyst bed (see Refs. [30,31]). With this technique, the absorbance of the UV/Vis charge-transfer (between O^{2-} and V^{5+}) band at *ca.* 400 nm, characteristic for vanadium species in the oxidation state +5 (V^{5+}), was detected [32]. The evaluation of the band intensity was performed according to the Kubelka–Munk function [33].

^{31}P and ^{51}V MAS NMR investigations were performed on a Bruker MSL-400 spectrometer at resonance frequencies of 161.98 and 105.25 MHz, with repetition times of 30 and 0.5 s, and with 4.800 and *ca.* 100.000 scans per spectrum, respectively. ^{31}P and ^{51}V nuclei were studied using 4 mm and 2.5 mm MAS NMR rotors with spinning rates of 8 kHz and 12.5–20.0 kHz, respectively. The quantitative ^{31}P MAS NMR studies of the number of phosphorous atoms in the proximity of V^{5+} species (P/V^{5+}) were carried out by comparing the signal intensities of the catalyst samples with that of an external intensity standard recorded with a repetition time of 120 s. This intensity standard consisted of a well-characterized silicoaluminophosphate SAPO-34 diluted with SBA-15 in a ratio of 1:4 [34]. For the $^{31}P\{^1H\}$ cross-polarization MAS NMR experiments, a contact pulse of 5 ms and a repetition time of 2 s were used.

Before the XRD and solid-state NMR characterization of the activated, reduced, and reoxidized catalyst samples, the corresponding materials were transferred from the fixed-bed laboratory reactor to the XRD sample carriers and into the MAS NMR rotors