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Time-resolved studies on correlations between dynamic electronic structure and selectivity of a $H_5[PV_2Mo_{10}O_{40}]$ partial oxidation catalyst

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Abstract

Time-resolved in situ X-ray absorption spectroscopy studies on an activated $H_5[PV_2Mo_{10}O_{40}]$ oxidation catalyst were performed to obtain correlations between the dynamic structure and the catalytic selectivity of the material. Both the geometric and electronic structures of the vanadium and molybdenum metal centers of the catalyst change dynamically under the reaction conditions used. Moreover, the selectivity of the catalyst exhibits a pronounced correlation with the degree of reduction and the solid-state kinetics of the reoxidation process. The corresponding extent of reoxidation curve can be simulated with a solid-state kinetic model assuming three-dimensional diffusion as the rate-limiting step. Thus, the partially reduced catalyst exhibits a rate constant of the bulk-diffusion limited reoxidation, coinciding with the temporal evolution of the selectivity of the catalyst.

Keywords: In situ; Heterogeneous catalysis; Structure–activity relationships; Molybdenum; Vanadium; EXAFS spectroscopy; Polyoxometalates; Time-resolution; Dynamic; Solid-state kinetics

1. Introduction

In situ studies on heterogeneous catalysts are indispensable in modern catalysis research. Reliable correlations between the structure of the catalyst and its catalytic performance can be determined only under relevant reaction conditions. These correlations need to be elucidated because they constitute the foundation of a knowledge-based design of novel heterogeneous catalysts [1]. Consequently, many structural analytic techniques, including X-ray absorption spectroscopy (XAS), have been used to study the bulk or surface structure of a catalyst under reaction conditions [2–7]. However, investigating a solid heterogeneous catalyst under steady-state reaction conditions yields little information on the dynamic nature of its surface and bulk structure. Heterogeneous catalysts are metastable materials whose structure and performance change dynamically under reaction conditions. Therefore, time-resolved measurements are needed to further elucidate the behavior of the electronic and geometric structure of a catalyst under changing reaction conditions. Monitoring the gas-phase composition during a catalytic reaction yields conventional kinetic information. Conversely, monitoring bulk structural changes reveals the solid-state kinetics of dynamic structural changes in the bulk of the catalyst under reaction conditions. In combination with simultaneous activity and selectivity measurements by suitable gas-phase analytical techniques, the desired correlations between the catalytic performance and the bulk structure dynamics are obtained.

Heteropolyoxomolybdates of the Keggin type (e.g., $H_3[PMo_{12}O_{40}]$) are active catalysts for the partial oxidation of alkanes and alkenes [8–12]. Because of their molecular structure, heteropolyoxomolybdates of the Keggin type have been frequently used as suitable model systems for more complex molybdenum-based mixed-oxide catalysts. However, the "real" structure of the Keggin ion under reaction conditions is not necessarily identical to the ideal structure of the corresponding as-prepared heteropolyoxomolybdate. In addition to the "ideal" (crystallographic) structure, the "real" structure comprises all deviations from the ideal structure that may be

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present in the bulk structure of the catalyst. We have recently shown that the onset of catalytic activity during thermal activation of $H_3[PMo_{12}O_{40}]\cdot 13H_2O$ and $H_4[PVMo_{11}O_{40}]\cdot 13H_2O$ in propene coincides with a partial decomposition of the Keggin ion at ∼600 K and migration of Mo centers on extra-Keggin sites [13,14]. Here we report on correlations between the electronic structure and the catalytic selectivity of $H_5[PV_2Mo_{10}O_{40}]\cdot 13H_2O$ under steady-state and dynamic reaction conditions obtained from time-resolved in situ XAS investigations.

2. Experimental

2.1. Preparation of $H_5[PV_2Mo_{10}O_{40}]\cdot 13H_2O$

To begin the preparation, 16.89 g of MoO_3 (corresponding to 11.73 mmol Mo_{10}) and 2.134 g of V_2O_5 (corresponding to 11.73 mmol V_2) were suspended in 650 ml of water in a three-necked 1000-ml flask equipped with a condenser. Commercial phosphoric acid [H_3PO_4 (∼82.5%)] was diluted by a factor of 100, and the exact concentration was determined by titration with NaOH. Then 81 ml of this 0.825% H_3PO_4 solution (11.73 mmol P) was added dropwise to the boiled and stirred suspension of the metal oxides. After complete addition of the phosphoric acid, a clear amber-colored solution was obtained. The solid product was isolated by removing the solvent in a rotary evaporator at ∼90 °C and dried in a vacuum desiccator [15,16]. Thermal analysis studies (TG/DTA-MS) confirmed the amount of ∼13 molecules of "crystal water" per Keggin ion in as-prepared $H_5[PV_2Mo_{10}O_{40}]\cdot 13H_2O$ and a thermal stability similar to that of $H_4[PVMo_{11}O_{40}]\cdot 13H_2O$.

2.2. X-ray diffraction

X-ray diffraction (XRD) measurements were performed on a *STOE STADI P* diffractometer (Cu$K\alpha_1$; Ge primary monochromator) in a range of 5–100° in 2θ with a step width of 0.01° and a measuring time of 10 s/step. Structural refinements to the experimental diffraction patterns were performed using the TOPAS v 2.1 software (Bruker AXS). Structural data used in the XRD and XAS analyses were taken from the Inorganic Crystal Structure Database (ICSD).

2.3. XAS

In situ transmission XAS experiments were performed at the V K-edge (5.465 keV, Si 111) and the Mo K-edge (19.999 keV, Si 311) at beamlines E4 and X1, respectively, at the Hamburg Synchrotron Radiation Laboratory (HASYLAB). The storage ring operated at 4.4 GeV with injection currents of 150 mA. The in situ experiments were conducted in a flow reactor at 1 bar in flowing reactants (flow rate, 30 ml/min; heating rate, 5 K/min to the specified reaction temperature). The gas-phase composition at the cell outlet was continuously analyzed using a noncalibrated mass spectrometer in a multiple-ion detection mode (Omnistar, Pfeiffer).

The heteropolyoxomolybdate was mixed with boron nitride (∼7 mg HPOM and ∼30 mg BN) and pressed with a force of 1 ton into a 5-mm diameter pellet. This resulted in edge jumps of $\Delta\mu_x \sim 1.5$ at the Mo K-edge and $\Delta\mu_x \sim 0.2$ at the V K-edge. $H_5[PV_2Mo_{10}O_{40}]\cdot 13H_2O$ was activated in 10% propene at 300–723 K. Extended XAS studies at the Mo K-edge revealed an intact Keggin structure of the activated $H_5[PV_2Mo_{10}O_{40}]\cdot 13H_2O$. Under isothermal reaction conditions (673, 698, and 723 K), the gas-phase composition was rapidly changed from oxidizing (10% propene and 10% oxygen in He) to reducing (10% propene in He) reaction conditions.

X-ray absorption fine structure (XAFS) analysis was performed using WinXAS version 3.1 software [17]. Background subtraction and normalization were carried out by fitting linear polynomials to the pre-edge and post-edge regions of the absorption spectra, respectively. The extended X-ray absorption fine structure (EXAFS), $\chi(k)$, was extracted using cubic splines to obtain a smooth atomic background, $\mu_0(k)$. The pseudoradial distribution function $FT(\chi(k)k^3)$ was calculated by Fourier transformation of the k^3-weighted experimental $\chi(k)$ function, multiplied by a Bessel window, into the R space. EXAFS data analysis was performed using theoretical backscattering phases and amplitudes calculated with the ab initio multiple-scattering code FEFF7 [18]. Single-scattering and multiple-scattering paths in the Keggin ion model structure were calculated up to 6.0 Å with a lower limit of 2.0% in amplitude with respect to the strongest backscattering path. EXAFS refinements were performed in R space simultaneously with magnitude and imaginary part of a Fourier-transformed k^3- and k^1-weighted experimental $\chi(k)$ using the standard EXAFS formula [19]. The structural parameters determined by a least-squares EXAFS refinement of a Keggin model structure to the experimental spectra are (i) one overall E_0 shift, (ii) Debye–Waller factors for single-scattering paths, (iii) distances of single-scattering paths, and (iv) one-third cumulant for the Mo–O or V–O distances in the first coordination shell and one-third cumulant for all remaining scattering paths. Coordination numbers (CNs) and S_0^2 were kept invariant in the refinement.

3. Results and discussion

This section comprises two parts. The first part establishes that the structure of as-prepared $H_5[PV_2Mo_{10}O_{40}]$ and its structural evolution on thermal activation is similar to that of $H_4[PVMo_{11}O_{40}]$ as described previously [14]. $H_5[PV_2Mo_{10}O_{40}]$ was used because the increased V content makes it more suitable for in situ XAS studies at the V K-edge. The second part of the manuscript describes reversible changes in the local structure around the V centers and the correlation between the time-dependent evolution of the Mo average valence and the catalytic performance of material under rapidly changing reaction conditions (reducing and oxidizing).