Site Identification on Heteropolyacid Catalysts using CO & CO_2 and Transmission & Diffuse Reflectance IR Spectroscopy

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Introduction

Heteropolyacid-based catalysts are used in the industrial production of methacrolic acid from methacrolein [1]. Unfortunately, the (thermal) stability and thus the lifetime of these catalysts is unsatisfactory. Activity and instability though may be unseparably linked; there are indications that not the heteropolyacid itself but a partially decomposed, not yet fully identified structure constitutes the active phase [2]. Here, we seek to identify the sites on structures formed in various thermal treatments of a family of catalysts consisting of $H_4PVMo_{11}O_{40}$ and its cesium salts.
Infrared spectroscopy so far has been mainly used for the analysis of the constitution of heteropolyacids [3,4]; few publications deal with site identification by adsorption of probe molecules such as pyridine [5] or CO [6]. We selected CO and CO_2 as probes in order to analyze for Lewis and Brønsted acidic and basic sites.

Experimental

$H_4PVMo_{11}O_{40}$ was prepared through dissolution of the according amounts of MoO_3 and V_2O_5 in H_3PO_4 and subsequent water removal. $Cs_xH_{4-x}PVMo_{11}O_{40}$ (x=2-4) were obtained through addition of a Cs_2CO_3 solution to the heteropolyacid solution in the desired stoichiometry and subsequent water removal.
For transmission IR spectroscopy / CO adsorption, samples were pressed (320 MPa) into self-supporting wafers ($\approx$25 mg cm^{-3}), activated in vacuum (final pressure $1*10^{-4}$ Pa) at 523, 673, or 773 K. Spectra were recorded with increasing CO pressure using a Perkin Elmer S 2000 at 4 cm^{-1} resolution. For diffuse reflectance / CO_2 adsorption, samples were filled into a gold cup and activated in a flow of dry N_2 at 473 or 773 K. CO_2 was purged through the cell at 298 K for 30 min, gas phase CO_2 was removed by purging with N_2. Spectra were recorded at 1 cm^{-1} resolution using a Graseby Specac "Selector" attachment with environmental chamber placed in a Bruker ifs 66.

Results

CO adsorption was only observed on Cs salts; the free acid had a surface area of < 5 m^2 g^{-1} and yielded a wafer of poor transmission. Up to 5 different band positions can be identified after activation (Fig. 1). The band at 2163 cm^{-1} is only pronounced with $Cs_2H_2PVMo_{11}O_{40}$ activated at 523 K; it is attributed to CO adsorbed on OH groups [6]. The band is not observed after activation at 773 K, consistent with dehydroxylation. The band at 2152 cm^{-1} arises from CO adsorbed on Cs$^+$ [6]. The band at 2138 cm^{-1} is often ascribed to physisorbed / liquefied CO. Such bands usually develop at elevated CO pressures once the bands of chemisorbed CO have been saturated. We detected this band at CO pressures of 0.2 Pa and, as the band 2133 cm^{-1}, it may represent coordinatively unsaturated Mo/V cations. Only $Cs_4PVMo_{11}O_{40}$ showed at band at 2144 cm^{-1} that is tentatively attributed to a second Cs$^+$ species.

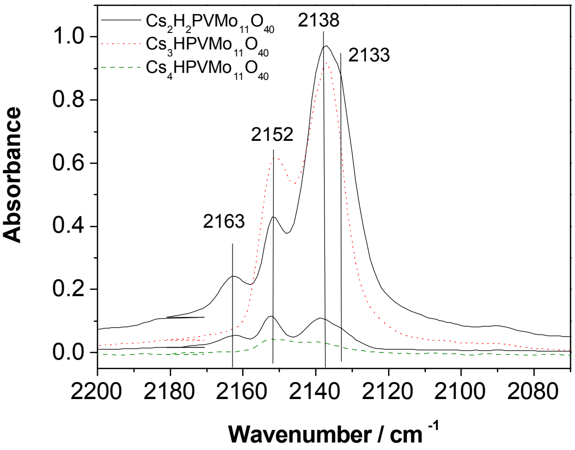

Figure 1: Adsorption of CO at 77 K after activation at 523 K. Spectra of samples in vacuum subtracted. CO pressure 0.002 and 6.3 (Cs_2X), 5.4 (Cs_3X), and 6.0 (Cs_4X) hPa.

CO_2 adsorption was observed on all samples. Carbonate formation was never observed, as expected for a weakly basic anion. The spectra revealed several bands from adsorbed CO_2. Fairly certain is the interpretation of the a band at 2341 cm^{-1} as CO_2 adsorbing on Cs$^+$. In analogy to the CO adsorption, a band at 2352 cm^{-1}, which was only observed for $Cs_2H_2PVMo_{11}O_{40}$, is thought to arise from interaction with OH groups. A band at 2320 cm^{-1} was only detected for $Cs_4PVMo_{11}O_{40}$ and $H_4PVMo_{11}O_{40}$, the low frequency may indicate adsorption of CO_2 on reduced metal cations. Bands at 2347 and 2332 cm^{-1} may indicate further non-cesium Lewis sites.

Both CO and CO_2 adsorption suggest the presence of weakly acidic Lewis sites on various HPA compounds after thermal treatment, indicating oxygen-deficient Keggin units.

References

[1] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.

[2] G. Mestl, T. Ilkenhans, D. Spielbauer, M. Dieterle, O. Timpe, J. Kröhnert, F.C Jentoft, H. Knözinger and R. Schlögl, Appl. Catal. A: General, 210 (2001) 13-34.

[3] A. Bielański, A. Małecka, L. Kubelkova, J. Chem. Soc. Faraday Trans. I 85 (1989) 2847.

[4] B.W.L. Southward, J.S. Vaughan, C.T. O'Connor, J. Catal. 153 (1995) 293.

[5] E.M. Serwicka, K. Bruckman, J. Haber, E.A. Paukshtis, E.N. Yurchenko, Appl. Catal. 73 (1991) 153.

[6] T. Saito, G. Koyano, M. Misono, Chem. Lett. (1998) 1075.