



A microcalorimetric study of the adsorption of propane on MoVTenb oxide

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Introduction

Polycrystalline, mixed MoVTenb oxides have been reported to show high selectivity and activity in the oxidation of propane to acrylic acid. The most relevant crystal structure in C-H activation of propane is the orthorhombic, bronze-like M1 phase [1]. Hydrogen abstraction and formation of propylene in the first step has been attributed to isolated V sites located on terminating lattice planes. In the present work, the adsorption of propane on the surface of M1 has been studied by microcalorimetry. For this purpose, a series of highly crystalline, phase-pure M1 catalysts has been synthesized. The investigation is aimed at a deeper understanding of the mechanism of propane activation.

Experimental

M1 (Tab. 1) was prepared applying different methods including precipitation (catalyst **M1-a**) [2] and hydrothermal synthesis at high temperature and pressure (catalyst **M1-b**) [3]. Microcalorimetry was performed on SETARAM Calvet calorimeters combined with a vacuum-gas-dosing apparatus [4]. Samples were pretreated in high vacuum at 423 K for 2 h. Propane (99.95 % purity) was adsorbed, desorbed and subsequently re-adsorbed at 313 K.

Results and discussion

The characteristics and catalytic properties of two M1 catalysts that show the most prominent differences in propane oxidation to acrylic acid are summarized in Table 1. At propane conversion of approximately 50%, the selectivity to acrylic acid differs by an order of magnitude. The chemical composition of the two crystalline M1 catalysts is similar. Electron microscopy revealed differences in the microstructure. Compared to **M1-a**, the mean particle size (length and width) of the rod-like M1 particles in **M1-b** is significantly reduced. This is reflected in an increased BET surface area of the nano-structured material.

Table 1. Properties of highly crystalline, phase-pure M1 catalysts

Catalyst (ID)	BET surface area [m ² g ⁻¹]	Mo:V:Te:Nb [at-%] as measured by EDX	Propane conversion [mol-%]	Selectivity to acrylic acid [mol-%]
M1-a (6059)	8.8	62 : 17 : 6 : 15	47	62
M1-b (5737)	13.3	64 : 15 : 6 : 15	56	5

Microcalorimetry was applied to follow the interaction of propane with the M1 surface at 313 K (Fig. 1). Fig. 1a shows the differential heat of adsorption as a function of the coverage. Compared to V₂O₅ ($\Delta H_{\text{ads},303\text{K}}=37$ kJ/mol) or V_xO_y/SBA-15 ($\Delta H_{\text{ads},313\text{K}}=40$ kJ/mol) [5,6], the initial heat of adsorption on **M1-a** is high. The heat remains constant at approximately 60 kJ/mol with increasing coverage demonstrating the presence of homogeneously distributed and energetically uniform adsorption sites. The adsorption sites on **M1-b** seem to be less

uniform, which is reflected in decreasing heat of adsorption with increasing coverage. At higher coverage ($> 30 \mu\text{mol/g}$), the heat decreases rapidly and reaches the heat of condensation of propane (-19 kJ/mol) indicating that in this range the monolayer is completed and multilayer adsorption proceeds. Thus, in contrast to N_2 adsorption at 77 K , nearly the same monolayer adsorption capacities of $40\text{-}50 \mu\text{mol/g}$ can be estimated for the two M1 catalysts (inset Fig. 1b). Desorption and subsequent re-adsorption of propane reveal that even at the low temperature of 313 K , propane adsorption on MoVTenb oxide is not completely reversible. Fig. 1b shows the adsorption isotherms in the region of Langmuir adsorption. The amount of propane, re-adsorbed on M1-a, is slightly reduced, suggesting that either a fraction of propane is irreversibly adsorbed or that the catalyst surface loses adsorption sites by reconstruction. No further changes have been observed during the third re-adsorption (not shown here). On M1-b, the few sites adsorbing propane strongly ($\Delta H_{\text{ads}} \sim 65 \text{ kJ/mol}$) are not observed in the re-adsorption experiment (Fig. 1a).

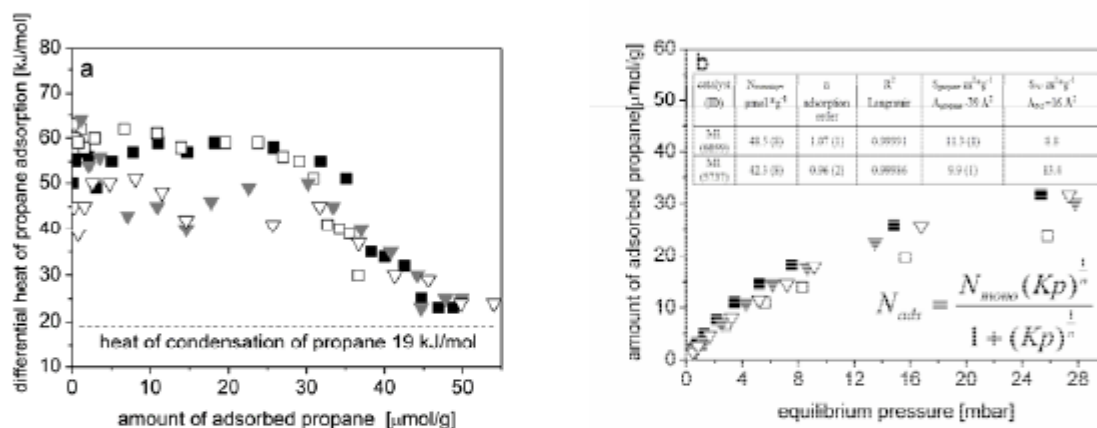


Figure 1. Propane adsorption and subsequent re-adsorption at 313 K on M1-a (■ ads; □ re-ads) and M1-b (▼ ads; ▽ re-ads); inset: results of fitting the data with a Langmuir model.

Conclusions

Highly selective M1 is characterized by comparatively strong adsorption of propane. The heat of adsorption is independent of the coverage suggesting homogeneous distribution and uniformity of adsorption sites. Nano-structuring of M1 results in weaker adsorption ($\Delta H_{\text{ads}} \sim 45 \text{ kJ/mol}$) and inhomogeneity, which may be connected with low the selectivity.

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