

Propane activation over vanadia clusters on different catalysts

S. Wrabetz, P. Kube, S. Carey, A. Trunschke and R. Schlögl

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dept. of Inorganic Chemistry,
Berlin, 14195, Germany, wrabetz@fhi-berlin.mpg.de*

Introduction

The catalytic cycle is generally composed of absorption/desorption steps, and surface reaction processes that all may have an impact on surface properties. The 1st step is the adsorption followed by activation of the reacting molecules. For a detailed and deeper understanding of the mechanism of propane oxidation, we need information about the catalytic performance of the catalyst, thermodynamic data of high accuracy, quantitative data as the number of catalytic relevant adsorption sites and their energetic distribution, and the knowledge about the nature of the catalyst surface during reaction.[1] Finally, it may be possible to describe a structure reactivity relationship. Moreover, quantitative data provide a basis for theoretical modelling.[2]

The present study concerns four V-containing model catalysts with substantial structural diversity, which all catalyse the oxidative dehydrogenation of propane (ODP). This multi-method study including kinetic measurements, microcalorimetry, bulk chemical analysis by XRF and surface analysis by in situ XPS enables us to suggest a structure-reactivity relationship for V-containing catalysts in the ODP.

Results and discussion

Differential heats of adsorption of the reactant propane were measured at 40°C for phase-pure bulk mixed oxide MoV & MoVTeNb (M1), V₂O₅ and silica-supported vanadium oxide. The catalysts were pre-treated in the calorimeter cell in the reaction feed under steady-state conditions. Several adsorption/desorption cycles were performed in the calorimeter cell. The amount of adsorbed molecules was determined volumetrically. In addition, all four catalysts were studied in corresponding kinetic experiments. Table 1 shows the apparent activation energy in propane oxidation, the differential heat of propane adsorption, the resulting estimated barrier for propane activation [1] and the consumption rate of propane normalized to propane adsorption surface sites.

Table 1: Reaction rates and kinetic parameters in the oxidative dehydrogenation of propane

	MoV oxide	V ₂ O ₅	MoVTeNb oxide [1]	V _x O _y /SBA15 [1]
E _{app.}	74 kJ/mol	66 kJ/mol	80 kJ/mol	110 kJ/mol
ΔH _{ads} [*]	40 kJ/mol	70 kJ/mol	63 kJ/mol	44 kJ/mol
Estimated barrier	114 kJ/mol	136 kJ/mol	143 kJ/mol	154 kJ/mol
mmol/(A _{ads.-site} [*] h)	1.47*10 ⁻¹⁹	8.0*10 ⁻²⁰	6.92*10 ⁻²⁰	2.89*10 ⁻²¹
* differential heat of propane adsorption at 50% coverage of propane				

The estimated intrinsic barrier for all studied V-catalysts increases in the order MoV oxide < V₂O₅ < MoVTeNb oxide < V_xO_y/SBA-15, which is in agreement with a decrease in the normalized consumption rate of propane in the same order. Comparison with DFT calculations [3] interestingly suggests that the cluster size of the active surface vanadium oxide ensembles decreases in the order MoV oxide > V₂O₅ > MoVTeNb oxide > V_xO_y/SBA-15.

Conclusion

A structure reactivity relationship can be retrieved by a combination of kinetic measurements, the determination of the heat of adsorption and DFT calculations. Higher rates of propane oxidation are correlated with lower barriers for propane activation and seem to be linked with larger vanadium oxide cluster size.

References

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