From model systems to technical catalysts: Nanostructured catalysts in activation of propane studied by electron spectroscopies and theory

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Introduction and Objectives

The activation of C-H bonds in alkanes is catalyzed by metal surfaces, acid sites or metal oxides implying great diversity in the chemistry of the active species, the type of reaction intermediates and elementary steps. The project presented here is focused on oxidative C-H activation and oxidation of propane for synthesis of olefins or oxygenates over Mo and V oxides. Selectivity in alkane oxidation relies on the nature of oxygen species and the molecular structure of the catalyst in terms of concepts such as "site isolation" and co-operation of H abstraction on O insertion functionalities [1]. Thus, an improved understanding of relations between the reaction network and the catalyst surface structure under working conditions is a key issue. Here, we study both technical catalysts like phase-pure multi-metal oxides ($MoVTeNbO_x$) that are characterized by high crystallinity and purity with respect to undesired amorphous admixtures and, in an effort to model the surface of these complex bulk oxides, mono-dispersed vanadium oxide species anchored on the surface of a host phase (mesoporous silica SBA-15, pristine or modified by Mo, Ti). Both the technical catalysts and the model systems have been investigated under working conditions, i.e. in the presence of reactive gases at a pressure of about 50 Pa at elevated temperatures up to 450 °C using near ambient pressure X-ray photoelectron spectroscopy (XPS) and by applying a recently developed methodology using near ambient pressure soft X-ray absorption spectroscopy near the O K-edge (O K-NEXAFS) [2]. The catalytic performance of the catalysts has been verified by on-line mass spectrometry.

Results and Discussion

Fig. 1a shows the evolution of oxygen species of dehydrated VO_x/SBA-15 model catalysts with increasing V loading. The O K-NEXAFS was analyzed by comparing the experimental spectra with theoretical spectra of model clusters obtained by simulations using state of the art density functional theory (DFT). Contributions of V-O-V bridges could be identified on the VOx/SBA-15 model catalysts at low V loadings (≤ 8wt%) providing clear evidence of the co-existence of different vanadia species including non-monomeric arrangements (Fig. 1b).

For $MoVTeNbO_x$ catalysts it was found that the elemental composition of the outer surface responds dynamically on the addition of steam to the O_2/C_3H_8 feed. Depletion in Mo content and a significant enrichment with Te and V was observed. An analysis of the $V2p_{3/2}$ XP core level spectra reveals the evolution of V^{5+} species that is related to the acrylic acid abundance, i.e. a close relationship between catalytic performance and V^{5+} sites (Fig. 1c). The Te/V abundance ratio remains constant. Thus, it is suggested that a monolayer of Te/V entities on top of the crystalline bulk phase constitutes the active surface of $MoVTeNbO_x$ during selective propane oxidation to acrylic acid [3].

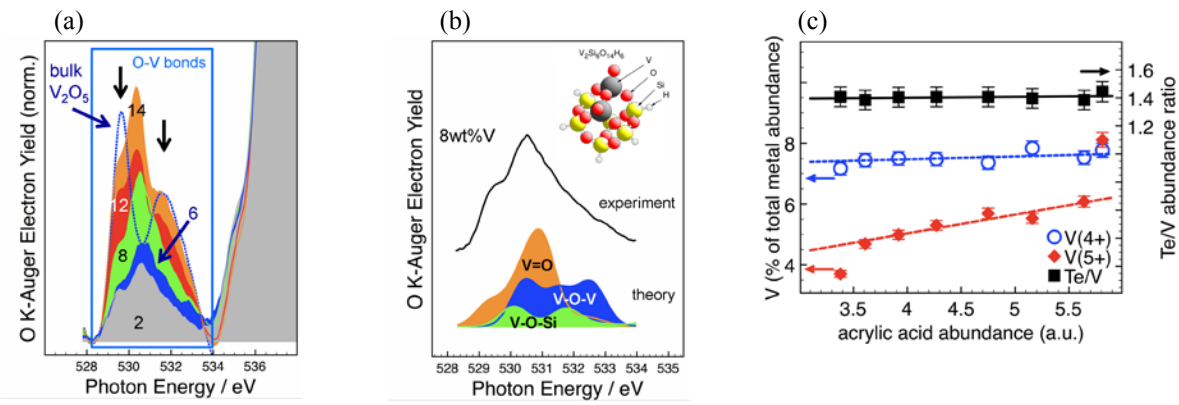

Figure 1. (a) O K-edge spectra in 50 Pa of O_2 at 420 °C showing the evolution of oxygen species (marked with arrows) with V loading (2wt% - 14wt% as indicated) on SBA-15. (b) Experimental O K-edge spectrum of 8wt%V/SBA-15 is compared with theoretical spectra derived from DFT cluster calculation. The contribution of different bonding configuration to the total spectrum is indicated. (c) Relationship between the acrylic acid abundance and the surface element content of V^{5+} species, V^{4+} species and the Te/V abundance ratio of $MoVTeNbO_x$ catalyst in the feed of propane, oxygen and water vapor at 420 °C.

Conclusions

Near ambient pressure XPS provided direct detailed insight into the redox chemistry of a complex oxidation catalyst such as MoVTeNb oxide. In the case of model systems like VO_x/SBA-15 a comparison of experimental O K-NEXAFS spectra with theory allows to differentiate between different bonding configuration of the transition metal oxide species under relevant conditions, i.e. in the dehydrated state at reaction temperature. Thus, near ambient pressure XPS and NEXAFS with their inherent surface sensitivity are a probe than can substantially assist other methods to obtain an in-depth understanding not only of model systems but also materials that are close to a technical catalyst.

References

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