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Comparative mechanistic studies on oxidative dehydrogenation of ethane and propane over model catalysts

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The major challenge in oxidative dehydrogenation (ODH) of alkanes to olefins is the limited control of undesired parallel and consecutive total oxidation pathways. Most heterogeneous catalysts are characterized by a pronounced multi-scale complexity preventing a profound investigation of straightforward structure-activity-correlations thus hindering a basic understanding of reaction mechanisms that would enable a rational catalyst design.

In the present study, we investigate three model catalysts with well-defined and characterized structure. A complex bulk MoVTeNb oxide composed of the M1 crystal phase that contains vanadium oxide surface species as active sites [1] is compared with sub-monolayer vanadium oxide dispersed on silica (6% VO_x/SBA-15) [2] and oxidized carbon nanotubes (O-CNT) stabilized by P_2O_5 that contain quinone groups as potential alkane activating sites without possessing redox-active metal ions [3] and no bulk oxygen. We performed a formal kinetic investigation applying the same reaction conditions in oxidative dehydrogenation of ethane and propane over the three catalysts as a basis for comprehensive mechanistic studies that address active sites and reaction mechanism in the oxidative activation of C-H bonds in alkanes.

Experimental

The oxidative dehydrogenation of ethane and propane were carried out in an 8-fold parallel reactor set-up (Integrated Lab Solutions, Berlin). Product analysis was performed by an on-line gas chromatograph (Agilent 7890) equipped with TCD and FID. The variation of the reaction conditions includes the reaction temperature (360-420°C), propane feed concentration (6-14%), oxygen feed concentration (3-7%), water feed concentration (0-40%), and space velocities (5000-105000 ml g^{-1} h^{-1} for M1 and 1500-3300 ml g^{-1} h^{-1} for 6V/SBA-15 and P/O-CNT, respectively). A plug flow single tube reactor was used for isotope tracer experiments under steady state conditions applying a mass spectrometer (QMA 400 from Pfeiffer) and a gas chromatograph (Agilent 7890) for product analysis.

Results and Discussion

Fig. 1 illustrates the selectivity to the olefin as a function of alkane conversion, demonstrating that the chemically complex M1 catalyst shows a high selectivity. The apparent activation energy (E_a) of propane and ethane activation increases in the sequence M1<P/O-CNT<6V/SBA-15 (Tab. 1). Differences in the formal reaction order (RO) in particular with respect to oxygen indicate differences in the reaction mechanism. Whereas the formation rate of CO_2 in comparison to CO is higher on the P/O-CNT catalyst, CO is the dominating carbon oxide over the V-containing catalyst. Contributions of O-CNT burning are discussed. Acids are formed over V-containing catalysts in dry and wet feed in noticeable amounts, whereas no oxygenates are observed in the product mixture over carbon as catalyst.

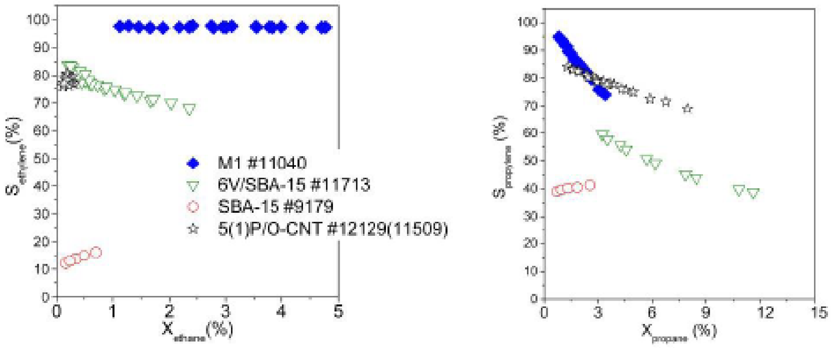

Fig. 1. Selectivity to olefin in the ODH of ethane (left) and propane (right); T = 360 to 420°C, F/W = 5000-105000 ml g^{-1} h^{-1} for M1 and 1500-3300 ml g^{-1} h^{-1} for 6V/SBA-15 and P/O-CNT, Feed $C_3H_8/O_2/N_2$ = 10:5:85.

Table 1. Comparison of formal kinetics (E_a and RO) for the ODH of propane and ethane

catalyst	ODH of ethane			ODH of propane		
	RO_{ethane}	RO_{oxygen}	E_a [kJ/mol]	$RO_{propane}$	RO_{oxygen}	E_a [kJ/mol]
M1	0.89	0.06	86	0.79	0.12	85
P/O-CNT*	0.56	0.40	109	0.55	0.48	97
6V/SBA-15	0.78	0.24	128	0.72	0.27	108
SBA-15	0.78	0.07	137	0.57	0.24	114

*5% P_2O_5 in ODH of ethane, 1%P_2O_5 in ODH of propane

Additional steam in the feed does not affect the activity of carbon, but increases the activity of M1, while the alkane conversion over silica supported vanadium oxide is decreased. Differences with respect to alkane and oxygen activation will be discussed in view of the different nature of the active sites on the three catalysts.

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