STRUCTURE-PERFORMANCE RELATIONSHIPS IN SUPPORTED VANADIA CATALYSTS UNDER WORKING CONDITIONS BASED ON COMPLEMENTARY OPERANDO RAMAN-GC AND IN SITU XANES SPECTROSCOPIES

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Catalysts with large surfaces are much more complex than the model single crystals. To single out the active site under real working conditions of the catalyst is an enormous task. It requires a combination of techniques and the development or adaptation of techniques, which allow measurements under catalytic conditions (high temperatures and high pressures). This is the field of *in situ* spectroscopy. We have recently developed a new methodology that combines the determination of catalyst activity/selectivity and its molecular structure in a single experiment (1,2). We have named this methodology "*operando*" (Latin for "working").

We will present Raman studies to assess structure-activity relationships on supported oxides (namely V, Cr, Mo) during alkane and ammonia activation (ammoxidation). In addition, a combination of in situ Raman, XANES, and EPR spectroscopies is used to study the nature of the interaction between V and Ce in the ceria-supported vanadia catalysts for ethane oxidative dehydrogenation. Vanadium oxide species disperse on ceria up to 9 V atoms/nm2 of support. Surface V5+ species closely interacts with ceria support promoting a reduction of surface Ce4+ to Ce3+. Upon heating or during reaction surface vanadia reacts with ceria support forming a CeVO4 phase. The active site appears to be V5+–O–Ce3+ for both systems. The redox cycle for oxidative dehydrogenation appears to be associated with Ce, rather than with V sites (3).

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References

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