

Isotopic studies of ethane oxidative dehydrogenation on Ni-Nb-O selective catalyst

Zinovia Skoufa¹, Eleni Heracleous² and Angeliki A. Lemonidou^{1,2*}
¹Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece
²CPERI/CERTH, 6th km Charilaou-Thermi road, Thermi, 57001, Greece
*alemonidou@cheng.auth.gr

Introduction

NiNbO mixed oxides constitute low temperature, highly active and selective catalysts for ethane ODH, exhibiting one of the best catalytic performances [1, 2]. The catalyst with the optimum formulation, Ni_{0.85}Nb_{0.15}, exhibits an ethylene yield of 46% at 400 °C [2]. In continuation of previous mechanistic studies [3], in this work we conducted and report herein advanced isotopic experiments in an attempt to further elucidate the elementary reaction steps of ethane ODH over Ni_{0.85}Nb_{0.15}, focusing on the determination of the rate determining step (RDS) and the participation of lattice oxygen in the activation of ethane.

Experimental

Temperature programmed reaction (TPRe) experiments were performed on Ni_{0.85}Nb_{0.15}. The preparation, physicochemical characterization, and evaluation of the catalytic performance of the catalyst in ethane ODH was reported in detail previously [2]. For the determination of the kinetic isotope effect for the C-H activation step, experiments with the following reactant feed compositions were conducted: 1% C₂H₆/1% O₂/He, 1% C₂D₆/1% O₂/He and 0.5% C₂H₆/0.5% C₂D₆/1% O₂/He. The participation of lattice oxygen in ethane ODH was approached with a 1% C₂H₆/1% ¹⁸O₂/He experiment. In all experiments the temperature was increased from ambient to 400°C with a rate of 10 °C min⁻¹. Before each experiment the catalyst (50mg) was pre-treated under 10% O₂/He flow at 450°C for 0.5h. The exit of the U-type quartz reactor was monitored by a quadrupole mass analyzer.

Results/Discussion

In all TPRe experiments, reaction onset was observed in the temperature range of 260-280°C, with ethylene and CO₂ both detected as primary products. Starting with the experiments with deuterated ethane, important differences were observed in reactants consumption and products formation compared to unlabeled ethane. In the C₂H₆/C₂D₆/O₂ experiment, unlabeled H₂O was recorded first, proposing favorable activation of the C-H over the C-D bond. As the activation of deuterated ethane proceeded with increasing temperature, the catalyst surface was enriched in D-atoms leading to the formation of HDO and D₂O later on. Quantification of the experimental results allowed the calculation of the kinetic isotope effect (KIE) for C-H bond activation. Throughout the entire temperature range, the measured consumption rates for C₂H₆

were higher than those for C₂D₆ both for the separate C₂H₆/O₂, C₂D₆/O₂ experiments and for the competitive C₂H₆/C₂D₆/O₂ reaction (Fig. 1) and a value of KIE=3 was recorded. The strong isotope effect (KIE>>1) for the C-H bond activation provides evidence that this step is the RDS in ethane ODH over the NiNb catalyst, and indicates participation of surface oxygen species (lattice or chemisorbed), since it is lower than the maximum theoretical value calculated according to literature [4,5] from translational, rotational, electronic, and vibrational partition functions.

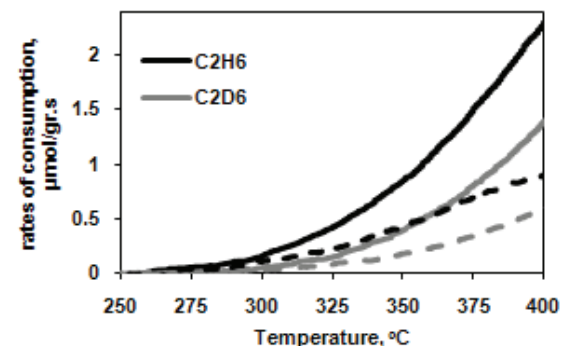


Figure 1: C₂H₆ and C₂D₆ consumption rates in C₂H₆/O₂ and C₂D₆/O₂ (solid lines) and C₂H₆/C₂D₆/O₂ (dashed lines) TPRe experiments

The participation of catalyst lattice oxygen in the ethane ODH reaction over Ni_{0.85}Nb_{0.15} was verified by the results of C₂H₆/¹⁸O₂ temperature programmed isotopic experiments. C¹⁶O₂ and H₂¹⁶O were the first products recorded followed by cross-labeled and ¹⁸O-isotopes, indicating the involvement of lattice oxygen in both the selective and unselective reaction pathways. Furthermore, throughout the experiment, neither ¹⁶O₂ nor ¹⁶O¹⁸O were formed, indicating irreversible oxygen dissociation.

Conclusions

The advanced temperature programmed isotopic experiments performed in this work show that, much like a typical Mars van Krevelen mechanism, the ODH reaction over Ni_{0.85}Nb_{0.15} catalyst proceeds via activation of C-H bonds by lattice oxygen, while gas phase oxygen reoxidizes the catalyst surface via irreversible dissociative chemisorption.

References

1. F. Cavani, N. Ballarini and A. Cericola, *Catal Today*, **127**, 113 (2007)
2. E. Heracleous, A.A. Lemonidou, *J. Catal.*, **237**, 162 (2006)
3. E. Heracleous, A.A. Lemonidou, *J. Catal.*, **237**, 175 (2006)
4. K. Chen, E. Iglesia and A.T. Bell, *J. Catal.*, **192**, 197 (2000)
5. A. Ozaki, *Isotopic studies of Heterogeneous Catalysis*, Academic Press, Tokyo, 1977