

Graphite as a selectivity controller of VAIO mixed (hydr)oxides for propane oxidative dehydrogenation

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Introduction

Heterogeneous catalytic oxidative dehydrogenation (ODH) reactions remain relevant to both industry and academia [1]. The major challenge in ODH is to control selectivity at high alkane conversion; where the alkenes are rapidly converted to CO_x. Supported vanadium oxides are classical catalytic systems for ODH [1,2]. The activity and selectivity of these materials is a function of the structural and molecular configuration of the vanadium oxide [1]. Vanadium-aluminium mixed hydroxides (VAIOs) are precursors of “VAION” oxynitrides which have presented interesting catalytic performance in ammoxidation reactions [3]. In this work, the performance of graphite modified VAIOs in the propane ODH reaction was evaluated.

Experimental

VAIO mixed hydroxides (V/Al ratio=0.25) were prepared by co-precipitation as presented in [4]. Graphite (G), 1 and 7wt.%, was added to the synthesized hydroxide VAIO powders during tableting. A part of the produced tablets were calcined 4h at 773K. The catalysts were marked according to their graphite content and pre-treatment using the nomenclature: VAIO-xG-NC,C, where, x=nominal graphite content; NC=non-calcined; and C=calcined. Characterization of the materials at different stages was carried out using techniques such as N₂ adsorption-desorption isotherm at 77K, XRD, Raman spectroscopy, XPS and hydrogen TPR. The propane ODH reaction was performed on a U-shape quartz reactor at 723 and 748K with a total gas flow of 40mL/min of composition C₃H₈/O₂/N₂= 10/15/75 (vol.%). The reaction products were analyzed using an on-line GC provided with FID and TCD detectors. Catalytic results were expressed in terms of the molar conversion of propane (X_{C₃H₈}) and oxygen (X_{O₂}) and the selectivity to propylene (S_{C₃H₆}) [5].

Results/Discussion

Figures 1a and 1b show the catalytic performance of the VAIO-xG-NC catalysts at the two different reaction temperatures. VAIO-0G-NC presents the highest propane and oxygen conversion at both temperatures. For this catalyst, selectivity to propylene drastically drops

when increasing reaction temperature: S_{C₃H₆}=0.57 at 723K and S_{C₃H₆}=0.18 at 748K. Such drop in propylene selectivity is accompanied by the complete conversion of gaseous oxygen (X_{O₂}=0.99) and a marked raise in propane conversion (X_{C₃H₈}=0.47). Propane conversion for VAIO-xG does not strongly depend on graphite loading. Furthermore, the catalysts containing graphite present a higher selectivity to propylene, regardless the reaction temperature. The highest selectivity to propylene was registered for VAIO-1G-NC, S_{C₃H₆}=0.76 at X_{C₃H₈}=0.11. Considering the registered trends one can say that graphite is playing a role in the dynamics of the ODH reaction mechanism. Changes in the hydrogen TPR patterns of the catalysts support this idea. The behaviour of the calcined catalysts goes in the same direction and relates the catalytic performance to the nature of the surface oxygen species of VAIO-xG. In addition, XRD, XPS and Raman analyses demonstrate that graphite does not alter the structural and oxidation state of vanadium and aluminium species of VAIO materials. In particular, Raman put in evidence the existence of a mixture of isolated VO_x species and metavanadate [(VO₃)_n]²⁻ species in the VAIO-xG-NC catalysts which are further transformed into decavanadates [V₁₀O₂₈]⁶⁻ and V₂O₅ species [14] during calcination.

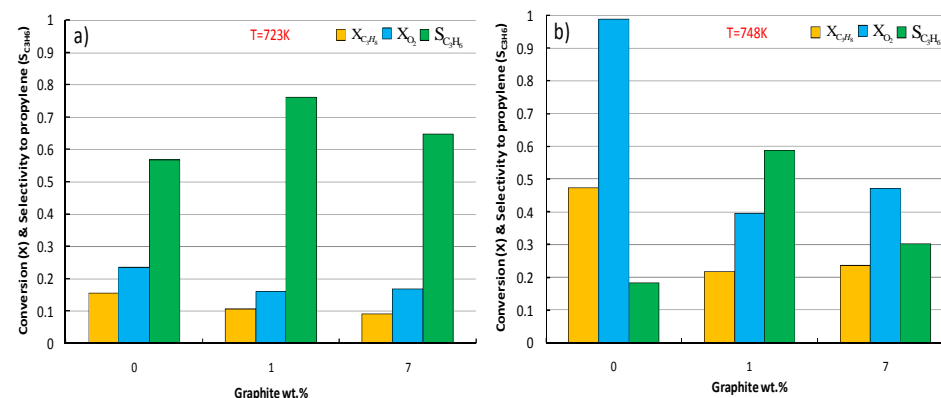


Figure 1. Catalytic performance, X_{C₃H₈}, X_{O₂}, and S_{C₃H₆}, of VAIO-xG-NC as a function of graphite loading: a) T=723K, b) T=748K.

References.

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