



VO_x/c-Al₂O₃ catalyst for oxidative dehydrogenation of ethane to ethylene: Desorption kinetics and catalytic activity

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ABSTRACT

This study reports ethane oxidative dehydrogenation (ODH) using lattice oxygen. Ethane ODH is studied under an oxygen-free atmosphere employing a 10 wt.% VO_x supported on c-Al₂O₃. TPR and TPO show that the prepared 10 wt.% VO_x supported on c-alumina catalyst is a stable catalyst over repeated reduction and oxidation cycles. XRD shows the absence of V₂O₅ bulk surface species and a high dispersion of VO_x on the support surface. Experiments are carried out in the CREC Fluidized Bed Riser Simulator at 550–600 °C and pressures close to atmospheric conditions. Reactivity tests show that the prepared ODH catalyst displays 6.5–27.6% ethane conversion and 57.6–84.5% ethylene selectivity in the 550–600 °C range. Metal–support interaction is assessed using ammonia TPD. This provides the desorption energy for both the bare c-Al₂O₃ support and for the VO_x/c-Al₂O₃ catalyst. A slightly increased desorption energy is found when using the V-loaded catalyst. This shows low metal–support interactions and as a result, a well dispersed VO_x catalyst phase with high availability of lattice oxygen for ODH. These findings are confirmed with XRD, showing no changes with respect to the XRD for the c-Al₂O₃ alumina support. This proves that there are no other species formed due to the interaction between the VO_x surface species and the Al₂O₃ support.

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1. Introduction

Light olefins, specifically ethylene and propylene, represent the most important building blocks of the petrochemical industry. Steam cracking of hydrocarbon feedstock (ethane, LPG, or naphtha) has been the major source of light olefins accounting for 70% of total olefin production [1]. Other methods for olefin production such as fluidized catalytic cracking (FCC) and direct dehydrogenation are also in use. Fluidized catalytic cracking (FCC) is the second most frequently used process for olefin production accounting for 28% of total gasoline production, with ethylene and propylene being in yields of 1–2% and 5%, respectively.

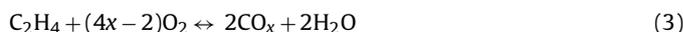
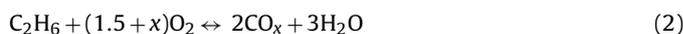
Current conventional processes for olefin production suffer from several limitations related to their high energy requirements due to the endothermic nature of the reaction, coke formation, selectivity control and thermodynamic constraints [1–7]. A number of alternative technologies have been investigated for olefin production [8–24]. These are currently being viewed as more and more attractive given the increasing demands for ethylene and propylene. Oxidative dehydrogenation (ODH) is an alternate method for

olefin production that does not suffer from the drawbacks of traditional methods. As an exothermic process, ODH can overcome the thermodynamic limitations of the non-oxidative dehydrogenation by formation of water, as a stable product. Moreover, ODH displays a large and positive equilibrium constant, decreasing at higher temperatures. Furthermore, the presence of oxygen limits coking and extends therefore catalyst usage. Moreover, light paraffins ODH can be operated at lower temperatures than either the thermal or the non-oxidative catalytic processes. So, ODH can thus offer potential increases in per-pass yields and energy savings while producing the desired olefins. Given that the formation of combustion products is thermodynamically favorable; selectivity control in ODH, reaction (1), is a major challenge. Undesired carbon oxides can be formed either by direct alkane combustion, reaction (2), or by deep oxidation of produced olefins, reaction (3). Thus, a catalyst for this reaction should be designed to prevent the undesirable reactions leading to carbon oxides [25–30].

Desired reaction:



Undesired reactions:



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