

Kinetic Study of the Oxidative Dehydrogenation of Propane (ODP) on promising model catalyst type VOx/TiOy/SBA15

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Introduction

Despite ODP has been extensively studied [1], its commercial application is still a big challenge. Bridging the gap between a detailed catalyst characterization, quantum chemical calculations, and kinetic studies (experimental and modelling), the last mentioned plays an important role to help to elucidate, or corroborate a proposed ODP reaction mechanism. From our data, plus a literature review, we are still far away from of a possible ODP industrial application. However, like it will be show in this work, using certain catalysts and operation conditions, the yield toward propylene is “acceptable” if we compare to those obtained by the majority of the catalysts in the ODP literature. To determine the economical attractiveness for an industrial process, one should consider the productivity, expressed in by means kilograms of desire product/kilogram of catalyst/hour, as a useful number to estimate if a catalyst can be consider either a candidate to scale-up or to substitute it by a better one if it is already applied at industrial scale. As pointed out by Cavani et. al. [1]: One is the productivity limit below which the productivity is too low to be of interest for commercial application. The highest productivity data found in literature are between 5.47 and 9.36 kgpropylene/kgcatalyst/hour using V/MCM48 catalysts [2]. However, taking into account only data under ODP conditions where homogeneous gas phase reaction as well as total oxygen conversion are excluded, the productivity has an upper limit of 2 kgpropylene/kgcatalyst/hour for all the catalysts containing vanadium [1]. In this study, we will present a detailed experimental kinetic study as well as kinetic modelling, of promising catalysts (from our previous studies) based on both, stability and productivity.

Experimental

The catalytic measurements were performed at ambient pressure in U-shaped fixed bed quartz reactors (i.d 6 mm). The feed consisted of synthetic air (20,5% O₂ in N₂) and propane, which were fed in the ratio 2:1 (C₃H₈/O₂/N₂ = 17,2/8,6/34,3). The experiments were performed at temperatures ranging from 440 up to 520 °C. The catalyst mass and the total flow rate were

varied from 1,5 to 250 mg and from 20 to 140 cc/min, respectively. The feed and the product components leaving the reactor were analyzed by an on-line gas chromatograph (GC, Shimadzu 2014) equipped with two packed columns (HayeSep Q and molecular sieve 13X).

Results/Discussion

Figure 1 shows both, the tested catalyst matrix (left), and the productivity as a function of propane conversion at 500°C (right). The tested catalyst-matrix provided us the basis to select the most promising VOx/TiOy/SBA15 catalyst for ODP.

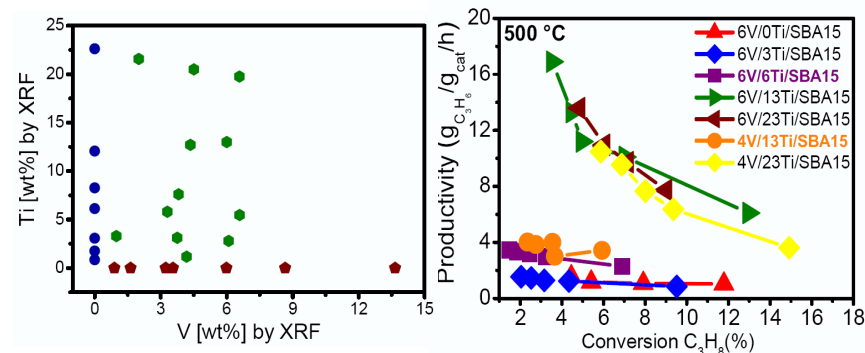


Figure 1. Productivity as a function of propane conversion at 500°C. Catalyst mass: 2-50 mg. Flows: 20 – 140 cc/min.

Under our conditions, the highest productivity values prevalent for all the catalysts with 23% wt Ti loading (Figure 1). However, the productivity towards propylene drop at longer residence times indicating that propylene easily burn into CO and CO₂ (Figure 1 right). Moreover, the catalysts 6V/6Ti/SBA15 and 4V/13Ti/SBA15 showed stable behaviour varying the residence times indicating that the propylene combustion occurs in less extent (Figure 1 right). Since the productivity data obtained with those catalysts are twice as high as those reported in Ref. [1], they will be extensively studied under ODP like it was done previously with low loading catalysts [3] in order to reveal the structure activity relationship behind this improvement in performance.

References.

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