

Influence of vanadium loading on the activity and selectivity of V/AlGaPO catalysts in the propane ammoxidation

M. A. Soria*, E.M Gaigneaux, P. Ruiz

Institute of Condensed Matter and Nanosciences – IMCN, Division Molecules, Solids and Reactivity – MOST, Université Catholique de Louvain, Croix du Sud 2/17, 1348 Louvain-la-Neuve, Belgium *e-mail address: patricio.ruiz@uclouvain.be

Introduction

Conversion of propane into acrylonitrile (ACN) by ammoxidation is an attractive route to the conventional propylene ammoxidation. However, the reaction conditions to activate the C-H bond of propane are more energy-demanding, which has a negative effect on selectivity. Much attention has been paid to the activity of various vanadium-based catalysts in propane ammoxidation. In a previous work, we have evidenced the possibility to dramatically boost the ACN selectivity of a $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ catalyst in the ammoxidation of propane by supporting vanadium oxide on it [1]. The present contribution deals with the study of the influence of V loading on the activity and selectivity of V/AlGaPO catalysts in the propane ammoxidation.

Experimental

Catalyst preparation: $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ support was prepared by the sol-gel method. V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ catalysts (2, 5 and 8% wt. of V) were prepared by impregnating the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ support with an aqueous solution of NH_3VO_4 . The solvent was evaporated, then dried at 110°C overnight and calcined in air at 500°C for 3h. **Characterization techniques:** Samples were characterized by BET-surface area, X-ray diffraction (XRD), NH_3 chemisorption, Raman spectroscopy and Temperature Programmed Reduction (TPR). **Catalytic Activity:** catalytic tests (0.1 g of catalyst, 28 ml/min total flow) were carried out in a conventional fixed bed quartz micro-reactor at atmospheric pressure and at 500, 530 and 550°C. Feed composition: $\text{C}_3\text{H}_8:\text{O}_2:\text{NH}_3=1.25:3:1$, balanced with He.

Results/Discussion

In the Fig. 1 one can note that propane conversion (XC_3H_8) increases with reaction temperature regardless of vanadium loading. In the whole temperature range studied, the 5V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ catalyst shows by far the highest activity. The selectivity towards acrylonitrile (SACN) over 2V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ and 8V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ increases with temperature but on 5V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ it reaches a maximum at 530°C and then decreases as the temperature is further increased. At a given temperature, the SACN strongly depends on V loading (Fig. 1): it increases as the V amount grows from 2 to 5 wt.% and then decreases when the V amount is increased up to 8 wt.%. 5V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ is, in general, the most selective catalyst.

XRD shows for the three samples V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ that, while they remained amorphous during the synthesis when V is absent, the impregnation of V identically induced their crystallization. The presence of the V in the sample favours the crystallization of $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ during preparation, which is interesting since pure amorphous $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ is stable even at 950°C [2]. Raman spectroscopy and XRD show the presence of crystalline V_2O_5 in the three V-based catalysts. XRD *in situ* measurements performed over the sample containing a 8% wt. of V in the same conditions as those used for calcination (air atmosphere, 500°C, 3h) shows that the support begins to crystallize at 450°C while V_2O_5 does at 500°C. This suggests that the vanadium species being able of inducing the support's crystallization are not crystalline V_2O_5 . All the V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ samples have specific surface areas and pore volumes smaller than their corresponding carriers: the higher the vanadium loading, the higher the decrease. This is likely caused by the blocking of the pores of the support by the crystallites of V_2O_5 . The reducibility of vanadium on the various samples depends on the loading showing the following trend (TPR- H_2):

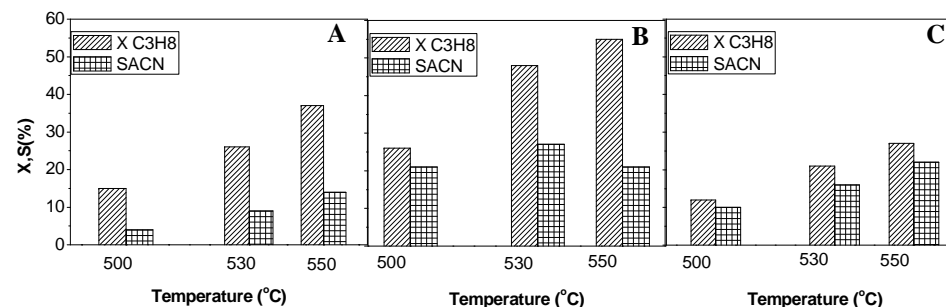
$$2\text{V}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4 > 5\text{V}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4 > 8\text{V}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$$


Fig.1. XC_3H_8 and SACN as a function of reaction temperature in the propane ammoxidation over: (A) 2V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$, (B) 5V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ and (C) 8V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$.

Our earlier study revealed the presence of a synergistic effect between V_2O_5 and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ [1]. The results of the present work seem to indicate that the synergy effect is higher in the 5V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ catalyst. Such an effect is even sharper at 530°C. XRD and physisorption of N_2 suggest that the extent of the synergy is not due to textural or structural changes. The propane conversion and ACN selectivity appear to be closely related to the redox properties of V catalysts. The intermediate reducibility of 5V/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ catalyst could be more suitable to enhance the extent of the synergy between V_2O_5 and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$, which would explain its higher catalytic performances.

References.

1. M.A. Soria, P. Ruíz, and E.M. Gaigneaux, *Catal Today* 128 (2007) 168-175.
2. V. Peltier, R. Conanec, R. Marchand, Y. Laurent, S. Delsarte, E. Guéguen, P. Grange, *Mat. Sci. Eng. B* 47,177 (1997)177.