Operando Raman-GC Study of Propane Selective Oxidation over Alumina -supported V_2O_5 and P_2O_5 Monolayer Type Catalyst

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Introduction and Objectives

Much attention has recently been devoted to the surface of bulk catalysts. Most critical phenomena in catalysis occur at the surface, which features differ significantly from those of the bulk. VPO materials are efficient catalysts for acrylonitrile production by propane ammoxidation reaction [1,2]. In order to understand the structure-activity relationship and the nature of the active site, *operando* Raman–GC analyses were employed to follow the states of vanadium and phosphorous species on alumina support during ammoxidation. V_2O_5 and P_2O_5 were supported on "Raman silent" γ-alumina by incipient wetness impregnation at a total V+P loading of two monolayers, which under reaction conditions lead to incipient formation of VPO crystallites possessing a high surface-to-volume ratio. The presence of VPO nanocrystals supported on alumina facilitates investigating the interaction between alumina-dispersed vanadia (V^{5+}) and VPO-lattice vanadium ions (V^{4+}). Thus it becomes possible to study surface species phase transformations near the surface, and relate changes in activity and selectivity to variations in composition and structure.

Results and Discussion

Vanadium and phosphorous supported γ-alumina catalysts were prepared by incipient wetness impregnation. Previous characterization by TPR, UV-Vis and XPS analyses confirm the predominance of V^{5+} in a fresh catalyst while a vanadyl pyrophosphate phase forms under reaction conditions. *Operando* Raman spectra of the VP/Al catalyst show that V^{5+} reduces to V^{4+} at 500 ^oC and the V^{5+}=O feature at 1022 cm^{-1} decreases in intensity, while a band due to $(VO)_2P_2O_7$ (V^{4+}) appears at 923 cm^{-1} (see Fig. 1). This suggest a combination of dispersed vanadium oxide and phosphorous into such VPO phase during reaction. The selectivity to acrylonitrile increases with increasing reaction temperature, and it shifts from acetonitrile to acrylonitrile just before the Raman band characteristic of $(VO)_2P_2O_7$ appears.

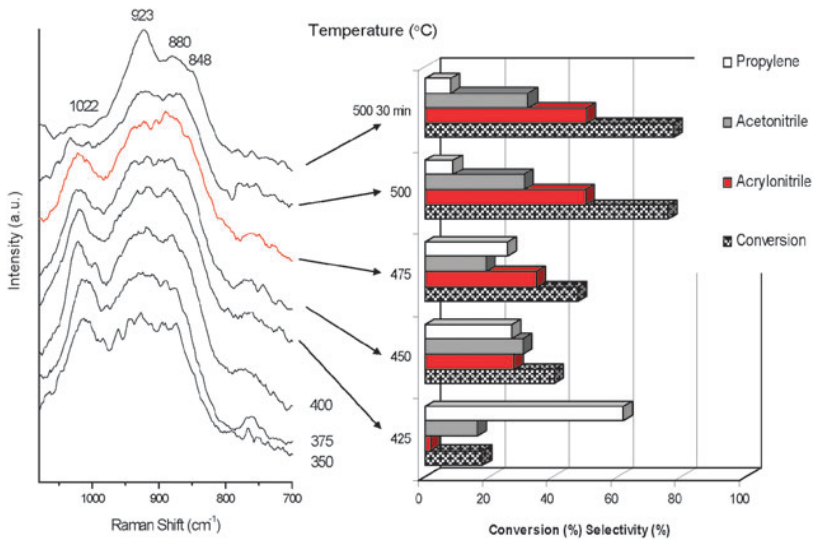

Figure 1 *Operando* Raman-GC study with product selectivities and propane conversion of VP/Al catalyst during propane ammoxidation reaction

The highest amount of the acrylonitrile is obtained in the presence of a slightly reduced catalyst, with high V^{4+} content, while a specific $V^{5+}/V^{4+}/V^{3+}$ equilibrium is probably reached under reaction conditions (seen by the bands at 1023, 927, 875 cm^{-1}). The oxidized sample (after exposure to air at 500 ^{o}C for 30 min) containing dispersed V^{5+} surface species is significantly more reactive towards propane, but acetonitrile becomes the main reaction product.

Conclusions

Dispersed V^{5+} species are stabilized on a lumina support; subsequently, vanadyl pyrophosphate phase forms during ammoxidation reaction. The stabilization of V^{4+} as $(VO)_2P_2O_7$ shifts the selectivity to acrylonitrile but an equilibrium between $V^{5+}/V^{4+}/V^{3+}$ rules during ammoxidation reaction. Catalysts containing higher amount of dispersed vanadium surface species (V^{5+}) is more active, but also more selective to acetonitrile.

References

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