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OXIDATIVE DEHYDROGENATION OF PROPANE AND n-BUTANE OVER ALUMINA SUPPORTED VANADIUM CATALYSTS

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Abstract - **Structural properties of vanadium dispersed species on γ-$A1_20_3$ are investigated with the scope to detect changes related with V loading in the oxidative dehydrogenation (ODH) of propane and n-butane. XPS, FTIR, and FTIR of absorbed pyridine were used to study the nature of vanadium supported species.**

Tetrahedral V^{5+} and probably V^{4+} species were detected. For vanadium loadings higher than 4.3 % wt octahedral species were also observed.

In the n-butane ODH reaction, the selectivity to ODH products decreases when vanadium content increases. However, for propane ODH, the selectivity seems to be independent of vanadium loadings.

Low oxygen/alkane feeding ratios favor selectivity to olefins. It is also shown that low V loading catalysts reach selectivities as good as best reported V-Mg-O catalyst.

Keywords – **Oxidative Dehydrogenation; Vanadium Catalysts; propane; n-butane.**

I. INTRODUCTION

Vanadium oxide dispersed on metal oxide supports exhibits interesting catalytic properties for partial oxidation of alkanes, aromatics and olefins (Bielanski and Haber, 1979; Dadyburjor at al., 1979; Mamedov and Cortés Corberán, 1995; Blasco *et al.*, 1995). The activity and selectivity of vanadia supported catalysts are deeply modified by the structure and physicochemical properties of the dispersed species supported on the surface (Dadyburjor *et al.*, 1979; Mamedov and Cortés Corberán, 1995; Yoshida *et al.*, 1988; Eon *et al.*, 1992; Koranne *et al.*, 1994).

MgO supported vanadium was reported as a very selective catalyst in the oxidative dehydrogenation of propane and n-butane (Kung and Chaar, 1988), while γ-$A1_2O_3$ supported vanadium catalyst was found to present a good selectivity to olefin products for ethane ODH but a poor selectivity in the ODH of n-butane (Concepcion *et al.*, 1994).

The acid-base character of the support explained this different behavior. On MgO, a support with basic properties, the interaction between vanadium species and the supports leads to the formation of vanadate compounds. In the case of more acid supports, such as SiO_2 or $A1_2O_3$ a weak interaction is expected leading to less dispersed vanadium species on the surface which, in turns favors the formation of V_2O_5 crystallites (Blasco at al., 1995; Galli at al., 1995).

Alumina-supported vanadia has been the object of several structural investigations (Haber *et al.*, 1986; Nag *et al.*, 1988; Eckert and Wachs, 1989; Andersen and Kung, 1992; Michalakos *et al.*, 1993). These studies show, in general, that at low loading vanadium form highly dispersed amorphous phases, whose structure changes from isolated tetrahedral vanadium, to polyvanadates species at medium loading. Crystalline V_2O_5 also appears at high loading in addition to amorphous vanadia phases.

The binding strength of oxygen lattice has been postulated as the parameter that governs activities and selectivities of these catalysts (Yoshida *et al.*, 1988). In this way VO_4 tetrahedra formed at low vanadium contents are related with high selectivities to alkenes because all the oxygen ions in these species are bridged between V and the metal ions of the support oxide (Michalakos *et al.*, 1993; Corma *et al.*, 1993a).

Other authors considered that -V_2O_7- units favor alkane ODH and suggested that the bridging oxygen ion between two vanadium ions (V-O-V) plays an important role in the propane ODH. The removal of' this oxygen results in a local structural change from the -V_2O_7- unit to two edge-sharing square-based -VO^{3-}- units where vanadium is present as V^{4+} cations (Eon *et al.*, 1994). These stabilized V^{4+} ions were postulated as responsible for the dehydrogenation selectivity of pyrovanadate structure.

As V^{4+} ions are also present in selective ODH catalysts like Mg pyrovanadate and Mg orthovanadate (Kung and Kung, 1992; Gao *et al.*, 1994), Mamedov and Cortés Corberán (1995) suggest that a certain extent of reduction is needed for the selective dehydrogenation of alkanes. But they also emphasize that a good selectivity can be achieved by controlling reaction conditions (temperature and alkane to oxygen ratio).

The aim of this paper is to further study the nature of active sites and the influence of the acid-base character of the vanadium supported catalysts on the selectivity for the ODH of propane and n-butane. For this purpose V/γ-$A1_2O_3$ catalysts have been prepared with different degrees of coverage using incipient wet impregnation techniques.

II. EXPERIMENTAL

A. Catalyst Preparation

Alumina support was Aldrich, surface area 132 m^2g^{-1}. Catalysts were prepared by impregnation of the support with an aqueous solution of ammonium metavanadate (from Fluka p.a.). The impregnated samples were dried