OXIDATIVE DEHYDROGENATION OF PROPANE OVER (Mo)-Sm-V-O CATALYTIC SYSTEM. ROLE OF THE DIFFERENT PHASES

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Abstract - The (Mo)-Sm-V-O catalytic system has been exhaustively studied in the propane oxidative dehydrogenation reaction. In order to obtain different surface arrangements, simple oxides (V₂O₅, Sm₂O₃ and MoO₃), SmV mixed oxides with different Sm/V molar ratio and SmVO₄ impregnated with vanadium, samarium or molybdenum were prepared. The function that the possible arrangements play has been identified. A slight samarium excess favors total combustion causing a strong drop of selectivity, therefore, it is necessary to avoid it. On the other hand, vanadium excess constituting surface vanadium oxide species (VOₓ) notably increases the catalytic activity while a higher vanadium amount leads to crystalline V₂O₅ formation and the catalyst behavior tends to that of bulk V₂O₅. Molybdenum at low concentrations constitutes surface molybdenum oxide species (MoOₓ) which showed to be highly selective in propane ODH. High contents of molybdenum favor the formation of crystalline MoO₃, thus, causing an important catalyst deactivation. Finally, a comparison with other known efficient vanadium based catalysts is made and hence, the potentiality of (Mo)-Sm-V-O catalysts is shown.

Keywords - oxidative dehydrogenation, propane, vanadium, samarium, molybdenum.

II. EXPERIMENTAL SECTION

A. Catalysts preparation

Simple oxides. V₂O₅ was prepared by calcination in air of NH₄VO₃ (Mallinckrodt) at 450°C for 4 h. Sm₂O₃ and MoO₃ from commercial origin were used.

Mixed oxides. Samples with atomic ratios Sm/V = 0.8, 1 and 1.2 were prepared by the citrate method (Courty, 1973). Sm(NO₃)₃.6H₂O (Fluka), NH₄VO₃ (Merck) and citric acid (Aldrich) were used as reagents. A citric acid solution with a 10% excess over the number of ionic equivalents of cations was prepared. Transparent solutions of samarium nitrate and ammonium metavanadate were prepared and added to the citric acid solution in such concentration that the Sm/V atomic ratio was equal to that in the resulting catalysts. The resulting solution was concentrated in a Rotavapor at 70°C under reduce pressure until the solution became viscous. Then, it was dried to obtain amorphous organic precursor. The solid obtained was decomposed in air of 400°C for 4 h and finally calcined at 600°C for 3 h. These catalysts were denoted as SmVₓ, where x = 0.8, 1 or 1.2 indicates the Sm/V atomic ratio.