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DEHYDROGENATION AND OXIDATIVE DEHYDROGENATION OF ALCOHOLS ON SILICA SUPPORTED CHROMIUM CATALYSTS

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Abstract - The catalytic activity of Cr/SiO_2 (0.43 to 2.8% chromium by weight), prepared by the ion exchange method, for the dehydrogenation (573 K to 613 K) and oxidative dehydrogenation (503 K to 558 K) of alcohols has been investigated. The results obtained are consistent with the hypothesis that the Lewis pyridine centers of chromium are the active sites for alcohol dehydrogenation. At 593 K the selectivity to aldehyde is 70% while selectivity to acetone is 62%, for pure dehydrogenation. The dehydrogenation rate of the secondary alcohol is one order of magnitude higher than that observed for primary ones. The catalytic activity for oxidehydrogenation is 12 times higher than for pure dehydrogenation and the reaction rate of primary alcohols are higher than for secondary ones. When the ratio of oxygen to alcohol partial pressures is 1:2 or above, the selectivity to aldehydes reach values of 97%, 89% and 80%, for ethanol, propanol and butanol, respectively, while the selectivity for secondary alcohols remains as in dehydrogenation (≈ 60%).

Keywords - Chromium catalysts; ion exchange; alcohol; dehydrogenation; oxidehydrogenation.

1.INTRODUCTION

Silica is an important material in catalysis due to its stability and mechanical strength, and more specifically to the hydroxyl groups on its surface. These surface groups of silica are potential cation exchange sites for transition metal ions; which is the base of the "ion exchange method" to prepare well disperse and active catalysts. However, the limiting factor that determines the exchangeability of a cationic specie is the pKa of the silanol proton (pKa > 9) onto the silica (Lunsford *et al.*, 1988).

Different chromium complexes have been used to prepare these materials, such as chromium (III) acetylacetonate by deposition of the complex from the gas phase or hexa aquo chromium ions $[Cr(H_2O)_6]^{+3}$ by ion exchange. Nevertheless the size of the complex in the first case or the basic character of the ligand in the second, are not adequate to ensure the interaction, leading to a very low exchange (White, 1993).

In general, the chromium catalysts are prepared by the conventional impregnation procedure. It is well known that these chromium-based catalysts are used in very important industrial processes such as the polymerization of ethylene, hydrogenation and dehydrogenation of hydrocarbons, gas phase oxidation, etc. (Rao *et al.*, 1996; Sarbak, 1995; Chudek *et al.*, 1996; Joseph *et al.*, 1995). The catalytic conversion of alcohols into aldehydes and ketones is essential for the preparation of many synthetic intermediates in organic chemistry, as was recently pointed out by Friedrich (1999).

In this paper, the study of alcohols dehydrogenation and oxidehydrogenation performances of silica supported chromium catalysts,