EFFECT OF THE ACID-BASE PROPERTIES OF Mg-Al MIXED OXIDES ON THE CATALYST DEACTIVATION DURING ALDOL CONDENSATION REACTIONS

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Abstract— The effect of chemical composition of Mg-Al mixed oxides on both the acid-base properties and the deactivation process during the gas phase self-condensation of acetone was studied. The activity and selectivity for acetone oligomerization depended on the catalyst acid-base properties. Mg-rich catalysts selectively yielded mesityl oxides whereas Al-rich Mg$_y$Al$_{1-x}$O$_x$ oxides produced mainly isophorone. The initial deactivation rate, increased linearly with the density of surface basic sites, thereby suggesting that although Mg$_y$Al$_{1-x}$O$_x$ oxides promote the self-condensation of acetone by both acid- and base-catalyzed mechanisms, the deactivation rate would be closely related to the surface basic properties. The Mg$_y$Al$_{1-x}$O$_x$ activity declines in the acetone oligomerization reaction due to a blockage of both base and acid active sites by a carbonaceous residue formed by secondary reactions. The amount and the nature of the carbon deposits were characterized by temperature-programmed oxidation technique. Mg$_y$Al$_{1-x}$O$_x$ and Al$_2$O$_3$ formed more and heavier coke than pure MgO but the latter deactivates faster. The deactivation rate and coke composition are defined by the nature of the active site involved in the coke-forming reactions at different catalyst compositions rather than by the carbon amount or polymerization degree.

Keywords— Catalyst Deactivation, Acetone Oligomerization, Acid-Base Catalysis

I. INTRODUCTION

Mg-Al mixed oxides obtained by thermal decomposition of anionic clays of hydrotalcite structure, present acidic or basic surface properties depending on their chemical composition (Di Cosimo et al., 2000). These materials contain the metal components in close interaction thereby promoting bifunctional reactions that are catalyzed by Brönsted base-Lewis acid pairs. Among others, hydrotalcite-derived mixed oxides promote aldol condensations (Reichle, 1985), alkylation (Velu and Swamy, 1996) and alcohol eliminations (Di Cosimo et al., 2000). In particular, we have reported that Mg-Al mixed oxides efficiently catalyze the gas-phase self-condensation of acetone to α,β-unsaturated ketones such as mesityl oxides and isophorone (Di Cosimo et al., 1998a). Unfortunately, in coupling reactions like aldol condensations, basic catalysts are often deactivated either by the presence of byproducts such as water in the gas phase or by coke build up through secondary side reactions. Deactivation has traditionally limited the potential of solid basic catalysts to replace environmentally problematic and corrosive liquid bases. However, few works in the literature deal with the deactivation of solid bases under reaction conditions. Studies relating the concerted and sequential pathways required in the deactivation mechanism with the acid-base properties of the catalyst surface are specially lacking. In this work, we studied the deactivation of Mg-Al mixed oxides in the gas phase oligomerization of acetone. We prepared and characterized calcined Mg-Al hydrotalcites with Mg/Al atomic ratios of 1-9. The effect of composition on both the surface and catalytic properties as well as the catalyst deactivation were investigated by combining several characterization methods with catalytic data.

II. METHODS

A. Synthesis Procedures

Mg/Al hydrotalcite with Mg/Al atomic ratios (y) of 1, 3, 5 and 9 were prepared by coprecipitation of Mg(NO$_3$)$_2$·6 H$_2$O and Al(NO$_3$)$_3$·9 H$_2$O at 333 K and pH = 10. After drying overnight at 348 K, precursors were decomposed in N$_2$ at 673 K in order to obtain the Mg$_y$Al$_{1-x}$O$_x$ mixed oxides. More experimental details are given elsewhere (Di Cosimo et al., 2000). Reference samples of Al$_2$O$_3$ and MgO were prepared following the same procedure.

B. Methods for the Sample Characterization

The crystalline structure of the samples was determined by powder X-ray diffraction (XRD) methods. Acid site densities were measured by temperature-programmed desorption (TPD) of NH$_3$ preadsorbed at room temperature. The structure of CO$_2$ chemisorbed on hydrotalcite-derived samples was determined by infrared spectroscopy (IR). CO$_2$ adsorption site