

CHARACTERIZATION AND CATALYTIC ACTIVITY OF ZIRCONIUM DIOXIDE PREPARED BY SOL-GEL

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Abstract — Zirconia samples prepared from $Zr(n-OC_3H_7)_4$ and $ZrOCl_2$ were characterized by XRD, BET surface area, TG-DTA, TEM/SEM, FTIR, and D_2O exchange. Oxides obtained from the alkoxide contain two types of hydroxyl groups at 3704 and 3597 cm^{-1} , which do not exchange with D_2O . Those obtained from $ZrOCl_2$ produced three types of hydroxyl groups at 3774, 3733 and 3671 cm^{-1} , which do exchange with D_2O . Surface acidity was determined by FTIR of adsorbed lutidine. Only Lewis acid sites were found on samples from $ZrOCl_2$ hydrolysis. FTIR spectra of calcined samples exhibited strong absorption bands in the 1800 to 1000 cm^{-1} region, which are ascribed to various types of carbonate and bicarbonate species. These ones are strongly adsorbed on the surface oxide and they are removed only after 3 hours at 600 °C in stream of H_2 . Samples derive from the alkoxide precursor restore the original carbonate species after exposure to O_2 at 600°C. Catalytic activity for *i*-propanol dehydration/dehydrogenation showed the absence of basic centers and an intermediate dehydration activity between that of silica and alumina.

Key words — Zirconium oxide, zirconia, acidity, FTIR, 2,6-lutidine.

I. INTRODUCTION

Zirconia is a very important ceramic material with growing application to heterogeneous catalysis both as active material and support. For example, Miller and Grassian (1995) have tested the decomposition of NO on zirconia nanoparticles and suggested that it occurs in Lewis acid sites. Yokoyama *et al.*, 1992) have found a correlation between the surface acid-base properties and the activity to reduce carboxylic acid to aldehydes. Various authors (Nakano *et al.*, 1979; Ferino *et al.*, 2000; He and Ekerdt, 1984a and He and Ekerdt, 1984b) have reported on the catalytic activity of zirconia to the selective dehydration of secondary alcohols to terminal alkenes as well as to the hydrogenation of CO to isobutane.

Zirconium oxide can be prepared by the sol gel technique (Brinker and Scherer, 1990) using inorganic precursors, like $ZrOCl_2$, or metalorganic ones, as zirconium alkoxides.

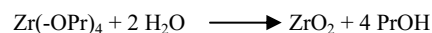
The aim of this work was the characterization of zirconia pure samples, prepared from $ZrOCl_2$ or $Zr(n-OPr)_4$, as well as to establish a correlation between superficial properties and preparation methods.

II. EXPERIMENTAL

A. Sample preparation

A 0.01 M aqueous solution of $ZrOCl_2 \cdot 8H_2O$ was neutralized by slowly adding 1M solution of NH_4OH to the gel formation. The gel was washed with absolute ethanol to negative chloride test.

0.1 M solutions of $Zr(n-OC_3H_7)_4$ in absolute ethanol were mixed with 0.1 M water/ethanol solutions (Davies *et al.*, 1995 and 2000). A white fine precipitate appeared immediately after mixing both solutions. The molar ratio water/alkoxide, *h*, was fixed at 2 and 16. Molar ratio equal to 2 is considered the stoichiometric one in accord to the following equation (Brinker and Scherer, 1990):



For both preparations, solvent was removed at 60°C in a vacuum rotary evaporator and solids were dried overnight at 120°C. Finally, samples were calcined at least for 3 hours at 600°C

B. Characterization methods

Self-supporting wafers (7 mm diameter) for FTIR analysis were obtained from dried samples and then calcined up to 600°C for three hours. FTIR studies were performed in a quartz cell which had KRS5 windows. The cell, connected to a vacuum system (10^{-2} Torr), allows *in situ* thermal treatment of samples from room temperature up to 600°C. All FTIR spectra were obtained at room temperature with a Bruker IFS 88 (4 cm^{-1} resolution).

After evacuation at 300°C and cooling down to room temperature, D_2O vapor was admitted into the cell followed by taking the FTIR spectra at increasing evacuation temperatures. Acidity studies were performed using 2,6-dimethylpyridine (2,6-lutidine) as probe molecule following a similar procedure to that with D_2O . Treatments with a stream of H_2 and O_2 up to 600°C were followed to analyze the evolution of carbonates.