

Diffuse Reflectance Spectroscopy Study of the Thermal Genesis and Molecular Structure of Chromium-Supported Catalysts

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The diffuse reflectance spectra of a series of chromium-supported silica aluminas, with varying SiO₂ content, have been investigated before and after drying and after calcination, successive CO reductions, and recalcination. The molecular structure of chromium before drying is influenced by the isoelectric point (IEP) of the supports. It is concluded that the lower the IEP of the support, the higher the amount of surface dichromate. After calcination at 720 °C, Cr is anchored to the surface without changing the chromate:dichromate ratio. Reduction results in the formation of octahedral Cr³⁺, pseudooctahedral and pseudotetrahedral Cr²⁺. A higher silica content of the support, a higher reduction temperature, and a higher calcination temperature result in a deeper reduction of the supported Cr. Recalcination restores the initial chromate:dichromate ratio on each support; however, small quantities of Cr³⁺ remain in the samples. This deeper reduction and reversibility can be explained by the low OH content of the supports calcined at 720 °C.

Introduction

Chromium-supported catalysts are usually prepared by impregnation of a chromium salt onto the support, followed by drying and calcination. During the calcination procedure, the thermodynamically favored reaction " $\text{CrO}_3 \rightleftharpoons \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{2}\text{O}_2$ " does not take place (or only to a small extent) in the presence of an oxide support. This phenomenon is generally explained by the anchoring of Cr onto the support (=stabilization). However, the molecular structure of the anchored Cr⁶⁺ species and the kind of interaction between Cr and the support are points of discussion in the literature.

The surface complex is considered to be chromate and/or dichromate,¹⁻⁸ but also the presence of polychromates^{9,10} and highly distorted monochromate¹¹ is claimed. Several types of interactions of the surface complexes are proposed in the literature. Most investigations assume an esterification reaction between chromic acid and the hydroxyl groups of the supports, resulting in the formation of surface chromates and/or dichromates (and polychromates).^{1,4,8,12} The exothermal peak in differential thermal analysis (DTA) curves of Cr-supported catalysts around 250 °C is ascribed to this reaction.⁸ Additional evidence comes from infrared (IR) investigations, indicating a consumption of OH groups by depositing Cr on the support.³ This OH consumption is proportional to the quantity of deposited Cr. Recently, Turek et al. have shown that on Al₂O₃ this OH consumption starts from the more basic OH groups to the more acidic groups, indicating an acid-base type reaction.¹³ McDaniel has followed the reaction between CrO₂Cl₂ and silica, observing the release of HCl.^{1,5} This can be explained only by the reaction of surface hydroxyls with the Cr precursor.

A similar reaction between CrO₃ and the support is envisaged by Wittgen et al.,¹⁴ Ellison et al.,¹⁵ Iwasawa et al.,¹⁶ and Hogan.¹⁷ In accordance with Turek et al.,¹³ Ellison et al.¹⁵ and Fubini et al.¹⁸ suggest a decondensation of the polyanions, followed by chemisorption of the monomeric species, while Bhutani et al.¹⁹ suggest a ligand-exchange reaction between Cr and Sb₂O₃.

In a previous study we have reported the quantification of Cr²⁺, Cr³⁺, and Cr⁶⁺ by diffuse reflectance spectroscopy (DRS) after calcination at 550 °C, successive CO reductions and recalcination.² On the calcined catalysts chromate and dichro-

TABLE 1: Characteristics of the Supports

SA- <i>n</i> with <i>n</i> =	BET surface area (m ² /g)	pore vol (mL/g)	pore size (nm)
0	365	2.0	3-9
20	337	1.7	1.5-8
40	329	1.4	1.5-7
60	253	1.0	1.5-10
100	735	0.8	1-3

mate are present with traces of Cr⁵⁺. The dichromate:chromate ratio is the highest for silica, zero for alumina, and in between for silica alumina. After reduction three new species were formed: octahedral Cr³⁺, pseudooctahedral Cr²⁺ and pseudotetrahedral Cr²⁺. On alumina only octahedral Cr³⁺ and small portions of octahedral Cr²⁺ were observed, while on silica and silica alumina the Cr²⁺:Cr³⁺ ratio increases with the silica content.

In this work three subjects will be studied systematically: (1) the interaction between Cr and the support before and after drying, after calcination and after rehydration; (2) the influence of the SiO₂:Al₂O₃ ratio of the amorphous supports on the molecular structure of supported Cr after calcination; (3) the influence of a high-temperature calcination (720 °C) and the SiO₂:Al₂O₃ ratio of the amorphous supports on the speciation of reduced and recalcined Cr.

Experimental Section

Sample Preparation and Characterization. *Preparation.* A series of SiO₂:Al₂O₃ was prepared following a modified method of Chen et al.²¹ They are indicated as SA-*n*, where *n* is the weight percentage of SiO₂. The appropriate amounts of tetraethylorthosilicate (TEOS) and aluminum triisopropoxide (Al(*i*P)₃) were mixed in 128 mL of ethanol during 30 min at room temperature. After addition of 35 mL of 1 M HCl, the acid hydrolysis started and the suspension was mixed for 1 h. The resulting gel was dried at 60 °C and 100 °C for 8 h and calcined at 550 °C for 16 h. The obtained samples were crushed. SiO₂ was prepared following a procedure described previously.² The Cr catalysts were prepared by the incipient wetness method with chromium(VI) oxide (CrO₃). The chromium loading was 0.2 wt %.

Characterization. The characteristics of the supports were measured by dynamic N₂ adsorption on an Omnisorp 100 (Coulter), after pretreatment in vacuum at 200 °C for 8 h. These characteristics are given in Table 1.

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