

A Quantitative Diffuse Reflectance Spectroscopy Study of Supported Chromium Catalysts

Bert M. Weckhuysen,* Leo M. De Ridder, and Robert A. Schoonheydt

Centrum voor Oppervlaktechemie en Katalyse, K.U. Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium

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The diffuse reflectance spectra of chromium supported on alumina, on silica, and on silica–alumina have been investigated after calcination, CO reduction, and recalcination. A method for quantifying the Cr⁶⁺, Cr³⁺, and Cr²⁺ concentrations was developed. After calcination at 550 °C, the chromate:dichromate ratio is ∞, 0.56, and 2.18 on respectively alumina, silica, and silica–alumina. Reduction results in the formation of three new species: octahedral Cr³⁺, octahedral Cr²⁺, and pseudotetrahedral Cr²⁺. On silica and silica–alumina, the relative proportions of these three species depend on the reduction temperature. On alumina, only octahedral Cr³⁺ and small amounts of octahedral Cr²⁺ were observed after reduction. Recalcination reestablishes the chromate:dichromate ratio; however, this regeneration is complete only on silica. On alumina and silica–alumina, about one-third and two-thirds respectively of the total Cr content remain as Cr³⁺. The sensitivity of Cr⁶⁺ to reduction is greater on silica than on alumina and silica–alumina. This is indicated by the increase of the Cr²⁺:Cr³⁺ ratio from alumina over silica–alumina to silica.

Introduction

Chromium on silica (Cr/SiO₂) is the famous Phillips catalyst for the polymerization of ethylene under relatively low pressures.¹ This catalyst is the basis for the Phillips particle-form process in the production of high-density polyethylene,² and the use has been extended to the production of linear low-density polyethylene³ and the copolymerization of ethylene and butene-1.⁴ Chromium on silica–alumina (Cr/SiO₂·Al₂O₃) catalyses the polymerization of propylene⁵ and chromium on alumina (Cr/Al₂O₃) catalysts are active in the dehydrogenation of alkanes, in dehydrocyclization, and in catalytic reforming.⁶

The Phillips catalyst is one of the most studied and yet most controversial systems,⁷ while the studies of Cr/Al₂O₃ and Cr/SiO₂·Al₂O₃ are more limited. All these studies deal with the formation and nature of the chromium species on the catalyst surface or with the associated problem of identifying the valence state of the species which are responsible for catalysis. Different techniques, such as infrared spectroscopy (IR),⁸ diffuse reflectance spectroscopy (DRS),⁹ X-ray photoelectron spectroscopy (XPS),¹⁰ Raman spectroscopy,¹¹ and electron spin resonance (ESR),¹² were used. There is a general consensus that the detectable oxidation states are Cr⁶⁺, Cr⁵⁺, Cr³⁺, and Cr²⁺. However, the coordination geometry of these surface complexes and the degree of polymerization of Cr on the surface are a matter of debate.

After calcination, most of the Cr is stabilized as Cr⁶⁺ on the SiO₂ and Al₂O₃ surfaces; only the exact mechanism of stabilization and the molecular structure of the stabilized Cr⁶⁺ species are points of discussion. According to Hogan and McDaniel, only chromate is formed on the SiO₂ surface,^{13,14} while other research groups favor the formation of dichromate.^{15–19} Raman studies on Cr/SiO₂ give evidence for mono-, di-, tri-, and tetramers under hydrated conditions²⁰ and highly distorted monochromate under dehydrated conditions.²¹ On Al₂O₃, mostly chromate is formed after calcination.^{17,22} However, Raman studies reveal the presence of monomers and dimers under hydrated conditions²⁰ and polymeric oxide species under dehydrated conditions.²³ To our knowledge, the molecular structure of Cr on SiO₂·Al₂O₃ is not yet reported in the literature.

Reduction of the calcined catalysts results in the formation of traces of Cr⁵⁺, Cr³⁺, and Cr²⁺, but the relative proportion of these species depends on the reduction temperature and on the

support. The coordination of the reduced species is unclear. Cr³⁺ is mostly thought of as octahedral, but according to Myers and Lunsford, a small part can be in a lower symmetry.²⁴ Cr²⁺ can be unsaturated, tetrahedrally coordinated, and square-planar.^{18,19,26,29}

Table I give a survey of DRS absorption bands and proposed assignments. All these DRS studies are qualitative, describing the different oxidation states formed after calcination and reduction. However, the data of different groups cannot be easily compared because of differences in pretreatments and Cr loadings. Therefore, the purpose of this work is a quantitative study of chromium-supported catalysts by DRS. This technique allows the quantitative determination of Cr²⁺, Cr³⁺, and Cr⁶⁺ after calcination, reduction, and recalcination at least at small loadings. The redox behavior of Cr on Al₂O₃, SiO₂, and SiO₂·Al₂O₃ will be discussed.

Experimental Section

Sample Preparation and Characterization. 1. Preparation. SiO₂ and SiO₂·Al₂O₃ were home-made. SiO₂ was prepared by mixing 2 vol parts H₂O at pH 2 (adding HCl) and 1 vol part tetraethyl orthosilicate (TEOS) during 5 h at room temperature. The mixture was titrated under stirring to pH 6 with a NH₄OH solution of pH 9.5. After 16 h of gelation, the gel was dried at 130 °C for 72 h and calcined at 250 and 550 °C for respectively 3 and 16 h. The so-obtained cake was crushed. SiO₂·Al₂O₃ with 40 wt % SiO₂ was prepared following a modified method of Chen et al.³³ TEOS (35.5 g) and aluminum triisopropoxide (65.36 g) were mixed in 128 mL of ethanol during 30 min at room temperature. After adding 35 mL of 1 M HCl, the hydrolysis started and the solution was mixed for 1 h. Acid hydrolysis resulted in a sol and a flocculated phase, suggesting a heterogeneous SiO₂·Al₂O₃. The gel was dried at 60 and 100 °C for 8 h for both and calcined at 550 °C for 16 h. The SiO₂·Al₂O₃ cake was crushed. Al₂O₃ was delivered by Rhône Poulenc (reference number EC 21/581/88). The Cr catalysts were prepared by the incipient-wetness method with chromium(VI) oxide (CrO₃). The chromium loadings were 0.1, 0.2, 0.4, and 0.8 wt %.

2. Characterization. The characteristics of the supports were measured by dynamic N₂ adsorption on an Omnisorp 100 (Coulter), after pretreatment in vacuo at 200 °C for 8 h. SiO₂ had a BET surface area of 735 m²/g, a pore volume of 0.8 mL/g, and a pore size of 1–3 nm. SiO₂·Al₂O₃ had a BET surface area

* To whom correspondence should be addressed.