

DRIFTS and DRS studies of Phillips ethylene polymerization catalysts

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Abstract

Formation of the $\text{CrO}_3/\text{SiO}_2$ catalyst prepared by the reaction of CrO_3 vapor with silica pre-dehydroxylated at 250–800 °C was studied by the DRIFT and DRS methods. It was found that CrO_3 reacts with the silica OH-groups at 250 °C to produce various chromate species and water. The latter is removed from the catalyst surface by vacuumation at 250 °C. It was found the nature of CrO_3 interaction with silica and the structure and composition of the surface species depend on silica dehydroxylation temperature. The reactions of CrO_3 with the silica dehydroxylated at 250, 400 and 800 °C yielded, respectively, monochromates; mono- and dichromates; polychromates. The catalyst activity at ethylene polymerization strongly increases with increasing dehydroxylation temperature, especially in the range of 250–400 °C. The results obtained prove di- and polychromates to be the active components of the Phillips type chromium-oxide catalysts from which the active centers are formed at interaction of the active component with co-catalyst (AlEt_3) and ethylene. Active centers contain the surface organo-chromium compounds with chromium ions in low oxidation states (lower than Cr(VI)).

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1. Introduction

Chromium-oxide catalysts (Phillips catalysts) for ethylene polymerization are known since the late 1950s. Although the catalysts have been studied intensively, numerous questions regarding the structure and composition of the surface chromium species, mechanisms by which they convert to active centers of polymerization, structure and composition of these active centers remain open and are still discussed in literature [1–9].

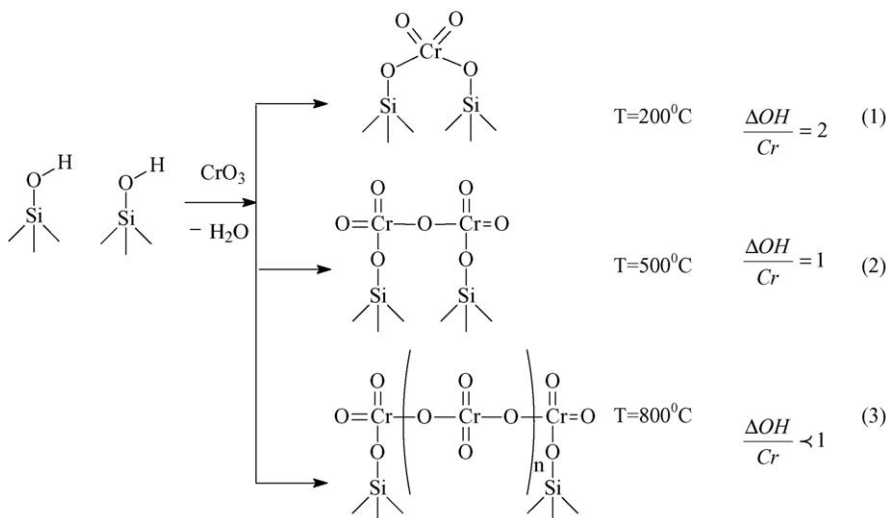
Phillips catalysts are usually prepared by impregnating of silica with an aqueous solution of a chromium compound, for example, CrO_3 , chromium acetate, chromium nitrate, etc. During subsequent activation in a flow of dry oxygen or air at 400–800 °C, Cr(VI) species of various composition are assumed to form on the catalyst surface [1,2,6–9].

The composition of surface chromium species in Phillips catalysts has been studied by various methods. Based on gravimetric measurements, Hogan [10] suggested monochromates to be the predominant species on the surface of the $\text{CrO}_3/\text{SiO}_2$ catalyst activated at 150 °C. UV–vis studies performed by

Zeccina et al. [11] proved dichromates to form in the chromium-oxide catalysts activated at 500–600 °C. Later, XPS studies showed that during activation of the Phillips catalysts in the flow of dry air at 450–650 °C chromium oxide can anchor on silica support through ester bonds Cr-O-Si , yielding surface chromate species [1,12,13]. Weckhusen et al. studied the feasibility to identify mono- and dichromate species in the Phillips catalysts by UV–vis spectroscopy [14,15]. However, the method appeared applicable only for chromium-oxide catalysts supported on alumina or aluminosilicates. Richter et al., based on the laser Raman spectroscopy data [16], suggested that dichromates are formed predominantly in the Phillips catalysts prepared by impregnating aqueous chromic acid on silica, followed by calcination at 500 °C. Similar conclusions were suggested in other works on the base of Raman and IR spectroscopic data [17–19]. McDaniel [20,21] applied the method of gravimetric measurements for the studies of the reaction of CrO_3 with the silica OH-groups in the catalysts activated at various temperatures (200–800 °C). Amount of water losses in the catalysts calcined at various temperatures were measured and the data obtained were used to calculate the molar fraction of Si–OH groups reacted with CrO_3 . It was found that molar ratio of the reacted OH-groups to Cr content in the catalyst ($\Delta[\text{OH}]/[\text{Cr}]$) depends on the activation temperature and varied from 2

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Scheme 1. Formation of the surface chromates in the reaction between silica and CrO_3 .

(at 200 °C) to 1 (at 500 °C); at higher temperature $\Delta[\text{OH}]/[\text{Cr}]$ was considerably below 1. It was concluded that the activation temperature affects the formation of the surface chromium species (Scheme 1, Eqs. (1)–(3)).

However, the method of gravimetric measurements gives little chance for reliable differentiation of water released by the reaction of CrO_3 with Si–OH groups from water originating from dehydroxylation of silica upon the catalyst calcination. The DRIFTS method allows direct tracing the CrO_3 interaction with silica hydroxyl groups. However, it is necessary to exclude the using of aqueous solutions of chromium compound for preparing of chromium-oxide catalysts to get the reliable data by this method. In this work, we applied the DRIFTS and DRS methods to study the catalysts prepared by reacting CrO_3 vapor with the silica pre-dehydroxylated in vacuum at various temperatures (250–800 °C).

2. Experimental

All steps of catalysts synthesis and activation, DRIFTS and DRS studies were performed under vacuum. The “break seal” technique has been used for preparing and investigation of the catalysts.

2.1. Synthesis of catalyst

The measured sample of silica (Davison 952 (300 m^2/g)) was heated in air at 500 °C for 3 h, then placed into a glass or quartz ampoule and dehydroxylated in vacuum at 250, 400 or 800 °C for 4 h.

Dehydroxylated silica was mixed with a measured amount of CrO_3 powder (to yield 1 wt.% of Cr in the catalyst). It is known that CrO_3 is stable at heating up to 250 °C and sublimates at 180 °C [22]. The mixed components were heated at 250 °C for 1 h under periodic shaking (Stage 1, precatalyst $\text{CrO}_3/\text{SiO}_2$ (T_d), where T_d is the temperature of silica dehydroxylation). Then the catalyst was vacuumed at 250 °C for 1 h to residual pressure of 10^{-2} Torr (Stage 2, catalyst $\text{CrO}_3/\text{SiO}_2$ (T_d)).

2.2. DRIFTS and DRS study

The DRIFT and FTIR spectra were recorded on a Shimadzu FTIR-8300 spectrometer with an attachment DRS-8000 in the 400–6000 cm^{-1} range with a resolution of 4 cm^{-1} .

2.2.1. Calculation of the content of terminal OH-groups

In order to calculate the concentration of terminal OH-groups using DRIFTS data, we developed a special procedure, which allows to find the correlation between the concentration of Si–OH groups, calculated from the intensity of a.b. 3745 cm^{-1} in the FTIR spectra of silica samples dehydroxylated at various temperatures, and integral intensity of this absorption band on the DRIFT spectra of silica samples dehydroxylated at the same temperatures.

For FTIRS studies, the silica powder was pressed into pellets (mass typically $\rho = 10\text{--}15 \text{ mg}/\text{cm}^2$). The silica pellet was heated at 500 °C in air for 1 h, then placed in a special cell and dehydroxylated at 200, 400, 500, 600, 700 or 800 °C for 1 h at a pressure below 2×10^{-2} Torr.

Concentration of terminal OH-groups (ν_{OH} 3745 cm^{-1}) was calculated from FTIR spectra by Eq. (4):

$$C_{\text{OH}} = \frac{S}{A_0 \times \rho} \quad (4)$$

where S is the apparent integral absorption of the examine band (cm^{-1}), calculated as integral square of the observed a.b., A_0 the apparent integral absorption coefficient for OH-groups with concentration of 1 $\mu\text{mol}/\text{g}$ ($\text{cm}/\mu\text{mol}$), absorption coefficient of a.b. at 3745 cm^{-1} (A_0) equal to 3 ± 0.5 [23], C_{OH} the concentration of OH-groups ($\mu\text{mol}/\text{g}$) and ρ is the weight of the sample per 1 cm^2 beam (g/cm^2).

Data on the concentration of OH-groups measured by FTIRS for silica samples dehydroxylated at different temperatures are presented in Fig. 1.

Then the DRIFT spectra of silica powders dehydroxylated at the same temperatures (200, 400, 500, 600, 700 or 800 °C) were

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