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IR study of the interaction of hydroxyl groups of silica gel with Cr species of Phillips' type catalysts

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Spectroscopic evidence for the interaction of hydroxyl groups and chromium ions was obtained using a catalyst prepared from chromyl chloride. A new OH peak, observed at 3705 cm^{-1} after pumping away CO gas, is attributed to the direct interaction of OH with the low-valent chromium. This peak shifts to 3590 cm^{-1} on contact with O_2 at room temperature and it is assigned to a hydroxyl interacting with the oxidized chromium. New assignments are also proposed for IR bands of CO presorbed on the catalyst. The peak due to CO at 2188 cm^{-1} decreases as the OH intensity at 3705 cm^{-1} increases, suggesting that the former peak arises from adsorption on Cr(II) species to which two oxygen atoms are attached.

Keywords: Cr/SiO_2; ethylene polymerization; surface hydroxyl groups; FTIR; Phillips catalyst; CO adsorption

1. Introduction

Chromium/silica catalysts [1] of the so-called Phillips' type used for the polymerization of ethylene have given rise to much controversy ever since their discovery in the early 1950's. Difficulties in elucidating the active structure stem from the complexities of the catalysts themselves. In order to minimize the chemical non-uniformity of the catalyst, we have developed [2] a method of direct reaction between CrO_2Cl_2 and hydroxyl groups of the silica. This mode of preparation leads to better control of the early stages of polymerization of ethylene as well as to improvement of catalytic activity, indicating that the chromium sites are distributed in a much more uniform fashion in the new preparation than in the conventional samples.

Though little is known about the reaction mechanism, hydroxyl groups of the silica gel have been considered to play a significant role during the polymerization of the ethylene for three reasons. First, as unsupported chromium compounds do not show any activity [1], the OH groups of the silica are evidently necessary for the polymerization. Second, since methyl groups are presumably formed as end groups [3,4], the additional hydrogen atom from OH was postulated to participate in the initiation of the reaction. Finally, two types of divalent chromium ions were proposed [5,6] as active sites on the basis of IR measurements of presorbed CO. One of these is thought to consist of OH groups coordinated to the chromium. These results prompted us to investigate afresh the interactions between the hydroxyl groups of the silica and the reduced chromium ions using the new catalyst preparation.

2. Experimental

The catalyst was prepared in an in situ IR cell by contacting the vapour of CrO_2Cl_2 (Aldrich, 99.99%) at room temperature (r.t.) with a self-supporting disc of silica gel (Aldrich, Davisil grade 643) which had been outgassed at 450°C for 1 h, followed by calcining with O_2 at 650°C for 30 min. The sample was cooled to r.t. for IR measurement (Perkin-Elmer FT-IR 1725X), and then heated to 400°C for reduction with CO for 15 min. The sample was again cooled to r.t. under CO atmosphere for the second IR spectrum. Gas-phase CO was then pumped away for a required period. For oxidation at r.t., 3 Torr of O_2 was admitted into the cell and then pumped away.

3. Results and discussion

3.1. INTERACTION BETWEEN HYDROXYL GROUPS OF THE SILICA AND THE REDUCED Cr

After calcining with oxygen at 650°C, the catalyst had only isolated surface OH species showing a sharp band at 3747 cm^{-1}(see fig. 1 (a)). When the catalyst was reduced with CO at 400°C, the intensity of the band decreased and the band itself broadened (see fig. 1 (b)). (The spectrum was taken under CO atmosphere.) From the difference spectrum (fig. 2 (c)) changes were observed as a decrease at 3749 cm^{-1} and an increase at 3743 cm^{-1}, indicating that the band at 3747 cm^{-1} shifted slightly to lower frequency. Fig. 2 (a) shows an IR difference spectrum before and after evacuating CO. When gas-phase CO was evacuated, some portion of the changes observed in fig. 1 (c) was restored; that is to say, the band around 3743 cm^{-1} shifted to the one at 3749 cm^{-1}. If the changes were caused by a direct interaction between the OH and the reduced Cr ions [6], they could not have been restored merely by evacuating CO. Therefore, the OH may be perturbated only by CO and the reduced Cr ions. When the catalyst was continued to be evacuated at r.t., adsorbed CO gradually decreased (a spectrum is not shown here, see ref. [5]) and a new peak appeared at 3705 cm^{-1} (see fig. 2 (b)). The peak completely disappeared when the catalyst was contacted with oxygen at r.t. as shown in fig. 3 (c)

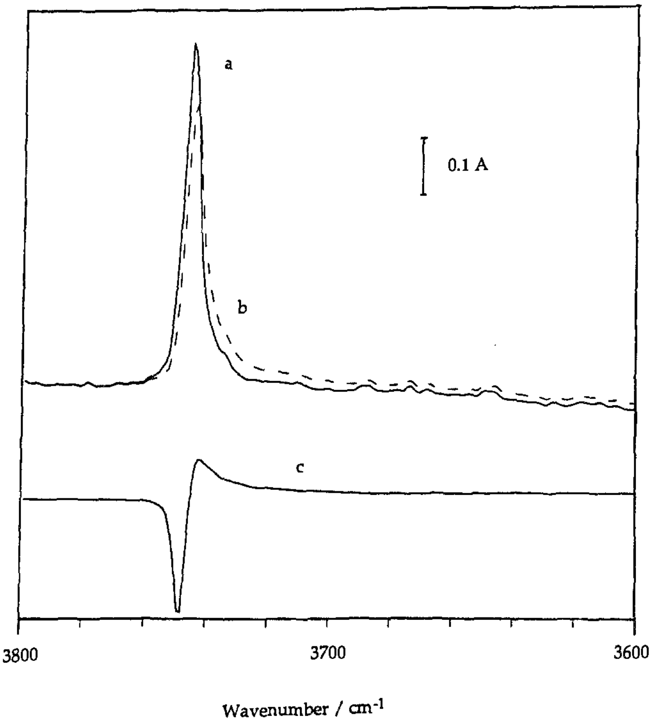

Fig. 1. IR spectra of OH stretching vibration region of the catalyst. (a) After calcining with O_2 at 650°C, measured in vacuo. (b) After reducing with CO at 400°C, measured under CO. (c) A difference spectrum of (a) from (b).

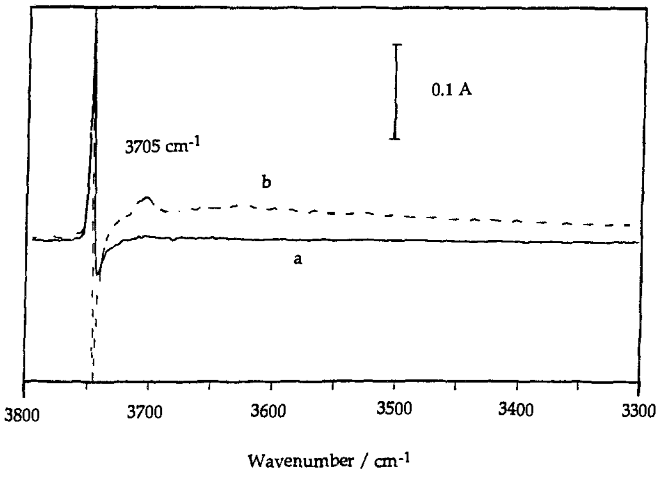

Fig. 2. IR difference spectra of a spectrum under CO from a spectrum after pumping away CO; (a) for 2 min; (b) for 60 min.

where a spectrum which had been taken before O_2 admission (fig. 3 (a)) was subtracted from a spectrum after contact with oxygen gas (fig. 3 (b)). And a new peak appeared at 3590 cm^{-1}. It was estimated by XANES data [7] that the oxidation state of the reduced Cr ions was a mixture of di and trivalent and that of the Cr ions exposed to O_2 was a mixture of tri and hexavalent.

The frequency of the OH stretching vibration mode of silica much depends on sorbates interacting with the OH group [8]. Nucleophilic sorbates shift it to much lower frequency than electrophilic ones do and the stronger the sorbates are, the lower the frequency of the OH. When CrO_2Cl_2 vapour was introduced onto a pure silica gel, the surface isolated OH species at 3747 cm^{-1} was observed [2] to shift to 3685 cm^{-1}. This shift was caused by hexavalent Cr adsorbing on oxygen atom of the OH. Since CrO_2Cl_2 desorbed at 420°C, it follows that this interaction is quite strong. On the other hand the higher frequency of the new peak at 3705 cm^{-1} indi-

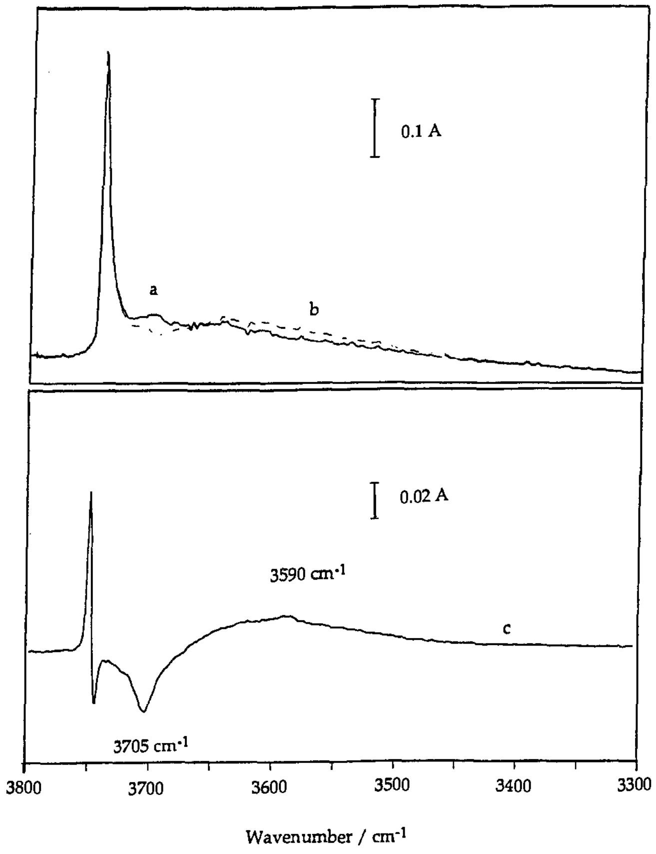

Fig. 3. IR spectra of OH region. (a) After pumping away CO for 90 min. (b) After admitting O_2 at r.t., then pumping away O_2. (c) A difference spectrum of (a) from (b).

cates that this interaction could be caused by weaker electrophiles. As this peak started to appear by desorbing CO from the reduced chromium atoms (fig. 2 (b)) and as it completely disappeared by oxidizing the chromium ions (fig. 3 (c)), we concluded that the electrophiles may be the reduced chromium ions which are coordinatively unsaturated. Though the oxidation state of the reduced chromium has not hitherto been precisely determined, it is generally thought to be divalent [1,5]. As divalent chromium ions would be weaker electrophiles than hexavalent ones, the smaller shift of the OH to 3705 cm^{-1} on the reduced catalyst than the one to 3685 cm^{-1} with CrO_2Cl_2 is in line with this interpretation. The other observed shift (to 3590 cm^{-1}) caused by oxidation at r.t. was much bigger than those above, and may be explained by an interaction between nucleophiles and the hydrogen atoms of the OHs. As a band at 905 cm^{-1}, assigned as a Cr=O stretching vibration mode [6,9], was also observed (spectrum not shown), the nucleophiles may be double-bonded oxygen atoms of the oxidized Cr species.

3.2. A PROPOSED ASSIGNMENT OF IR BANDS OF CO ON Cr

It is known [5,10] that the reduced Cr/SiO_2 catalysts adsorb CO at r.t., yielding three IR bands of CO stretching vibration modes at 2188, 2183 and 2178 cm^{-1} under CO atmosphere. The band at 2183 cm^{-1} vanishes as soon as gas-phase CO is pumped away, whereas both the bands at 2188 and 2178 cm^{-1} continue to decrease on successive evacuation, but with the one at 2188 cm^{-1} disappearing more slowly than that at 2178 cm^{-1}. The current assignments [5] are as follows: the band at 2178 cm^{-1} is due to CO adsorbed on divalent chromium ion (Cr_A species) which is bound to the silica through two oxygen atoms; the band at 2188 cm^{-1} to CO adsorbed on divalent chromium ion (Cr_B species) which is bound to the silica through two oxygen atoms with an additional oxygen coordinating to the Cr ion. A source of the additional oxygen atom has been proposed to be either Si–O–Si or Si–O–H. One more divalent chromium ion (Cr_C species) with two additional oxygen atoms is thought [5] not to adsorb CO at r.t.

After reduction with 6 Torr of CO the sample was cooled under CO atmosphere to r.t. and then gaseous CO was pumped away for 2 min (fig. 4 (a)); the sample was further outgassed for 1 h, followed by readmission of CO (6 Torr); finally, the CO was pumped away for 2 min (fig. 4 (b)). The band corresponding to the OH stretching region at 3705 cm^{-1} increased during the prolonged evacuation as shown in fig. 2 (b). This is interpreted to mean that the OH species interacts with the reduced Cr ions. When a new OH group coordinates a Cr ion, Cr_A should be converted into Cr_B and Cr_B into Cr_C. Unless the change of Cr_B to Cr_C is greatly preferred over that of Cr_A to Cr_B, Cr_A should decrease more than Cr_B. As the number of the adsorbed CO species at 2188 cm^{-1} decreased much more than that of the CO at 2178 cm^{-1} when the coordinating OH increased, it is plausible to assign the band at 2188 cm^{-1} to Cr_A species.

Since OH coordinates to a Cr ion by donating electrons the electron density of

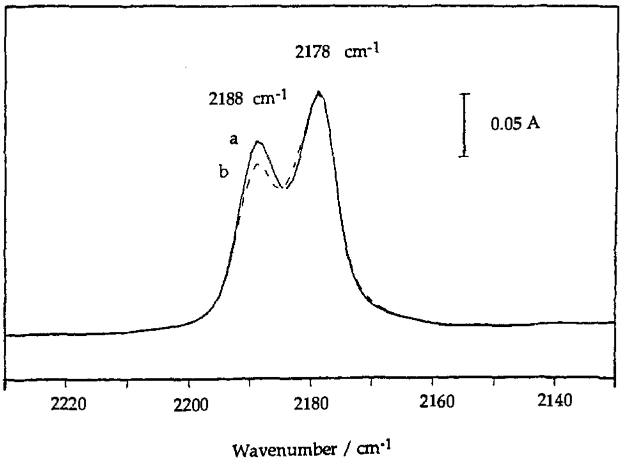

Fig. 4. IR spectra of CO stretching vibration region. (a) CO was pumped away for 2 min. (b) CO was readmitted after 1 h of evacuation at r.t. and CO was pumped away for 2 min.

the Cr increases so that the oxidation state of Cr_B should be lower than that of Cr_A. The frequencies of the IR bands of adsorbed CO are higher than those of gas-phase CO (2155 cm^{-1}) indicating that π backdonation from a Cr dπ orbital into the antibonding π^* at CO would be weaker than a σ bond between the carbon lone pair and a Cr dσ orbital. Therefore, CO would adsorb more strongly on a Cr of higher oxidation state. The assignment of the 2188 cm^{-1} band to the Cr_A is consistent with the result that CO band at 2188 cm^{-1} desorbs more slowly than the CO band at 2178 cm^{-1}.

4. Conclusion

Previously, hydroxyl groups of the silica gel were postulated to interact with the reduced chromium ions or even to participate in the polymerization but without any definitive supportive spectroscopic evidence from the OH group frequency. A recent report [6] identified OH peaks, but both the shapes and positions of the bands were not unambiguously assigned. As the catalysts prepared from CrO_2Cl_2 gave rather more uniform chromium species, it enabled us to observe delicate changes in IR spectrum of the OH region. A new OH peak was observed at 3705 cm^{-1} after pumping away gas-phase CO, the frequency of this peak and its complete disappearance by oxidation strongly suggesting that the OH groups interact with low-valent chromium ions. The inverse correlation of the OH at 3705 cm^{-1} to the IR band of CO at 2188 cm^{-1} offers a new proposition, namely that CO absorption at 2188 cm^{-1} arises from adsorption on the Cr_A species.

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