

CHARACTERIZATION OF SILICA SUPPORTED CHROMIUM COMPLEXES

M.L. PARENTIS*, N.A. BONINI and E.E. GONZO

Instituto de Investigaciones para la Industria Química - INIQUI - Universidad Nacional de Salta - UNSa - CONICET, Buenos Aires 177 (4400) SALTA, ARGENTINA.

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ABSTRACT

The Cr/SiO₂ catalysts were prepared via the deposition of mononuclear and binuclear chromium (III) ammine complexes on silica. The influence of the chromium loading and calcination temperature upon the type of species formed was determined. FTIR and Raman studies revealed the presence of Cr (VI) species as monomers and dimers in calcined catalysts and the existence of a chemical interaction between the complex chromium ions and the support. Furthermore, IR of adsorbed pyridine showed the presence of Lewis centers just before calcination. After calcination Brønsted sites were developed, these sites were related to the presence of Cr (VI) species. The relative concentration of such centers depends on the amount of chromium exchanged.

* Author to whom correspondence should be addressed.

INTRODUCTION

For many years, supported chromium catalysts have been applied in industry mainly in the polymerization of alkenes. Particularly the Phillips Catalyst, Cr/SiO₂, has been used to produce high-density polyethylene (Rebenstorf, 1991 a-c; Rebenstorf and Sheng, 1991, Ellison *et al.*, 1993; Blom *et al.*, 1994; Kantcheva *et al.*, 1995; Chudek *et al.*, 1996). Moreover, this catalytic system has also been applied to a great variety of other reactions such as hydrogenation and dehydrogenation of hydrocarbons (Sarbak, 1995; Rao *et al.*, 1996), dehydrocyclization of paraffins and oxidation of organic substrates. Gas-phase oxidation of methanol, ethanol and 2-propanol (Ritcher *et al.*, 1986; Kim *et al.*, 1992) and the liquid-phase oxidation of hydrocarbons and secondary alcohols (Ulagappan and Rao, 1996; Joseph *et al.*, 1995; Blau *et al.*, 1989; Lee and Ha, 1989) can be mentioned among them.

Despite these applications, controversy continues around the characterization of the chromium species and the active sites present in this catalytic system, mainly when low chromium loading is used.

Usually, catalysts were prepared by the conventional impregnation method while relatively few investigations have been devoted to the deposition or ion exchange of chromium complexes. In this way, the use of hexa aquo chromium ions (Lunsford *et al.*, 1988) and chromium acetylacetonate (Haukka *et al.*, 1994) leads to very low exchange levels. In the first case, the pK_a of the complex makes it an unlikely candidate for ion exchange onto silica and in the second case, the

relatively large size of the complex has a restricting effect on the amount of chromium bounded (Haukka *et al.*, 1994; White, 1993).

The present paper reports the preparation of silica supported chromium catalysts by ion exchange-deposition of ammine chromium complexes on the silica surface. The catalysts were characterized by thermogravimetry (TG-DTA), TPR, FTIR and Raman spectroscopy techniques.

The effect of chromium loading and calcination temperature on the nature of the acid sites were studied using I.R. spectroscopy of adsorbed pyridine.

EXPERIMENTAL

Silica Davison G62, calcined up to 750°C was used as support. It has a 260 m²/gr specific surface area and 160 Å mean pore diameter. The hydroxyl concentration was 1.32 mlec. OH/g SiO₂.

The chromium complexes used, acid rhodo chromium chloride [(NH₃)₅Cr-OH-Cr(NH₃)₅Cl₅·H₂O] and aquo penta-ammine chromium (III) nitrate [(H₂O)(NH₃)₅Cr(NO₃)₃], were synthesized following the techniques described by Brauer (1958).

The catalysts were prepared by the traditional ion exchange method previously described (Parentis *et al.*, 1996). After the exchange, the solid was washed with an ammoniacal solution (1:1).

In all cases, the samples were subsequently dried at room temperature (RT), at 110°C and calcined at 450°C in air stream for 4 horas. The amount of chromium exchanged was determined by atomic absorption spectroscopy after solubilization of the samples in HF. The results are shown in Table 1. The theoretical chromium loadings are shown in the first column. These values represent the amount of Cr that

would be obtained if all the chromium ions present in the original solution were exchanged.

TABLE 1
Chromium loadings

Catalysts	Chromium loading(%)
Ion Exchange - Rhodo Chromium Chloride	
5% (450 °C)	2.38
5% (110 °C)	2.52
5% (RT)	2.80
5% (450 °C) - Washed	0.24
2% (450 °C)	1.24
2% (110 °C)	1.46
2% (RT)	1.53
2% (450 °C) - Washed	0.03
1% (450 °C)	0.60
0.5% (450 °C)	0.31
Ion Exchange-AquoPenta-ammine Cr (III) Nitrate	
2% (450 °C)	1.50
2% (RT)	1.57

Specific surface areas were determined gravimetrically by the BET method (Table 2).

Thermogravimetric and Differential Thermal Analyses studies were performed on samples of 15-20 mg, in air, using a Thermal Analysis Unit Rigaku. A heating rate of 10°C/min from room temperature up to 800°C was used.

FTIR spectra were recorded on a Bruker IFS 88 Spectrophotometer.

To analyze the surface hydroxyl stretching region (4000 - 3000 cm⁻¹), self-supporting wafers of 20 mg/cm², (pressed at 4 tn/cm²) and an Infrared cell with KRS5 windows to carry out "in situ" pretreatments, were used. For recording the chromium-oxygen stretching region (1000-500 cm⁻¹) the samples were ground with KBr.

The Raman spectra were recorded on a Bruker IFS 66 Spectrometer with a resolution of 4 cm⁻¹.

Temperature Programmed Reduction (TPR) experiments were carried out in a conventional flow equipment fitted with thermal conductivity detectors.

The carrier, a mixture of H₂/N₂ (5% v), was flown through the sample (20-50 mg) at 35 ml/min. The temperature was increased at a constant rate of 10°C/min.

Pyridine (Py) adsorption study was carried out on pure samples (20 mg) using the infrared cell above described. The samples were evacuated 1 hr at 250°C and the spectrum baseline was recorded. Gaseous Py (8 mm Hg) was introduced inside the infrared cell at room temperature and the spectra corresponding to different evacuation periods and temperatures were recorded. Finally the "difference" spectra were obtained by subtracting the baseline spectrum from that of the evacuated sample.

TABLE 2
Specific Surface Areas

Catalysts	Surface Area (m ² /g)
SiO ₂	260
5% (450 °C)-Rhodo	254
5% (RT)-Rhodo	287
0.5% (450 °C)-Rhodo	265
2% (450 °C)-AquoPent	251

RESULTS AND DISCUSSION

Chromium analysis of the samples.

The chromium loading of the samples before and after different thermal treatments was determined by A.A. spectroscopy (Table 1). For catalysts prepared from the binuclear rhodochromic chloride complex an important loss of chromium was observed (15% w/w of the initial chromium value approximately) during the calcination process but not when the materials were prepared from the nitrate mononuclear precursor. The loss of chromium during the heating in air is related to the chloride ion present in the precursor that remains on the surface after the exchange process. So, during the heating, these ion forms HCl that reacts with surface oxidized Cr⁶⁺ to form CrO₂Cl₂. The chromyl chloride is a high vapor pressure compound (bp. 117°C), easily removed by the air flow. McDaniel (1982) reported a similar behaviour. The volatilization during the calcination process is accompanied by a deposition of a green compound, probably Cr₂O₃, on the upper cold section of the heating tube. This Cr₂O₃ would be formed, in the gas phase, from CrO₂Cl₂ by the reductive

character of the NH_3 (Fouad and Knözinger, 1991) that is simultaneously released when the samples were heated under the air flow.

From these results, the observed chromium loss is in agreement with both the complex decomposition and with a concomitant oxidation process of Cr^{3+} to Cr^{6+} to form CrO_2Cl_2 at low temperature. These transformations take place during the long time drying process at 110°C and/or at the 177°C exothermic process observed under the TG-DTA experiences as it will be further discussed.

DTA Studies

In Fig. 1, the thermograms (DTA) of SiO_2 and catalysts prepared with both kinds of complexes are shown. The plot exhibited by the support (Fig. 1a) monitors the free water endothermic desorption process between 40 to 130°C . After that, only a smooth and continuous loss of weight arising from condensation of geminal and vicinal silanol groups is observed. (Peri, 1984; Brinker and Scherer, 1990; Iler, 1977).

The thermal behaviour of 2% (RT) - Rhodo sample shows an endothermic peak at approximately 90°C and two exothermic transformations at 160 - 200°C and 290 - 340°C over the smooth process of water release previously described on the support. The observed loss of weight corresponding to the endothermic peak (12% of the total weight) was higher than the weight loss observed on the support. It corresponds to the simultaneous removal of water and ammonia from the silica surface.

On the other hand, the first exothermic peak at 177°C was not accompanied by a significant loss of weight. According to Fouad and Knözinger (1991), this transformation corresponds to the formation of Cr^{3+} oxygenated species (i.e., CrOOH) when free NO_3^- samples are heated in air. This species are "topochemically oxidized" during the second exothermic process to CrO_2 and CrO_3 .

During this second exothermic peak, the loss of weight represents 0.78% of the total weight. During this process, the oxidation to Cr^{6+} species and the simultaneous condensation with the hydroxyls of the silica surface, forming chromate and dichromate like species, probably take place.

The decomposition of this oxygenated species to non stoichiometric ones ($\text{Cr}_2\text{O}_{3+x}$) and their characteristic exothermic transformation ("glow phenomenon") to form crystalline Cr_2O_3 oxide was hard to observe because of the low amount of chromium on the samples and their interaction with the support.

The catalysts prepared from the mononuclear

chromium complex after drying in air at 110°C (Fig. 1c), show only one exothermic peak at approximately 330°C . This last transformation, similar for both kinds of catalysts, could be ascribable to the oxidation of Cr^{3+} to Cr^{6+} species, determined by other techniques as it will be discussed later.

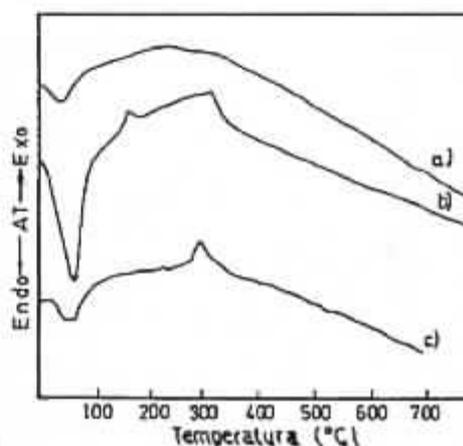


Fig.1: DTA curves of a) SiO_2 , b) 2% (RT) Rhodo, c) 2% (110°C) Aquo Pentammine. Heating rate $10^\circ\text{C}/\text{min}$. Static system in the presence of air.

The different behaviour observed over both kinds of catalysts must be related to the mono and binuclear character of the complexes, which is apparently preserved after the exchange process.

Infrared Spectroscopy Studies

1000 - 500 cm^{-1} region

Fig. 2 shows the absorption infrared spectra of the support and catalysts after different thermal treatments in the 1000 - 500 cm^{-1} region. The IR spectrum of silica is characterized by an intense peak at 804 cm^{-1} due to the Si-O-Si symmetric stretching vibrations and a weak band at 975 cm^{-1} which have been assigned to Si-OH bond vibrations (Perry and Li, 1991). After the exchange process and subsequent drying at room temperature or at 110°C , the band at 975 cm^{-1} disappears in both kinds of catalysts. As the treatment temperature increases, a new band at 970 - 975 cm^{-1} is observed. When the sample is calcined in air at 250°C or higher temperature, two additional bands at 957 and 905 cm^{-1} are developed. The intensity of the last two bands depends on the chromium loading.

The FTIR spectrum of the 5% Rodo catalyst calcined in air for 4 hours at 450°C shows, in addition to the previous peaks, two weak bands at 550 and 620

cm^{-1} which must be assigned to the presence of a small amount of bulk Cr_2O_3 (Fouard and Knözinger, 1991). The described behaviour is only observed when the catalysts are heated in air but not when the catalysts are treated under nitrogen or in vacuum. In these cases only the 804 cm^{-1} absorption band of the silica is observed.

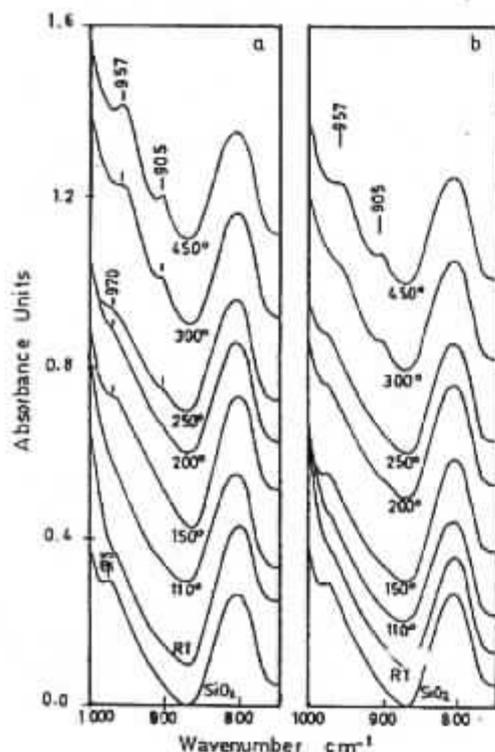


Fig. 2: IR spectra of a) 5% Rhodo, and b) 5% aquopentammine. Samples after different thermal treatments diluted in BrK.

From these results it can be concluded that the IR bands development is closely related to the exothermic processes previously described in the TG-DTA experiences. These absorption bands are assigned to the formation of $\text{Cr}=\text{O}$ surface species (Vuurman *et al.*, 1993; Sugimoto *et al.*, 1992) which are formed during the calcination as a consequence of the Cr^{3+} to Cr^{6+} oxidation process. The IR absorption bands in this region are not enough evidence to distinguish and identify unequivocally, the kind of Cr^{6+} surface species developed.

On the other hand, the colour of the samples reflects the presence of certain species. The catalyst dried at RT or 110°C shows a green colour which is characteristic of the presence of Cr^{3+} ions. During the calcination process from 110°C to 450°C it passes from green to red-brown at 200°C , and finally to a

yellow-orange colour, characteristic of the chromate and/or dichromate species (Jehng *et al.*, 1995). The final hue in the yellow-orange colour range depends on the amount of chromium in the catalyst. The samples treated in vacuum or under nitrogen atmosphere remain green between RT and 450°C .

Infrared spectra and chemical analysis reveal that about 90% of the chromium present in the catalysts can be removed if the samples are washed in water after calcination in air at 450°C whereas for the same catalysts dried at RT or 110°C or heated under nitrogen, the removal of the exchanged chromium complexes is not observed after washing the catalysts in identical conditions.

These results show the existence of a chemical interaction between the transition metal complex and the support after the ion exchange process and before being heated in air. The disappearance of the 975 cm^{-1} band and the decrease of the 3740 cm^{-1} band intensity (Fig. 3) confirm it. Moreover, the formation of water soluble Cr^{6+} oxidized species like monochromate, dichromate and/or chromic oxide during the calcination process is expected.

4000 - 3000 cm^{-1} region

The spectra of the 4000 - 3000 cm^{-1} IR region confirm the presence of ammonia ligands in the supported complex after the ion exchange process.

Again, the ammonia release from the sample is highly conditioned by its treatment in air or in vacuum.

Thus, in vacuum, at temperatures below 350°C , the spectrum of the 4000 - 3000 cm^{-1} region shows, besides the bands assigned to oxygen-hydrogen stretching vibration of free and associated hydroxyl groups, two other bands corresponding to the asymmetric and symmetric N-H stretching vibration of ammonia groups at 3382 and 3288 cm^{-1} respectively (Nakamoto, 1977). Conversely, these bands disappear at 200°C when the samples are heated in air. So, the ammonia removal is clearly associated to the first DTA exothermic process.

In this region a gradual decrease of the 3740 cm^{-1} absorption band intensity as the amount of chromium increases suggests that the ion exchange of complexes promotes an interaction of the chromium ions with the silica isolated hydroxyl groups. This behaviour is observed both in catalysts dried at room temperature or calcined in air at 450°C (Fig. 3). Certainly, the same hydroxyls groups that link the complex to the surface retain the Cr (VI) species formed after the oxidation process.

Monochromate, dichromate and polychromate species are reported as polydentated species that can show such behaviour.

If the catalysts calcined in air are washed, the 3740 cm^{-1} absorption band is restored. In this case the intensity of the band depends on the amount of chromium remaining in the catalyst after washing (Fig. 3).

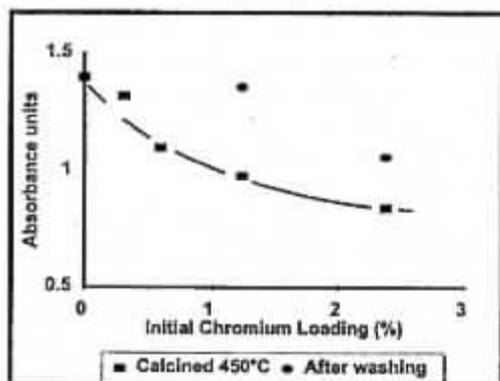


Fig. 3: Variation in the intensity of the free hydroxyl band at 3740 cm^{-1} with the chromium loading. Self supported samples evacuated at 450°C .

Raman Studies

It is well known that the Raman band position is indicative of chromium oxides present on the support (Hardcastle and Wachs, 1988), so while Cr (III) oxide compounds exhibit Raman bands in the $500 - 600\text{ cm}^{-1}$ region due to their lower oxidation state, Cr (VI) compounds exhibit bands in the $800 - 1000\text{ cm}^{-1}$ region. The particular spectral feature in the region can give additional information about the structural characteristics of the surface species.

The Raman spectra of different Cr/SiO₂ catalysts prepared from rhodochromic chloride and calcined at 450°C are presented in Fig. 4. It can be observed that all the catalysts show spectra with a band centered at $890-906\text{ cm}^{-1}$ with a broadening towards the low side frequencies.

This band must be assigned to the symmetric stretching vibration of the CrO₃ group inside the dimeric unit. The broadening towards lower frequencies is related to the presence of a small amount of monomeric surface chromate species. The shift of this band from 890 to 906 cm^{-1} indicates that the ratio of dimers/monomers increases with the chromium loading. The absorption band at 846 cm^{-1} , characteristic of the tetrahedral monomeric chromate species, is probably shifted to 880 cm^{-1} as a consequence of their interaction with the hydrated oxide support surface.

As the chromium loading increases, a new band at 962 cm^{-1} is developed as a shoulder due to the presence of non-terminal chromate units. This band

reveals that a portion of chromium is present as chromium oxide after the calcination process (Hardcastle and Wachs, 1988). The aquo catalysts show a similar behaviour (Fig. 4).

It must be taken into account that none of these bands in the $800 - 1000\text{ cm}^{-1}$ region is observed in high loading catalysts before calcination.

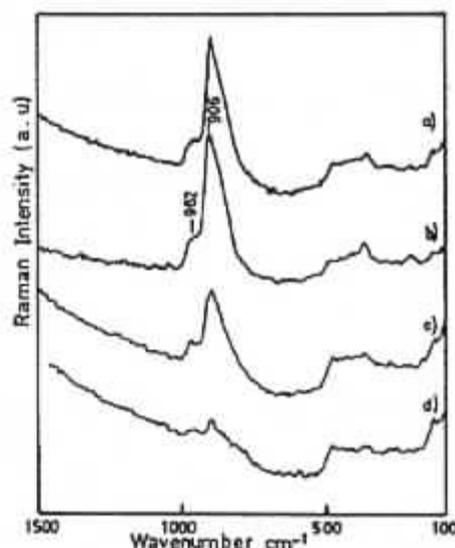


Fig. 4: Raman spectra of a) 2% (450°C) Aquo, b) 2% (450°C) Rhodo, c) 1% (450°C) Rhodo, d) 0.5% (450°C) Rhodo catalysts.

Finally, a band at 989 cm^{-1} was observed in the 5% (450°C) - Rhodo catalyst spectrum (not shown in the Figure). This band is associated with dehydrated chromium oxide species on the silica surface.

TPR experiences

The TPR profiles of the 5% Rhodo catalyst after different thermal treatments are shown in Fig. 5. It can be observed that while the 5% (110°C) catalyst shows a very low hydrogen uptake centered at 450°C , the hydrogen consumption increases as the temperature of calcination is raised. So, after treatment in air at 200°C a small and broad peak appears centered at 290°C approximately. This peak is clearly developed as we increase the calcination temperature. Finally, at 450°C , the TPR profile shows two well defined reduction zones at $250-350^\circ\text{C}$ and $370-500^\circ\text{C}$ respectively.

The presence of reduction peaks at temperatures of 200°C and higher is consistent with the 177 and 273°C exothermic peaks observed in the TG-DTA experiences and with the appearance of Cr (VI) species detected both by Raman and FTIR spectroscopy.

According to Zaki *et al.* (1996), the low temperature reduction peak is related to the presence of polichromate (dimers, trimers and higher) chromium species, while the high temperature peak must be assigned to the presence of monochromate compounds. Both of them were identified by Raman spectroscopy.

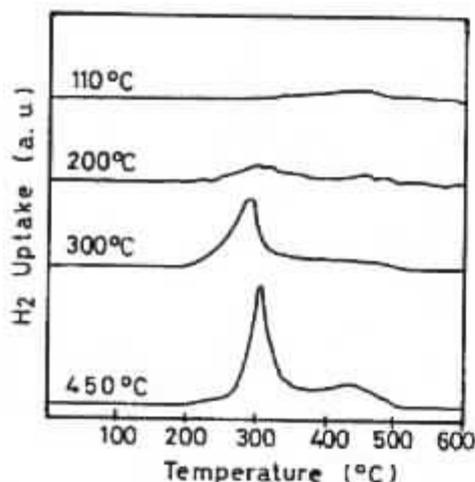


Fig. 5: TPR diagrams of 5% Rhodo catalyst after different thermal treatment.

Infrared Spectroscopy of Adsorbed Pyridine

The nature of the acid sites was determined by I.R. Spectroscopy of adsorbed Py.

When the 2% (RT)-Rhodo catalyst interacts with Py molecules at room temperature the characteristic IR absorption bands due to vibration modes of physisorbed and chemisorbed pyridine appear.

Fig. 6a shows the spectra obtained where it can be observed, not only the bands assigned to hydrogen bounded Py at 1598 cm^{-1} (8a mode) and 1447 cm^{-1} (19b mode) (Parry E.P., 1963), but also another group of bands centered at 1612 , 1579 , 1489 and 1450 cm^{-1} corresponding to 8a, 8b, 19a and 19b vibration modes of Lewis Py respectively (Buzzoni *et al.*, 1996). Evacuation of the sample during 2 hours at RT decreases the intensity of the bands related to hydrogen bounded Py, while evacuation for 45 minutes at $100\text{ }^{\circ}\text{C}$ completely removes them.

The disappearance of the 1598 cm^{-1} and 1447 cm^{-1} bands agrees with the regeneration of the 3740 cm^{-1} band due to free hydroxyl groups, which had disappeared following Py chemisorption.

On the other hand, the bands at 1612 , 1579 , 1489 and 1450 cm^{-1} , assigned to Py bounded to Lewis acid sites, remain after evacuation of the sample at $100\text{ }^{\circ}\text{C}$ and are not observed when Py

interacts with pure silica.

Influence of the calcination process.

After calcination of the catalysts at $450\text{ }^{\circ}\text{C}$, a decrease in the intensity of the Py bands associated with Lewis centers and the development of new bands at 1635 cm^{-1} and 1543 cm^{-1} is observed (Fig. 6c). These new bands remain after evacuation for 2 hours at RT, but a decrease in their intensity is observed after evacuation at $100\text{ }^{\circ}\text{C}$. They are assigned to the 8a and 19b vibration modes of pyridinium ion (Buzzoni *et al.*, 1996).

Similar behaviour was observed with the catalyst prepared from the mononuclear complex. The position of the bands indicates the presence of pyridinium ions and the decrease of band intensity with the thermal treatment is related to the acid site weakness (Chapus *et al.*, 1994). From these results, it can be concluded that both types of acid centers, Lewis and Brønsted, are present in calcined catalysts. The last ones are generated during the calcination process at $450\text{ }^{\circ}\text{C}$ and are probably associated with the Cr (VI) surface species detected by FTIR and Raman studies.

In order to determine if the Brønsted acid sites are related to these Cr (VI) ions, Pyridine chemisorption experiences were performed over the catalyst heated in air and in vacuum at different temperatures. The results are shown in Fig. 7, where it can be observed that Brønsted acid sites appear when the samples are heated in air at temperatures of $200\text{ }^{\circ}\text{C}$ or higher. The amount of these sites passes through a maximum at $300\text{ }^{\circ}\text{C}$ and slightly decreases at $450\text{ }^{\circ}\text{C}$. The development of Brønsted acid sites is clearly coincident with the previous oxidation process.

On the contrary, no Brønsted acid sites are observed when the catalyst, previous to pyridine chemisorption, is heated under vacuum. In this case the amount of Lewis acid sites remains similar in all the range.

These results propose that the Lewis acid sites are associated with Cr^{3+} ions linked to the support during the exchange process. The amount of these sites diminishes when the catalyst is heated in air at temperatures higher than $150\text{ }^{\circ}\text{C}$. Meanwhile, the Brønsted acid sites are developed through an oxidation process. These Cr^{3+} ions must be surface sites forming SiO-Cr bonds and not included into de silica framework. The substitution of Cr^{3+} tetravalent cations for Si^{4+} should generate a lattice negative charge; developing Brønsted acid sites (Conell *et al.*, 1987), that is not observed when the catalysts are heated in vacuum.

The observed Brønsted acid sites appear only

when the catalysts are heated in air at temperatures that induce the oxidation of Cr^{3+} ions to Cr^{6+} oxides.

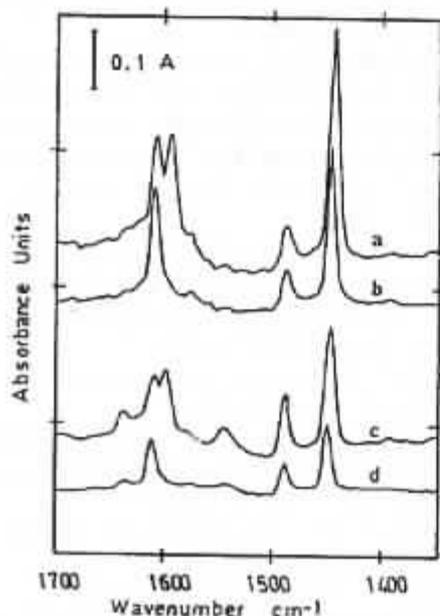


Fig. 6: Py interaction with 2% Rhodo. a) Dried (RT), Py evac. 2 hours. at RT, b) Dried at RT, Py evac. 2 hours. at RT and 45 min. at 100°C, c) Calcined at 450°C, Py evac. 2 hours at RT and d) Calcined at 450°C, Py evac. 2 hours at RT and 45 min. at 100°C.

These Cr^{6+} oxides were observed through the IR bands in the 1000 - 500 cm^{-1} region and identified by Raman spectroscopy as dichromate and monochromate species. They are held to the silica surface by hydroxyl groups and their hydrated forms develop weakly acid hydroxyl groups that protonate the Py molecule.

Similarly, Bandoz *et al.* (1996) determined, by potentiometric titration, the formation of highly acidic Brønsted centers (pKa: 5.49 and 7.14) when Cr^{3+} -intercalated Bentonites, were heated in air up to 473 or 573 K. These centers are related to the formation of Cr^{6+} hydrated oxides after calcination. Moreover, these authors report no changes in the amount and acid strength of the surface centers when the samples are heated in absence of oxygen at these temperatures.

Fig. 8 shows the effect of chromium loading on the amount of chemisorbed Py for a series of catalysts prepared from rhodo chromic chloride and calcined at 450 °C. The data were obtained by integrating the area under the 1543 cm^{-1} band (after evacuation of the samples at RT) for the Brønsted sites, and the area under the 1612 cm^{-1} band (after

evacuation 2 hours at RT and 45 minutes at 100 °C) for the Lewis sites.

A slight decrease in the amount of Py bounded to Lewis acid sites per chromium atom (calculated as the peak area / %Cr (u.a.)) as chromium loading increases is observed. This observation is accompanied by an increase in the amount of Brønsted type Py. Therefore, at low chromium loading (0.3% and 0.6% Cr) the amount of Brønsted Py remains in a low value and begins to increase for chromium concentrations greater than 0.7%.

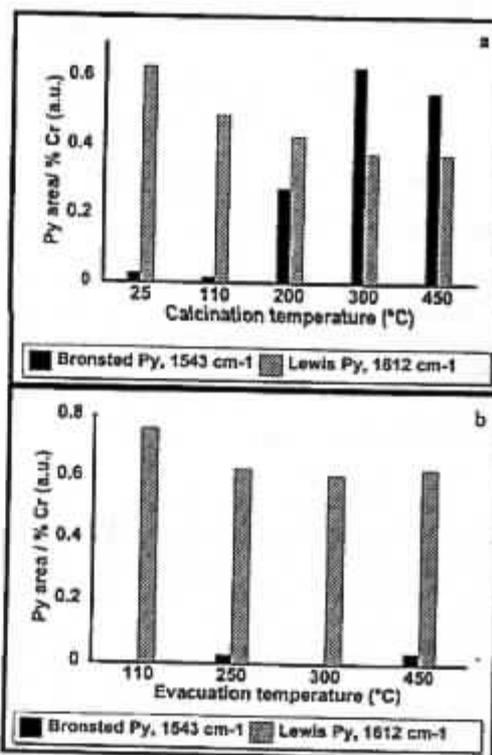


Fig. 7: Influence of the pretreatment conditions on Py chemisorption. a) 5% Rhodo catalysts heated in air at different temperatures, b) 5% Rhodo catalyst heated in vacuum at different temperatures. Self supported samples.

Pyridine adsorption on 5% (450°C) - Rhodo catalyst washed with distilled water and calcined again, leads to a spectrum in which the pyridinium ion characteristic bands are not observed and the amount of Py associated with Lewis centers increase up to a value consistent with the amount of chromium remaining in the catalyst after washing.

The following conclusions arose from these results:

a) The Lewis sites consist of coordinatively unsaturated Cr (III) ions attached to the support during the ion exchange process. The calcination step

leads to the formation of Cr (VI) species, which would be the precursors for the Brønsted acid sites generation.

b) The relative amount of Lewis/Brønsted sites in calcined catalysts depends on the amount of chromium deposited on the support.

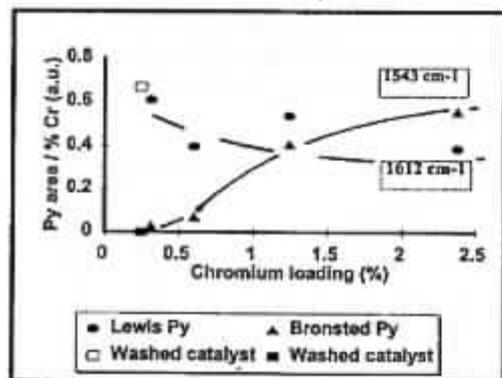


Fig. 8: Amount of chemisorbed Py vs. % Cr. ● and ▲ Rhodo Series, calcined at 450°C. □ and ■ 5% Rhodo (450°C) catalyst after washing with distilled water.

CONCLUSIONS

The deposition or ion exchange of mononuclear or binuclear chromium (III) ammoniacal complexes improves the exchange level obtained and leads to chromium contents up to 2.5%. The catalysts dried at RT or 110 °C, present chromium (III) ions in strong interaction with the support, so that they remain attached to the support after the washing experience.

The calcination of the catalysts leads to the complex oxidation and formation of Cr (VI) species, present as monomers and dimers, as it was determined by the IR and Raman studies. These species are present in a greater proportion in calcined catalysts with high chromium loading.

The non-calcined catalysts show the development of Lewis acid sites while the calcination process generates Brønsted acid sites.

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