

DEHYDROGENATION AND OXIDATIVE DEHYDROGENATION OF ALCOHOLS ON SILICA SUPPORTED CHROMIUM CATALYSTS

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Abstract - The catalytic activity of Cr/SiO₂ (0.43 to 2.8% chromium by weight), prepared by the ion exchange method, for the dehydrogenation (573 K to 613 K) and oxidative dehydrogenation (503 K to 558 K) of alcohols has been investigated. The results obtained are consistent with the hypothesis that the Lewis pyridine centers of chromium are the active sites for alcohol dehydrogenation. At 593 K the selectivity to aldehyde is 70% while selectivity to acetone is 62%, for pure dehydrogenation. The dehydrogenation rate of the secondary alcohol is one order of magnitude higher than that observed for primary ones. The catalytic activity for oxidehydrogenation is 12 times higher than for pure dehydrogenation and the reaction rate of primary alcohols are higher than for secondary ones. When the ratio of oxygen to alcohol partial pressures is 1:2 or above, the selectivity to aldehydes reach values of 97%, 89% and 80%, for ethanol, propanol and butanol, respectively, while the selectivity for secondary alcohols remains as in dehydrogenation ($\approx 60\%$).

Keywords - Chromium catalysts; ion exchange; alcohol; dehydrogenation; oxidehydrogenation.

1. INTRODUCTION

Silica is an important material in catalysis due to its stability and mechanical strength, and more specifically to the hydroxyl groups on its surface. These surface groups of silica

are potential cation exchange sites for transition metal ions; which is the base of the "ion exchange method" to prepare well disperse and active catalysts. However, the limiting factor that determines the exchangeability of a cationic specie is the pKa of the silanol proton ($pK_a > 9$) onto the silica (Lunsford *et al.*, 1988).

Different chromium complexes have been used to prepare these materials, such as chromium (III) acetylacetonate by deposition of the complex from the gas phase or hexa aquo chromium ions $[Cr(H_2O)_6]^{3+}$ by ion exchange. Nevertheless the size of the complex in the first case or the basic character of the ligand in the second, are not adequate to ensure the interaction, leading to a very low exchange (White, 1993).

In general, the chromium catalysts are prepared by the conventional impregnation procedure. It is well known that these chromium-based catalysts are used in very important industrial processes such as the polymerization of ethylene, hydrogenation and dehydrogenation of hydrocarbons, gas phase oxidation, etc. (Rao *et al.*, 1996; Sarbak, 1995; Chudek *et al.*, 1996; Joseph *et al.*, 1995). The catalytic conversion of alcohols into aldehydes and ketones is essential for the preparation of many synthetic intermediates in organic chemistry, as was recently pointed out by Friedrich (1999).

In this paper, the study of alcohols dehydrogenation and oxidehydrogenation performances of silica supported chromium catalysts,

prepared by the ion exchange method, is described.

Reference is made to previous characterization by thermogravimetry (TG-DTA), Fourier transform I.R. and Raman spectroscopy, temperature programmed reduction (TPR) and I.R. spectroscopy of adsorbed pyridine (Parentis *et al.*, 2000).

2. EXPERIMENTAL

The chromium complex acid rhodo chromium chloride $[(\text{NH}_3)_2\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_3\text{Cl}_2 \cdot \text{H}_2\text{O}]$ used as precursor in the catalyst preparation was synthesized in our laboratory following the technique proposed by Brauer (1958).

Silica Davison G62, calcined at 1023 K, which has a specific surface area of 260 m^2/g , a mean pore diameter of 16 nm and a surface hydroxyl concentration of 1.12 milieq. (OH)/g SiO_2 ; was used as support.

The catalysts were prepared according to the procedure previously developed (Bonini *et al.*, 1994a). After the ion exchange step, the material was washed with a (1:1) solution of ammonium hydroxide, filtered and dried at room temperature. Two types of catalysts are distinguished according to the pre-treatment used: one (dried) where the samples were simply dried at 383 K and the other (calcined) where the samples were subsequently calcined, in an air stream, at 723 K for 4 hours.

The chromium loading was determined by atomic adsorption spectroscopy after solubilization of the samples in FH.

Pyridine IR experiments were performed with a Bruker IFS 88 Spectrophotometer. The IR cell used and the procedure followed in these experiments has been previously described (Parentis *et al.*, 2000).

The catalytic reactions were carried out at atmospheric pressure in a glass flow reactor (id. = 5 mm) with a mass of catalyst ranging from 20 to 50 mg. Nitrogen was used as carrier gas. Feed flows were maintained between 180 and 300 $\text{ml}\cdot\text{min}^{-1}$. Most of the experiments were performed with an alcohol partial pressure of 5 KPa. The dehydrogenation

reactions were carried out between 573 and 613 K. The oxidative dehydrogenation were carried out at a lower temperature range of 503 to 558 K, with oxygen partial pressures ranging from 0.5 to 4.5 KPa in order to make the reacting system proceed under differential regime, with alcohol conversion below 10%. The reaction rates at different temperatures were obtained by changing this parameter following an aleatory law. Both reactants and products were analyzed on line with a gas chromatograph. The reaction rates were determined with catalyst particles small enough to eliminate resistances to internal and external transports (80 - 100 mesh).

The silica support exhibits some activity for the dehydrogenation of ethyl alcohol at or above 623 K.

3. RESULTS AND DISCUSSION

3.1 Chromium loading and pyridine adsorption

The chromium loading and the results of pyridine adsorption experiments, determined in a previous paper (Parentis *et al.*, 2000), are presented in table 1.

The resulting chromium loading of the catalysts prepared from the binuclear chromium complex is lower than the expected one, showing that not all the chromium ions present in the original preparation solution are exchanged; this phenomena is remarkably greater in catalysts with higher chromium loading. Nevertheless, the exchange level is low compared to those found with copper, nickel or copper-nickel complexes (Bonini *et al.*, 1994a; Bonini *et al.*, 1994b; Parentis *et al.*, 1996). A loss of metal was also observed during the calcination (723 K in air), probably due to the presence of chloride ions of the precursor, which form volatile compounds.

After calcination, a high percentage of chromium present on the catalysts is easily and quickly dissolved in water at room temperature, whereas for the catalysts dried at 383 K, it is not removed.

The amount of pyridine bounded to Lewis acid sites ($\text{L}\cdot\text{Py} - 1612 \text{ cm}^{-1}$) and to Brönsted

acid sites (BPY – 1543 cm^{-1}) are listed in table 1. On the catalysts dried at 110°C Lewis type pyridine is only observed, which is associated with Cr^{+3} ions linked to the support during the exchange process. After calcination, Cr^{+6} species detected by IR and Raman spectroscopy are formed, which would be the precursors for the Brönsted acid sites generation.

Table 1

Chromium loading and amount of Pyridine associated to Lewis and Brönsted acid sites.

Catalyst	Chromium Loading (%)	LPy (a.u.)	BPY (a.u.)
Precursor: Rhodo Chromium Chloride			
5%Dried	2.80	1.24	0
2%Dried	1.46	1.30	0
0.5%Dried	0.43	0.29	0
5%Calcined	2.38	0.95	1.33
2%Calcined	1.24	0.68	0.51
1%Calcined	0.60	0.23	0.04
0.5%Calcined	0.31	0.17	0.01

3.2 Dehydrogenation

After an initial period of about 15 minutes, during which the reaction rate of ethanol dehydrogenation slowly decreased, a constant value is achieved which remains stable over several hours (> 7 hours). The apparent activation energy remains constant and equal to $E_a = 25$ Kcal/mole, for the dried catalyst, irrespective of Cr loading. While for the calcined catalysts the activation energy varies between 29 and 23 Kcal/mole as Cr loading increases from 0.43 to 2.8 %.

The effect of chromium loading on the reaction rate is depicted in Fig. 1 for both types of catalysts.

The main observation is that the reaction rate per mole of chromium is high at low loading and it decreases appreciably as the loading increases reaching a constant value when the wt % Cr is greater than 2 %. We may derive added insight to these results if the

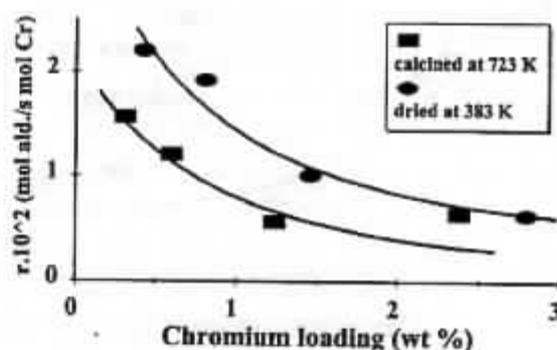


Figure 1. Dependence of ethanol dehydrogenation rate on Cr content (Cr precursor: rhodo chromium chloride). At 593 K and 5 KPa of ethanol.

reaction rate (mole of aldehyde /second per mole of chromium) is divided by the Lewis pyridine quimisorbed per mole of chromium (L Py), thus producing a reaction rate per surface site (Fig. 2)(Parentis *et al.*, 2000; Weckhuysen *et al.*, 1996). The fact that under identical conditions the same activity is found irrespective the pre-treatment procedure used in the catalyst preparation, is consistent with the hypothesis that the Lewis pyridine adsorption sites are the active sites for the dehydrogenation of alcohols. According to previous findings (Lunsford *et al.*, 1988), these Lewis centers are Cr (III) ions anchored to silica surface through OH species in the exchange process. These results also show increasing reactivities for the alcohol dehydrogenation as the Cr loading decreased. This behaviour, characteristic of the Phillips polymerisation catalysts (Lunsford *et al.*, 1988), is attributed to the presence of a low number of active centres consistent in isolated chromium ions anchored on the silica surface.

The selectivity to acetaldehyde at 593 K is around 70 %, being ethylene the only by-product observed.

The activities over the 2% Cr catalyst (dried), for the dehydrogenation of primary and secondary alcohols, with partial pressure of alcohols of 5 KPa at a standard reaction temperature of 593 K; are shown in Fig. 3. The activities are reported as the rate of reaction per mole of Cr, for the yield of

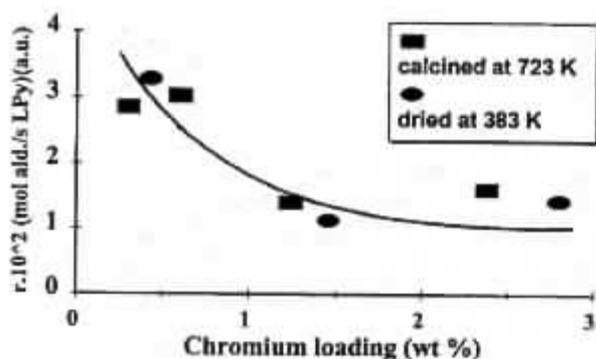


Figure 2. Effect of Cr loading on the specific (LPy) ethanol dehydrogenation rate. At 593 K and 5KPa of ethanol.

aldehydes (primary alcohol) or ketones (secondary alcohol). It can be seen that the rate of dehydrogenation of 2-propanol is one order of magnitude higher than the rate corresponding to primary alcohols.

The selectivities to aldehydes are around 70 %, meanwhile the selectivity to acetone is slightly lower (62 %). However, dehydration products are always found.

3.3 Oxidative dehydrogenation (ODH)

Whereas dehydrogenation is an endothermic process, ODH is exothermic. The role of oxygen is thought to be that it reacts with the hydrogen product, making the overall process exothermic and overcoming the equilibrium limitation. The rate of ethanol ODH was found to be 12 times faster than dehydrogenation rate at the same ethanol partial pressure and temperature.

The reaction rate increased with oxygen partial pressure (Table 2), being the rate per mole of chromium, for the catalyst dried, slightly above the rate on calcined ones. The apparent activation energy is constant, in the temperature range of 503 to 558 K and equal to 20 Kcal/mole for the dried catalyst, and independent of oxygen partial pressure. Over the calcined catalysts the activation energy varies between 24 and 18 Kcal/mole as partial pressure of oxygen increased from 0.5 to 4.5 Kpa.

The selectivity to acetaldehyde is also remarkably improved with this process. Over both types of catalysts, when the oxygen to

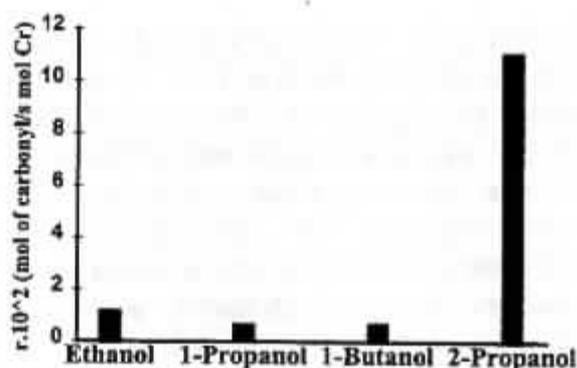


Figure 3. Dehydrogenation rate of different alcohols at 593 K. Alcohol partial pressure 5 KPa on dried 2% Cr/SiO₂.

ethanol ratio is higher than 0.5, near 1% of ethylene is observed as reaction product, increasing the selectivity to acetaldehyde, reaching values of $\geq 97\%$. This selectivity remains constant for oxygen to ethanol partial pressures ratio up to near one.

Table 2

Effect of oxygen pressure on ethanol oxidative dehydrogenation. Temperature 538 K. Ethanol partial pressure 5 KPa.

Catalyst	O ₂ Pressure (K.Pa)	r.10 ² (mole acet./s.moleCr)
2% Dried	0.5	1.45
	0.9	1.66
	2.2	1.92
	4.5	2.17
2% Calcined	0.5	1.05
	2.2	1.47
	4.5	1.67

The activities of the 2 % Cr (dried) for the ODH of primary and secondary alcohols are shown in Fig. 4. Contrary to pure dehydrogenation, the ODH reaction rate is higher for primary alcohols than for isopropanol. The rate increases as the primary alcohol's carbon chain increases.

In the oxidative process, the primary alcohols present a very high selectivity to aldehydes reaching values of 97%, 89% and 80%, for ethanol, propanol and butanol,

respectively, while the selectivity of isopropanol to acetone remain around 60 %.

Acetaldehyde, ethylene and CO_2 , were the main reaction products in the ethanol ODH. However, in the propanol and butanol ODH, acetaldehyde, methanol, CO_x , propene and butene, besides the major aldehydes (propanal, butanal) were found.

The way isopropanol decomposed gives important information on the catalyst acidity, due to the fact that it is easily dehydrated. If strong acid sites are present dehydration products are formed (Tatibouët, 1997). The observed selectivities, both in dehydrogenation and ODH of isopropanol (60% to acetone and 40% to propylene), revealed a high acidity of these catalysts.

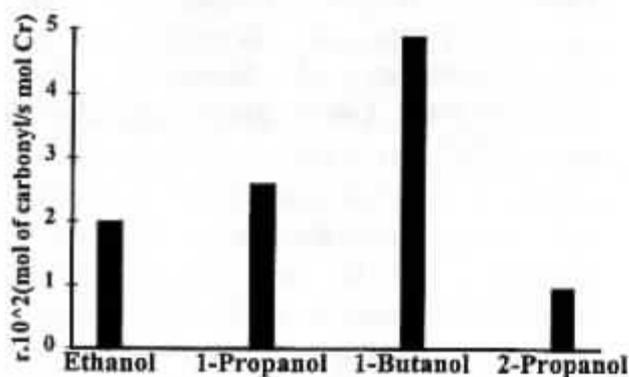


Figure 4. Oxidative dehydrogenation rate of different alcohols at 538 K. Alcohols partial pressure of 5 KPa on 2% dried Cr/SiO₂.

4. CONCLUSIONS

Supported chromium catalysts, prepared by the ion exchange method, are very interesting and promising for alcohols oxidative dehydrogenation. They are between 80 - 97% selective to aldehydes (primary alcohols) and approximately 60% to ketones (secondary alcohols); whenever the oxygen to alcohol partial pressures ratio is 0.5 or greater. The rate of reaction per mole of Cr is one order of magnitude higher than for pure dehydrogenation, meanwhile the activity for primary alcohols is higher than that for secondary alcohols.

These chromium catalysts are also active for the dehydrogenation of alcohols, the activity for the secondary alcohol being 10 times higher than for primary alcohols. However, in this case the selectivity to aldehydes or to ketones remains around 60%. A good correlation between the catalytic activity and the amount of Lewis pyridine adsorbed by the catalysts lead to the hypothesis that these chromium sites are the active sites for the dehydrogenation reaction.

Any discussion on the correlation between the catalytic performance in these reactions and the nature and physicochemical properties of the catalysts is still premature and further data will be required to establish final conclusions.

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