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## SILICA SUPPORTED CHROMIUM CATALYST. REACTIVITY STUDIES WITH ALCOHOLS

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### Abstract

Reaction rates of primary and secondary alcohols over chromium on silica catalysts prepared by the ion exchange method, in the presence and absence of oxygen, were measured. The effect of temperature and feed composition on activity and selectivity has been examined.

*Keywords:* Chromium catalysts, alcohol dehydrogenation and oxidehydrogenation

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## INTRODUCTION

Supported chromium catalysts are very important in the chemical industry for the production of several chemical commodities [1-3]. In particular, the dehydrogenation (DH) as well as the oxidative dehydrogenation (ODH) of alcohols are basic reactions from a practical aspect, because of the production of aldehydes and ketones, essential for the preparation of many intermediates in organic chemistry [4].

During recent years, much effort has been devoted to the preparation of supported chromium catalysts and, in general, the conventional impregnation procedure was employed. Nevertheless, different chromium complexes have been used to prepare supported chromium catalysts by novel methods like deposition from the gas phase or by ion exchange from solution of  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$  ions [5].

The aim of this work was to study the activity and selectivity of chromium on silica catalysts in partial oxidation reactions (dehydrogenation and oxidative dehydrogenation) of primary and secondary alcohols. The catalysts were prepared by ion exchange of binuclear pentaamminechromium(III) complex ions obtained in our laboratory, over silica gel used as support.

## EXPERIMENTAL

### Catalyst

Davison G-62 silica gel, calcined in air at 1023 K (250 m<sup>2</sup>/g, 80 – 100 mesh, mean pore size 10 nm) was used as support. The chromium complex  $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5\text{Cl}_5\cdot\text{H}_2\text{O}]$  synthesized in our laboratory was used as precursor in the catalyst preparation. The catalysts were prepared in a three-step procedure. In the first step the hydroxy groups of the silica surface were exchanged with  $\text{NH}_4^+$  ions by immersing a given weight of support (usually 10 g) in 300 mL of 1:1 aqueous-ammonium solution. In the second step the ammonia ions on the  $\text{SiO}_2$  surface were exchanged with the chromium complex ion. 100 mL of the complex solution was slowly dropped (30 min) into a stirred suspension of silica gel – ammonia solution. The chromium complex concentration was just sufficient to obtain the desired amount of chromium over the silica. The samples were filtered, washed and after dried at 383 K for 16 h. The Cr weight loading (0.4 to 3%) was obtained by atomic absorption spectroscopy. The resulting metal loadings were around the 70% of the calculated value, considering a 100% exchange from the chromium solution. In a previous paper [6] the catalyst characterization by Fourier Transform I.R. spectroscopy, TG-DTA, Raman spectroscopy and T.P.R., were described.

### Initial rate experiments

The reactions were carried out in an isothermal fixed-bed flow reactor at atmospheric pressure. The catalyst (usually 20-50 mg) was held between two layers of quartz wool inside a Pyrex glass reactor (5 mm internal diameter) connected to an on-line gas chromatograph. The height of the catalyst bed was about 2 to 3 mm. The reactor temperature was controlled within  $\pm 0.5$  K by a commercial device. Feeding the reactants diluted with nitrogen isothermal conditions were approached. The total flow rate varied between 180 and 300 cm<sup>3</sup>/min per minute (sccm). The variation in catalyst weight, total flow rate and reactant dilution was such that alcohol conversion was between 1 and 5%. The DH reactions were studied between 573 and 613 K. The ODH reactions

were carried out in a lower temperature range, *viz.* 503 to 558 K, with an oxygen to alcohol molar ratio between 0.1 and 0.9. Before each run the catalysts were stabilized under reaction conditions.

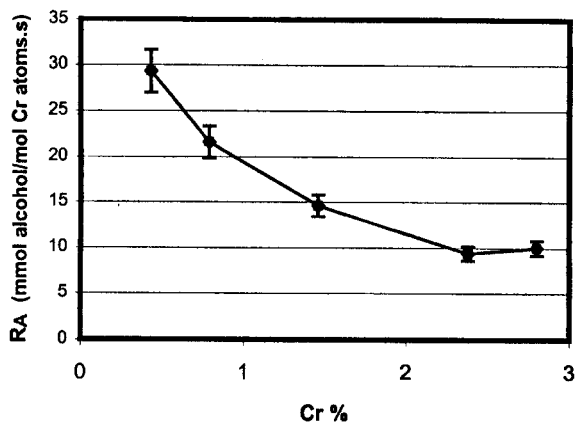
The silica support exhibits some activity for dehydrogenation at or above 623 K and was found practically inactive for ODH up to 523 K.

The catalytic activities (RA) were calculated from the moles of alcohol converted per mole of total chromium atoms per second.

## RESULTS AND DISCUSSION

### Alcohol dehydrogenation

The catalytic activity for ethanol dehydrogenation over Cr/SiO<sub>2</sub> catalysts at different chromium contents is shown in Fig. 1. The reaction rate decreases to 2% Cr and stays constant, at least, up to near 3% Cr (the maximum Cr loading reached by ion exchange). According to previous findings [6-7], at low chromium loading anchored surface chromium species prevail. As Cr content increases, labile species precursors of bulk chromium oxide increases and R<sub>A</sub> decreases appreciably. The main reaction products are acetaldehyde (70% selectivity at 593 K) and ethylene, in addition to chromium content.



**Fig. 1.** Ethanol dehydrogenation over Cr/SiO<sub>2</sub> catalysts at different chromium contents. 5 KPa of alcohol and 593 K

For all the chromium catalysts studied, the apparent activation energies for ethanol dehydrogenation are the same and equal to 25 kcal/mol in the temperature range of 573 K to 613 K.

The catalytic activities and selectivities on 1.46% Cr catalyst with an alcohol partial pressure of 5 kPa, at 593 K, for the dehydrogenation of primary and secondary alcohols are presented in Table 1. The silica supported chromium catalyst is an order of magnitude more active for secondary alcohols than for primary ones. The selectivities to aldehydes are around 70%, while the selectivity to acetone is a little lower and close to 62%.

**Table 1**

Activity-selectivity data for the dehydrogenation of different alcohols on 1.46% Cr/SiO<sub>2</sub>, 5 kPa of alcohol and 593 K

Alcohol	R <sub>A</sub> (mmol alcohol/mol Cr atoms s)	Selectivity(%)	
		Aldehyde/ketone	Alkene
Ethanol	14.6	69	31
1-Propanol	9.8	71	29
1-Butanol	9.7	73	27
2-Propanol	179.0	62	38

### Alcohol oxydehydrogenation (ODH)

Unlike direct dehydrogenation, the ODH is not equilibrium limited. The DH process is improved by adding a small amount of oxygen to the feed. This reduces the possibility of carbon deposition and reacts with the hydrogen product, making the overall process exothermic and improving the equilibrium limitation. Therefore, the oxidative dehydrogenation was studied at a lower temperature range than pure dehydrogenation and at four different oxygen concentrations. The ethanol ODH rate over 1.46% Cr/SiO<sub>2</sub> catalyst at 538 K was examined for oxygen to ethanol feed molar ratios between 0.1 to 0.9. Table 2 presents the effect of oxygen concentration on the catalytic activity (R<sub>A</sub>). For oxygen to ethanol molar ratios up to 0.9, the catalytic activity is slightly enhanced by the partial pressure of oxygen.

The apparent activation energy for ethanol ODH is 20 kcal/mol regardless of chromium loading and oxygen to ethanol pressure ratio, for temperatures between 503 and 558 K.

Comparing activity values obtained by extrapolating at the same temperature and alcohol pressure, the chromium catalysts are 15 times more active in oxidehydrogenation than for pure dehydrogenation of ethanol. Figure 2 shows the

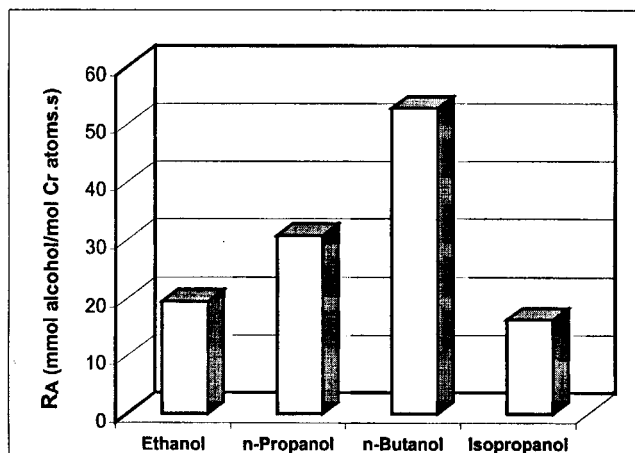
catalytic activity for the oxidative dehydrogenation of primary and secondary alcohols on 1.46% Cr catalyst at 538 K, with alcohol partial pressures of 5 kPa and 2.2 kPa of oxygen. The opposite behavior to DH is observed showing catalytic activities for primary alcohols higher than for secondary ones.

**Table 2**

Effect of oxygen concentration on the activity for ethanol oxydehydrogenation. Alcohol pressure 5 kPa, T = 538 K

$O_2$ /Alcohol molar ratio	$R_A$ (mmol alcohol/mol Cr atoms s)
0.00	1.7*
0.10	14.7
0.18	17.0
0.44	19.8
0.90	22.6

\* Extrapolated



**Fig. 2.** Oxydehydrogenation of different alcohols on 1.46% Cr/SiO<sub>2</sub>. 5 kPa of alcohol, 2.2 kPa of O<sub>2</sub> and 538 K

For all alcohols, in addition to the corresponding aldehyde or ketone, dehydration products and carbon dioxide, were detected. The selectivity to acetaldehyde is appreciably enhanced when ethanol reacts over chromium catalyst in the presence of oxygen. When the oxygen to ethanol ratio is equal to or higher than

0.4, the selectivity to acetaldehyde is 97%, meanwhile near 1% is the selectivity to ethylene and 2% that to CO<sub>2</sub>. These values remain constant at oxygen to ethanol molar ratios up to 0.9 (the maximum relation used in our experiments).

The selectivity to the corresponding aldehyde, for primary alcohols, is 97%, 89% and 80% for ethanol, *n*-propanol and *n*-butanol, respectively. Meanwhile selectivity of isopropanol to acetone remains the same as that for pure dehydrogenation, *viz.*, 59%, under the conditions specified in Fig. 2.

Experiments with catalysts calcined in air at 723 K for 4 h were performed. The catalytic activities over calcined catalysts are a little lower than those found on dried ones, but the same selectivity was observed.

## CONCLUSIONS

- a) Silica supported chromium can be promising catalysts especially for the ODH of alcohols, being very active and selective at relatively low temperatures, 503 – 558 K.
- b) Catalytic activity of SiO<sub>2</sub> supported chromium for DH of primary alcohols at 593 K is almost constant, the activity for isopropanol being an order of magnitude higher.
- c) Catalytic activity of SiO<sub>2</sub> supported chromium for ODH of primary alcohols decreases in the order: *n*-butanol > *n*-propanol > ethanol. Meanwhile the activity for isopropanol is 4 times lower than that for *n*-butanol.
- d) The selectivity to aldehyde for DH of primary alcohols is almost the same and near 70%, while the selectivity of isopropanol to acetone is around 62%. The selectivity to aldehyde for ODH of primary alcohols decreases in the order: ethanol (97%) > *n*-propanol (89%) > *n*-butanol (80%). The selectivity of isopropanol to acetone is low and equal to 59%, similarly to that found in DH.

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## REFERENCES

1. M.P. McDaniel: *Ind. Eng. Chem. Res.*, **27**, 1559 (1988).
2. K. Rao, K. Narayama, V. Rao, S. Masthan, P. Rao: *Indian J. Chem. Soc.*, **A35**, 656 (1996).
3. J. Chudek, G. Hunter, G. McQuire, C. Rochester, T. Smith: *J. Chem. Soc. Faraday Trans.*, **92**, 453 (1996).
4. H.B. Friedrich: *Platinum Metals Rev.*, **43**, 94 (1999).
5. M. White: *Catal. Today*, **18**, 73 (1993).
6. M.L. Parentis, N.A. Bonini, E.E. Gonzo: *Lat. Am. Appl. Res.*, **30**, 41 (2000).
7. D.S. Kim, J.M. Tatibouet, I.E. Wachs: *J. Catal.*, **136**, 209 (1992).