

## Ethanol dehydrogenation reaction to ethyl acetate on copper/copper chromite catalysts.

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### Introduction

In this paper the reaction of ethanol dehydrogenation to ethyl acetate in one step, promoted by a copper/copper chromite catalyst has been studied. A commercial catalyst have, surprisingly, shown high activity (about 65%) and selectivity (98%) in well defined condition of temperature (220-240°C), pressure (20 bars) and residence time (100 g h/mols) [1]. A discussion on the reaction mechanism and kinetics will be the main subject of this contribution.

### Experimental

Several kinetic runs have been performed in a stainless steel tubular packed bed reactor (i.d. 1.8 cm, length 30 cm) by changing the temperature in the range 200-260°C and the pressure from 10 to 30 bars. We operated with different amounts of catalysts, covering conditions corresponding to both differential and integral reactor. At this purpose, the reactor was filled with small spheres of glass, as inert material, and 2 g of catalyst or alternatively the reactor was completely filled with about 50 g of catalyst. We examined, therefore, a large field of residence times with the scope of an accurate kinetic analysis. The employed catalyst was a pre-reduced commercial copper chromite catalyst (BASF Cu-1234) supported on alumina and containing BaCrO<sub>4</sub> as promoter. The catalyst composition, provided by the supplier, is CuCrO<sub>4</sub>/CuO/Cu/BaCrO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> (45:1:13:11:30% b.w.). The catalyst was previously submitted, for 18 h, to a pretreatment with a flow stream of H<sub>2</sub>-N<sub>2</sub> mixture (H<sub>2</sub>/N<sub>2</sub>=6:94 mol/mol) 25 cm<sup>3</sup>/min, at a temperature of 200°C, with the aim to reduce completely the copper oxide on the catalyst surface. After the pretreatment, the catalyst was heated to the desired reaction temperature. The analyses of the reaction products have been made by a gas-chromatograph by both withdrawal online and by cooling and condensing with liquid nitrogen all the reaction products and un-reacted reagents. Ethanol was fed to the reactor with a mixture of H<sub>2</sub> 6% in N<sub>2</sub> as carrier gas. The presence of H<sub>2</sub> is important for obtaining high selectivities.

### Results/Discussion

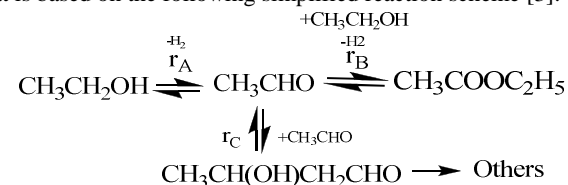
Copper is, normally, present in the catalysts composition in the form of oxide and must be reduced to metal to be active. For this reason all the proven catalysts have been submitted to the already described pre-treatment with a flow stream of hydrogen mixed with nitrogen for about 18 hours at 200°C. This pre-treatment is very important for the catalysts performances and the mentioned prolonged time is necessary for obtaining the highest conversion and selectivity. During the reduction copper oxide reduces to Cu<sup>0</sup>, while, copper chromite reduces, too to Cu<sup>0</sup> that grows epitaxially [2] on the spinel surface, while, H<sup>+</sup> formed during the copper chromite

reduction remains inserted into the spinel structure occupying old Cu<sup>2+</sup> sites for compensating the negative charges of the crystal lattice [2]. In Table 1, are reported some preliminary most significant results of conversion and selectivity.

**Table 1.** - Catalytic results over copper/copper chromite based catalyst. The dehydrogenation reaction were conducted at different pressure (10-20 bar), temperature (200-240°C) and at different contact time.

Cat. (g)	W/F (ghmol <sup>-1</sup> )	T (°C)	P (atm)	F <sub>EtOH</sub> (cm <sup>3</sup> /min)	F <sub>H<sub>2</sub>-6% N<sub>2</sub></sub> (cm <sup>3</sup> /min)	X (%)	S <sub>AcOEt</sub> (%)	S <sub>AcH</sub> (%)	S <sub>others</sub> (%)
50.70	97.4	220	10	0.5	25	51.1	96.1	2.9	1.0
50.70	97.4	220	20	0.5	25	54.8	98.9	0.8	0.3
50.70	97.4	240	20	0.5	25	61.2	98.5	0.9	0.6
50.70	32.5	220	20	1.5	25	47.2	96.9	1.9	1.2
2.07	3.9	220	10	0.5	25	25.9	67.6	26.3	6.0
2.07	3.9	220	20	0.5	25	25.3	79.2	16.8	3.9
2.07	3.9	240	20	0.5	25	31.74	77.0	18.2	4.7
2.07	1.3	220	20	1.5	25	13.74	53.6	40.4	6.0

For developing a kinetic model we considered the most accredited mechanism reported in the literature that is based on the following simplified reaction scheme [3].



Many other runs have been performed and interpreted with the mentioned kinetic model. The best values of selectivities have never obtained before and this open the possibility to simplify the industrial process being not necessary a further hydrogenation step for eliminating by products. We attribute the high selectivities obtained to the particular structure assumed by this commercial catalyst during the reduction with hydrogen and to the local acid environment of Cu<sup>0</sup> obtained from copper chromite. Probably also the presence of Al<sub>2</sub>O<sub>3</sub> as support and barium chromite as promoter could contribute to the high performance of the catalyst [4].

### References.

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