Influence of Cd on the Activity of Copper Chromite Catalyst in the Hydrogenation of Methyl Oleate

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The hydrogenation of methyl oleate was conducted on catalysts based on barium-copper chromite /γ- Al$_2$O$_3$ and respectively barium-copper chromite / γ - Al$_2$O$_3$ doped with Cd. The distribution of the acid strength of the prepared catalysts was determined by thermic desorption of diethyl amine in the temperature range from 20 to 600°C. Experiments were carried out on a laboratory echipament using a fixed bed catalytic reactor at a temperature of 160-250°C, pressure of 80-100 atm with a methyl oleate volume flow rate (VHSV) of 0.2-2h^{-1}and molar ratio hydrogen/ methyl oleate of 5-10/1. The main compounds identified were saturated fatty alcohols and saturated hydrocarbons. Ba-Cu chromite catalyst activity was superior to that of Cd-Ba-Cu chromite, probably due to an optimal distribution of the acid strength of the first catalyst.

Keywords: catalyst, hydrogenation, acidity, methyl oleate, selectivity

The hydrogenation of fatty acid esters to produce alcohols, either saturated or unsaturated is of great interest to industry. The fatty alcohols are chemicals used in the detergent industry, cosmetics and pharmaceutical applications or as auxiliary textile [1]. Their industrial production is now based on the hydrogenation of fatty acids or fatty acid methyl esters obtained by transesterification of vegetable oils, respectively by triglycerides hydrolysis of these oils, at high pressure and temperature (260-300°C and 247-296 atm) [2,3].

In one study, Ross D. Rieke et. al. [4] studied the hydrogenation of fatty acid methyl esters in the presence of copper chromite catalyst for the production of fatty alcohol, at a temperature of 200-300°C and a pressure of 135-203 atm. The catalyst used was a powdered copper chromite and the hydrogenation process was carried out in suspension. Copper chromite has been prepared by two different methods, and two catalysts prepared were tested in the hydrogenolysis of fatty acids methyl ester. The reaction was carried out in an autoclave at 280°C and 135-203 atm. Reaction rates were calculated through a reaction mechanism that took primarily into account the methyl-ester concentration.

Catalyst with a narrower particle distribution was 30% more active, was quickly filtered and it maintained the activity for a further some uses than catalyst with the larger particle distributions [4].

Copper chromite has been used as a catalyst in the preparation of unsaturated fatty alcohols. Its selectivity to the carboxyl group in the hydrogenation reaction of fatty acid esters is not high enough and therefore it require the presence of another metal for inhibiting the hydrogenation of the double bond. Although there are various studies on the hydrogenation of the methyl ester of copper chromite as a catalyst, these studies are limited to discussion about the secondary reactions that occur.

The addition of cadmium like oxide form [5], or carbonate at the based catalyst [6], has the effect of a rather selective hydrogenation, according to the ratio of the Cu-Cr-O:Cd catalyst. Further experiments have shown that chromium leads to a higher saturation of the double carbon-carbon bond, while the catalyst CuO/ CdO [5, 7]

yields to the obtaining of total or partial soaps of fatty acids i.e. by reacting of oxides with acid or fatty ester.

The use of copper and cadmium oleate metal soaps type favors obtaining of oleyl alcohol by hydrogenation in homogeneous catalysis, while other catalysts such as copper and tin oleates promotes the obtaining of stearyl alcohol [8]

When the metal soaps like copper and cadmium oleate are used as catalysts, hydrogenation of the oleic acid take place with formation of oleyl alcohol [9-12].

Waterman et al. [13], also reduced the methyl ester of oleic acid to oleyl alcohol by the addition of the Cu and Cd catalysts. Supposing that these catalysts were used in a mixture of colloidal of Cu and Cd in certain reaction conditions favor the reduction of these substrates. Optimum reaction conditions were: the molar ratio Cu / Cd of 6.1 / 2.7, initial temperature of 300°C and pressure of 190 atm. From the above data it is clear that the ratio Cu:Cd is essential for the selectivity and yield in unsaturated alcohol. The reaction product obtained in these catalytic systems based on copper and cadmium is inhomogeneous and contains black particles. Alcoholic filtrate obtained does not contain copper, but only cadmium oleate.

According to literature data the presence of cadmium catalysts is of major importance to achieve selective hydrogenation process towards obtaining of unsaturated fatty alcohol, while only in the presence of cadmium has been no reaction.

Although there are many studies that address the processing of bioresources towards obtaining biofuels [14-16], the number of publications that address the hydrogenation of bio-fatty esther to fatty alcohol is relatively low. In this paper we studied the influence of cadmium on the activity of copper chromite catalyst in the hydrogenation of methyl oleate.

Experimental part

The raw materials used in experiments were methyl oleate, copper nitrate trihydrate p.a.(Sigma-Aldrich), ammonium dichromate p.a.(Sigma-Aldrich), barium nitrate ACS reagent (Sigma-Aldrich), cadmium acetate dihydrate p.a.(Sigma-Aldrich), ammonia solution, nitric

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Peak Number	Component	Concentration, %
1.	Methyl Palmitate	2.79
2.	Methyl Palmitoleat	2.57
3.	Methyl Stearate	2.38
4.	Methyl Oleat-1n9	77.48
5.	Methyl Oleat-1n7	2.56
6.	Methyl Linoleat	12.22

acid, alumina powdered and electrolytic hydrogen purity from Linde Company. The composition of methyl oleate used in the experiment was determined by GS-MS analysis and are shown in table 1.
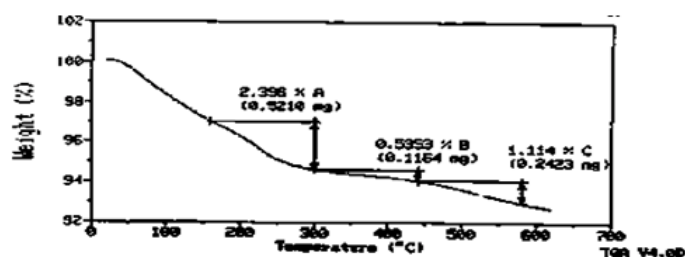

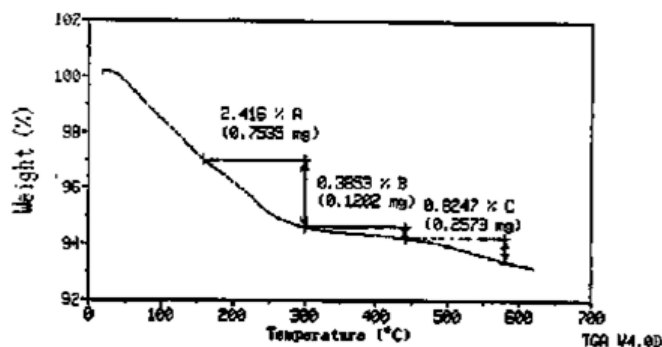Fig. 1. Diethylamine thermodesorption for Ba-Cu chromite / γ-Al$_2$O$_3$

Fig. 2. Diethylamine thermodesorption for Cd-Ba-Cu chromite / γ-Al$_2$O$_3$

The synthesis of catalysts where achieved by extrusion of copper chromite and barium with alumina followed by impregnation with solutions of aqueous solutions of cadmium acetate applying the method of filling the pores, at the cadmium concentration of 1%. Conditioning of the catalyst before and after impregnation was achieved by drying at 160°C for 4 h and calcination at 450°C for 6 h. Activation was achieved by reduction in a stream of hydrogen at 450°C for six hours.

Catalyst characterization was performed by determining the acid strength. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont Instruments *Thermal Analyst 2000/2100* coupled with a module *951 Thermogravimetric Analizer.*

The experimental program was performed in a continuous system and fixed bed catalytic reactor. The process was carried out in isothermal conditions. The temperature was regulated with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket. A metallic jacket for the mobile thermocouple was also placed in the axis of the reactor in order to measure the reaction temperature.

Reaction conditions were:
-pressure: 80-100 atm;
-temperature: 160-250°C;
-volume hourly space velocities of methyl oleate (VHSV): 0.2-2h^{-1};
-molar ratio hydrogen/ methyl oleate: 5-10/1.

The composition of the reaction mixture was performed by the method of gas chromatography coupled with mass spectrometry, equipped with capillary column with a length of 30 m having a diameter of 0.250 mm, whose fixed phase was polyethylene glycol (PEG) and He as mobile phase.

Results and discussions

Thermodesorption curves of diethylamine of the two catalysts are showed in figure 1 and 2. The concentration of acidic centers and the acid strength distribution where determined based on thermal desorption curves of diethylamine. Thermal desorption of diethylamine in temperature range 150-300°C corresponds to weak acids centers (area A), in the temperature range 300-450°C corresponds to medium acids centers (area B) and in the temperature range 450-600°C corresponds to the strong acids centers (area C).

Table 2 presents data on the distribution of strength acidity for the two catalysts, calculated based on thermal desorption curve.

From table 2 is observed a lower content in strong acidic centers (0.1128 meq./G) and of medium acidity centers (0.0527 meq./g) for Cd-Ba-Cu chromite/γ-Al$_2$O$_3$ in comparison with Ba-Cu chromite / γ-Al$_2$O$_3$ (0.1523 meq./g

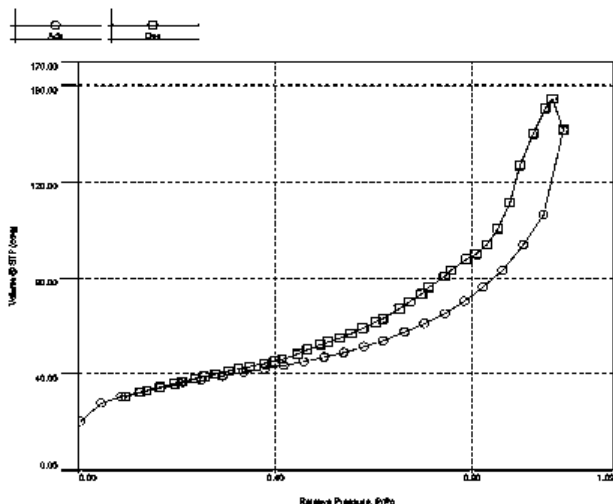| The type of the acidic centers	The acidity strength, meq./g	
	Ba-Cu chromite / γ-Al$_2$O$_3$	Cd-Ba-Cu chromite / γ-Al$_2$O$_3$
Weak acids centers	0.3276	0.3303
Medium acids centers	0.0732	0.0527
Strong acids centers	0.1523	0.1128
Totally acids centers	**0.5531**	**0.4958**

Fig. 3. Adsorption / desorption isotherm of nitrogen for Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst
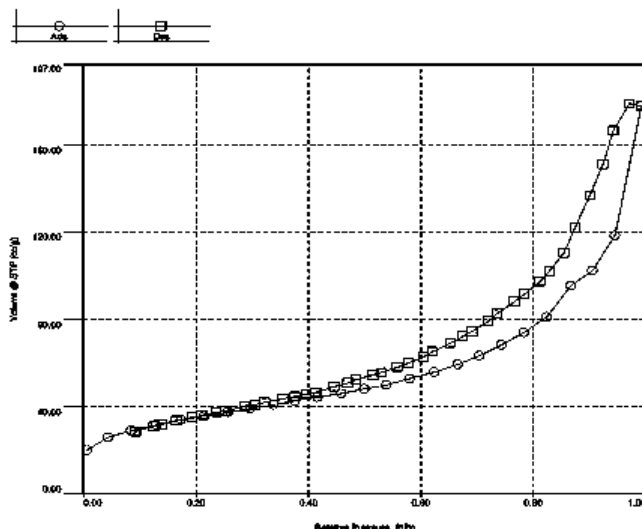

Fig. 4. Adsorption / desorption isotherm of nitrogen for Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst

Table 3

TEXTURAL DATES OF THE TWO CATALYSTS

Catalyst	Specific surface area, m^2/g	Total pore volume, cm^3/g	The pore diameter, nm
Ba-Cu chromite / γ-Al$_2$O$_3$	89.445	0.216	3.644
Cd-Ba-Cu chromite / γ-Al$_2$O$_3$	99.980	0.259	3.833

Fig. 5. Pore size distributions of Ba-Cu chromite / γ-Al$_2$O$_3$
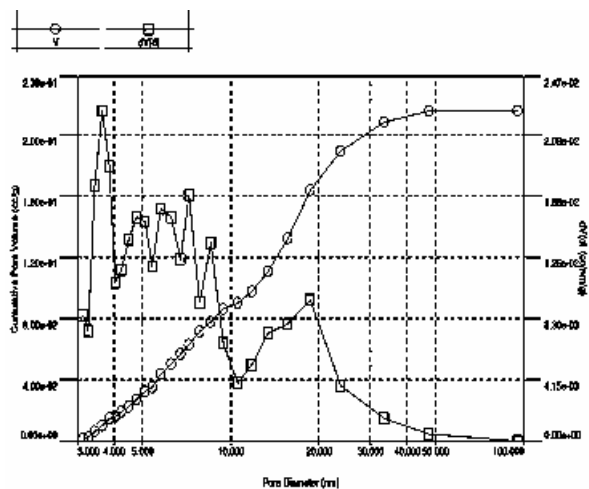

Fig. 6. Pore size distributions of Cd-Ba-Cu chromite / γ-Al$_2$O$_3$

for strong acidic centers and 0.0732 meq./g for medium acidity centers) and a lower concentration of weak centers acids for Ba-Cu chromite / γ-Al$_2$O$_3$ (0,3276 meq./G) in comparison with Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ (0.3303 meq./g). Overall the total concentration of the acidic centers for Ba-Cu chromite / γ-Al$_2$O$_3$ was higher than for Cd-Ba-Cu chromite / γ-Al$_2$O$_3$. It can be notice that after impregnating with cadmium, acidity of Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst diminishes.

The adsorption isotherms for the both catalysts are shown in figures 2 and 3. At relative pressures close to 1.0 is observed an increase in the volume adsorbed and the presence of a small hysteresis loop, this last area being associated with condensation of nitrogen in the mesopores.

Textural characteristics of the catalysts was determined by BJH method cumulative desorption pore volume, and are presented in table 3. The surface area and the total pore volume of the catalyst Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ had a higher value that for Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst.
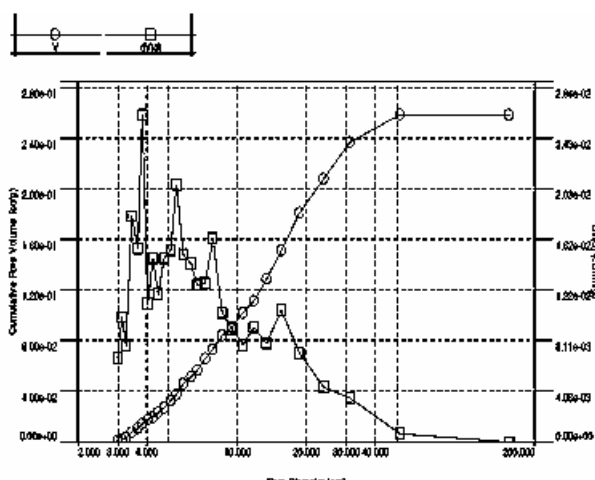
Figure 4 and figure 5 show that the both catalysts possesses a possesses a multimodal pore size distribution with a maximum centered around 37Å. This result could indicate that the multimodal pore structure of the both catalysts has been induced during theirs preparation.

The composition of reaction products obtained on the two catalysts in the hydrogenation of methyl oleate are different. Thus, in the case of Ba-Cu chromite / γ-Al$_2$O$_3$ are obtained saturated fatty alcohols at concentrations of over 50%, saturated hydrocarbons at concentrations of up to 10%, saturated ethers and aldehydes at concentrations of less than 1%. On the other hand when the hydrogenation of methyl oleate occurred on the catalyst Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ on a much larger contact time, were obtained only saturated fatty alcohols at concentrations of up to 24%.

The performance of Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst decreased after impregnation Cd as shown in figures 7-10.
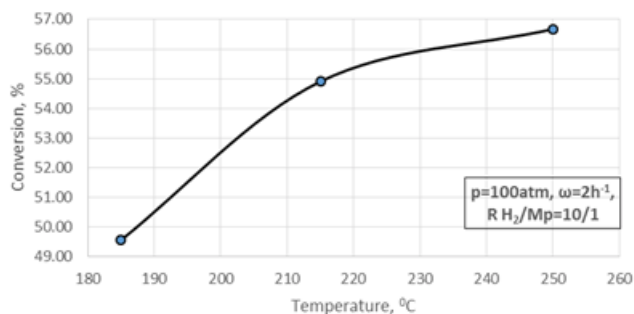
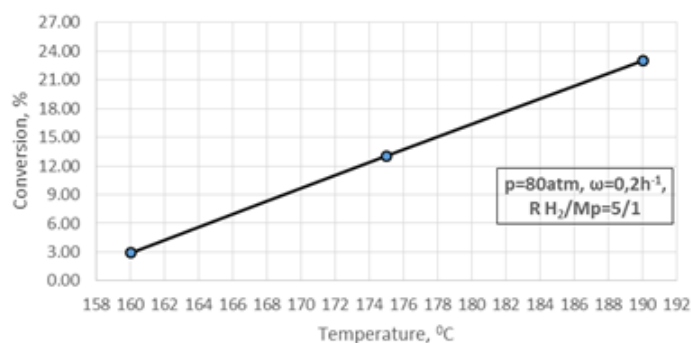Fig. 7. Conversion of methyl oleate on the catalyst Ba-Cu chromite / γ-Al$_2$O$_3$ as function of temperature

Fig. 8. Yield to saturated fatty alcohols and hydrocarbon on the catalyst Ba-Cu chromite / γ-Al$_2$O$_3$ as function of temperature

Fig. 9. Conversion of methyl oleate on the catalyst Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ as function of temperature

Fig. 10. Selectivity to saturated fatty alcohols on the catalyst Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ as function of temperature (Reaction conditions: p=80 atm., w=0.2h^{-1}, R H$_2$/Mp=5/1)

Thus, in figures 7 and 9 are seen that methyl oleate conversion increases with temperature, adding of cadmium reducing obviously the conversion. For Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst, saturated fatty alcohols were the main reaction product (fig. 8), reaction byproducts, respectively saturated hydrocarbons, were obtained at low yield, yield which increases with temperature. In the temperature range studied, for Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst yield in saturated fatty alcohols remains at high levels, and for Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst yield in saturated fatty alcohols increases with increasing temperature. Even if operating conditions were milder, adding cadmium did not favor getting the unsaturated fatty alcohols, selectivity in saturated fatty alcohols being 100% throughout the temperature range studied (fig. 10).

Thus selectivity to fatty alcohol is influenced by the distribution of acidity centers. Therefore, lowering the acidity of Ba-Cu chromite / γ-Al$_2$O$_3$ by adding cadmium diminishes hydrogenolysis reactions responsible for the formation of hydrocarbons. Probably the centers of strong acidity and medium acidity are responsible for the side reactions of hydrogenolysis.

Conclusions

Two catalysts based cuprum chromite with different concentrations of acidic centers were prepared by adding Ba and Cd, in order to test in hydrogenation of methyl oleate.

The Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst has a total acidity greater than the Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ catalyst, acidity due to a high concentration of strong and medium acids centers.

Hydrogenation experiments of methyl oleate were performed on the two catalysts in continuous system.

Ba-Cu chromite /γ- Al$_2$O$_3$ catalyst activity was superior to that of Cd-Ba-Cu chromite /γ- Al$_2$O$_3$, probably due to an optimal distribution of the acid strength of the first catalyst.

Lowering the acidity of Ba-Cu chromite / γ-Al$_2$O$_3$ by adding cadmium diminishes hydrogenolysis reactions responsible for the formation of hydrocarbons. The high
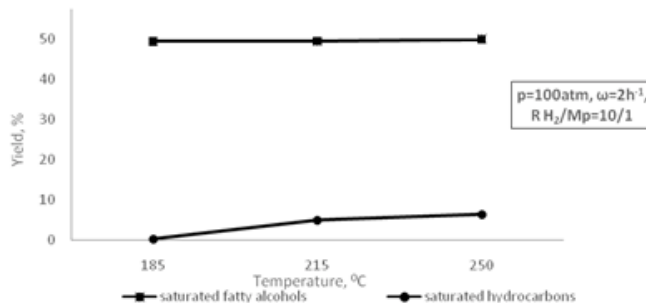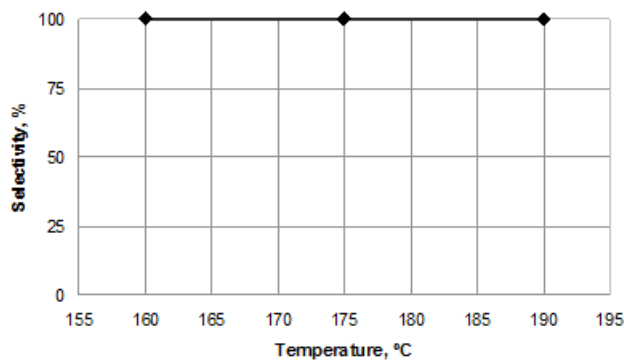
concentration of weak acids centers in the case of catalyst Cd-Ba-Cu chromite / γ-Al$_2$O$_3$ than in the case of catalyst Ba-Cu chromite / γ-Al$_2$O$_3$, is probably responsible for increasing of selectivity to fatty alcohols.

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