



OXIDATIVE DEHYDROGENATION OF ETHANOL OVER MgCrO CATALYSTS

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Received October 2, 2008. In final form February 2, 2009.

ABSTRACT

MgCrO catalysts have been prepared from the corresponding acetates following three different procedures and they were characterized by X-ray diffraction, BET specific surface area, FTIR and EPR. The characterization results revealed that a spinel highly organized with an excess of oxygen at the surface was obtained irrespective of preparation method. The initial crystallization temperature was around 450°C, lower than that required if the preparation was from oxides. The samples calcined at 500°C were tested in oxidative dehydrogenation of ethanol. They were active at 260°C with selectivity to acetaldehyde higher than 75%. The sample obtained by using citric acid led to a relatively lower CO_x formation due likely to a lower oxygen excess at the surface.

Keywords: catalysts, characterization methods, chemical synthesis, MgCr₂O₄, MgCrO catalysts, oxidative dehydrogenation of ethanol.

RESUMEN

Se prepararon catalizadores MgCrO a partir de los correspondientes acetatos por tres procesos diferentes y se caracterizaron por sus diagramas de polvo de difracción de RX, área superficial específica (BET), espectros infrarrojos y Resonancia Paramagnética Electrónica. Los resultados de la caracterización indican que una fase espinela altamente organizada, con un exceso de oxígeno sobre la superficie, es siempre obtenida. La temperatura inicial de cristalización fue alrededor de 450 °C, menor que la requerida si la preparación hubiese sido a partir de los óxidos. Las muestras calcinadas a 500°C fueron probadas como catalizadores en la reacción de deshidrogenación oxidativa de etanol. Ellas fueron activas a 260°C con selectividad a acetaldehído por encima del 75%. La muestra obtenida a partir de soluciones de ácido cítrico produce una relativamente menor formación de CO_x debido posiblemente al menor exceso de oxígeno en la superficie.

Palabras clave: métodos de caracterización, síntesis química, MgCr₂O₄, catalizadores MgCrO, deshidrogenación oxidativa de etanol.

Introduction

The transformation of ethanol from plant raw materials, particularly in countries that do not have any natural hydrocarbon resources, is a promising process for the production of various products such as acetaldehyde, ethyl acetate, acetic acid, ethylal, ETBE, etc. Acetaldehyde is a highly reactive compound and widely used as an intermediate in industrial organic synthesis. Recently, it has shown a good NO_x reduction capability [1]. Acetaldehyde can be produced by hydration of acetylene; vapor phase oxidation of butane, and oxidation or dehydrogenation of ethanol [2-5].

The MgCrO system has proved to be an efficient combustion catalyst [6] but as far as we know there has been no report on its use for the oxidative dehydrogenation of ethanol. In this work the preparation, characterization and activity of MgCrO catalyst are investigated.

Experimental

Catalyst preparation

MgCrO catalysts were prepared from an aqueous solution containing stoichiometric amount of magnesium acetate and chromium acetate. Three different procedures were employed.

(I) The first method consisted in the addition of 4.264 g of MgC₄H₆O₄·4H₂O to 8 g of (CH₃CO₂)₇Cr₃(OH)₂ dissolved in 10 ml of distilled water, followed by the addition of 50 ml of distilled water (pH=6). The dark green solution was magnetically stirred at 80°C until the solvent was almost completely evaporated. The solid was dried for 48 h at 80°C and finally it was calcined at different temperatures for 15 h in static air.

(II) A second sample was prepared by the procedure mentioned above but the pH of preparation solution was adjusted by a dropwise addition with hydrazine until pH = 9. The gel formation was observed at this pH. Evaporation, drying and calcination were as before.

(III) A third catalyst was prepared dissolving acetates in 50 ml of a 10 wt.% citric acid aqueous solution (pH = 2.2). Evaporation, drying and calcination were as before.

The catalysts were denoted as MgCrO-x being x a Roman numeral which indicates the synthesis method. Thus, MgCrO-I corresponds to the sample prepared for method I.

Catalyst characterization

The specific surface areas of catalysts were determined from the nitrogen adsorption isotherm at -196°C by the BET method. A Quantachrome Autosorb and 70 mg of sample previously degassed at 300°C for 6 h were used.

X-ray powder diffraction patterns, XRPD, were obtained with a Rigaku D-MAX-IIIIC diffractometer operated at 30 kV and 20 mA by using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm). The powdered samples were analyzed without previous treatment after deposition on a quartz sample holder. The identification of crystalline phases was made by matching with the JCPDS files.

The FTIR spectra were recorded by a Nicolet Protégé 460 Infrared spectrometer in the $1000\text{--}220$ cm^{-1} range with 32 scans at room temperature. The spectral resolution is better than 1 cm^{-1} . The sample was mixed with KBr and pressed into a thin wafer.

Electron paramagnetic resonance (EPR) measurements were obtained with a Bruker ER 200 spectrometer at room temperature. The spectra of polycrystalline samples placed into sealed glass capillaries were recorded at X band frequencies. Experimental conditions were: center field: 3400 G; field sweep: 3000 G; modulation amplitude: 0.4 G; microwave power: 0.6 mW; sweep time: 200 s; and microwave frequency: 9520 MHz.

Catalytic test

The catalysts (0.5–0.85 mm particles diameter) were tested in a Pyrex tubular fixed-bed reactor operated at atmospheric pressure and equipped with a jacket furnace. The reactor temperature was measured and controlled by a PID controller with a coaxial thermocouple. The feed was a mixture of ethanol, oxygen and helium. The total flow was 50 ml/min at room temperature and the catalyst weight was 400 mg. The flows of oxygen and helium were controlled by Matheson mass flow controllers. Ethanol was fed from a saturator which was immersed in a water bath. Its temperature was controlled by means of a Lauda RCS-R20C cryostat, ensuring temperature variations of less than 0.1°C . A molar ratio of ethanol: oxygen = 2 was used. The reactants and reaction products were alternately analyzed on-line by a Varian 3800 GC gas chromatograph equipped with a flame ionization detector and a methanizer. To prevent possible condensation all gas line connections and valves were wrapped with heating tapes. The catalytic values were obtained after running the reaction for one hour, when the steady state was reached.

Results and discussion

In Table 1, values of BET specific surface areas of samples calcined at different temperatures and after 15 h of exposure time are shown. Although a diminution in the specific surface area with increasing calcination temperature is expected to be occurred, the sintering rate is different among samples. In the case of MgCrO-I and MgCrO-II an almost linear decrease of surface area with an increase of calcination temperature is observed from 450° to 650°C . However, the surface area of MgCrO-III decreases exponentially. At high calcination temperature the crystallization of MgCr_2O_4 spinel takes place rapidly. During calcination two different phenomena can occur simultaneously, a release of H_2O and CO_2 from the initial precursor due to the reaction and a sintering of the decomposed solid (spinel phase).

In Figure 1, the XRPD patterns of MgCrO-I catalyst are shown. It can be seen that the precursor dried at 80°C is essentially amorphous. The characteristic peaks corresponding to MgCr_2O_4 spinel phase ($2\theta = 35.8^{\circ}$, 43.5° and 18.4° , JCPDS card 10-351) begins to be observed at 450°C . This temperature is lower than that required for preparation from oxides. In literature it has been reported that solid state reaction between MgO and Cr_2O_3 resulted in the formation of single-phase MgCr_2O_4 after heating for 3 h at 1100°C [7]. With increasing temperature an increase in the peak intensities accompanied by sharpening of the peaks is observed. Simulation by Rietveld

determines that the phase is highly organized and corresponds to a normal spinel. It is well known for Cr^{3+} has a great tendency to occupy the octahedral position [8]. Similar results are obtained for MgCrO-II catalyst prepared in the presence of hydrazine. Yoshida et. al [9] have reported the spinel formation by the hydrazine method from 480° to 540°C. At 80°C XRPD patterns of MgCrO-III reveal the characteristic peaks corresponding to citric acid which have disappeared after calcination at 450°C. From this temperature, XRPD patterns of three catalysts are similar. Then, it can be suggested the preparation method does not affect the distribution of Cr^{3+} and Mg^{2+} in the lattice. The XRPD analysis of used catalyst indicate no significant differences in the bulk structure after reaction, thus, if any catalyst changes occur they are limited to the surface.

Table 1. BET specific surface area of MgCrO catalysts.

Catalyst	Calcination temperature, °C				
	450	500	550	600	650
MgCrO-I	102	88	80	28	17
MgCrO-II	118	101	70	38	21
MgCrO-III	132	67	46	30	22

BET specific surface area expressed in $\text{m}^2 \text{g}^{-1}$

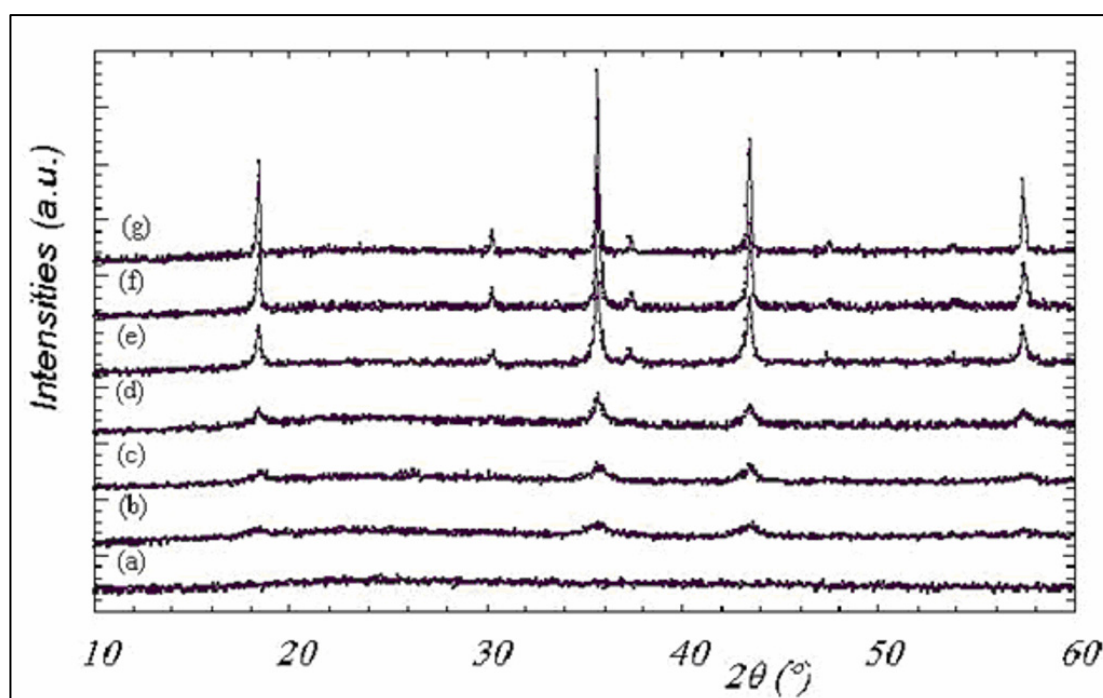


Figure 1. XRPD patterns of fresh MgCrO-I at different calcination temperatures. (a) 80°; (b) 450°; (c) 500°; (d) 550°; (e) 600°; (f) 650°C, (g) 1000°C.

FTIR spectra of fresh catalysts calcined at 500°C are shown in Figure 2. The vibrational behavior of these materials is expected to be rather complex, taking into account that the crystal lattice is built up by two different metal oxygen polyhedral. For the detailed analysis of such vibrational spectra the most correct procedure is a factor group analysis of the unit cell. The simplicity of the recorded spectra suggests a scarce impact of correlation field effects derivate from vibrational coupling in the unit cells and precludes an analysis of this type. On the basis of this simple argument one may predict that the Cr(III)O₆ units behave as approximately Oh “isolated” groups that dominate the spectroscopic behavior. The spectra show two strong and well-defined absorption bands, typical of spinel materials [10]. These bands are mainly assigned to the antisymmetric F_{1u} stretching (630 cm⁻¹) and F_{1u} deformational modes (484, 426 cm⁻¹) of the octahedral CrO₆ moieties [11]. Besides, the lower energy bands (275 and 252 cm⁻¹) are related to lattice modes. The bands at 934 and 893 cm⁻¹ are assigned to stretching modes Cr(VI)-O of CrO₄²⁻ as a consequence of the superficial oxidation of spinel phase, MgCr₂O_{4+x}. Similar results have also been postulated by others authors [12]. The three spectra are similar although the intensity of chromate bands is slightly lower on MgCrO-III fresh catalyst.

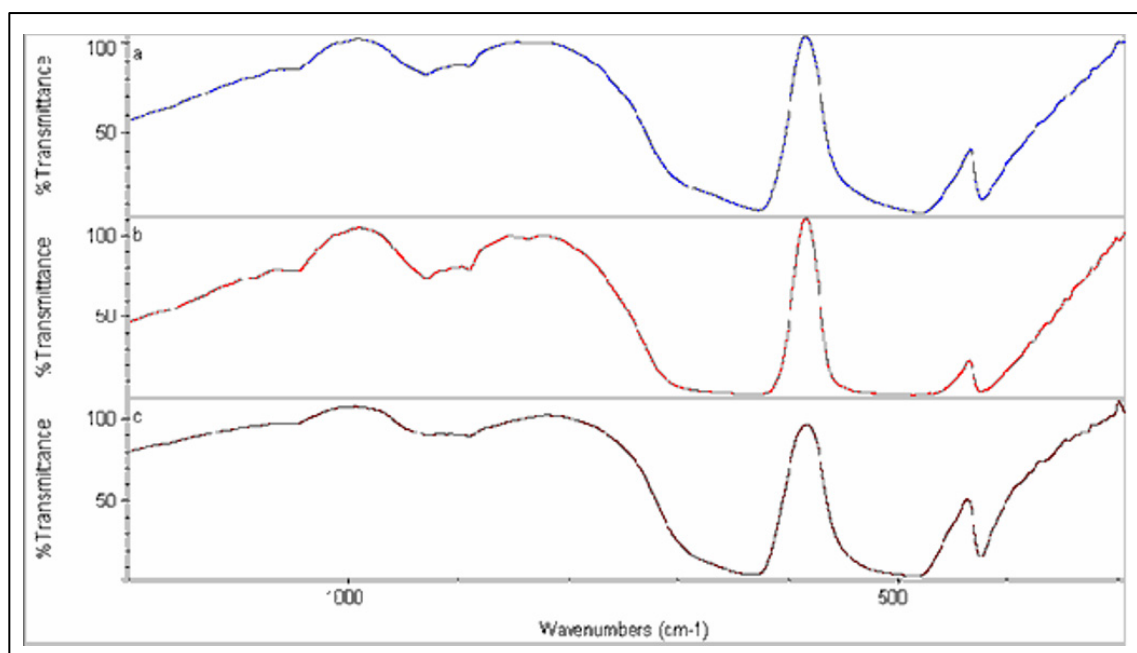


Figure 2. FTIR spectra of fresh MgCrO catalysts calcined at 500°C (a) MgCrO-II; (b) MgCrO-I; (c) MgCrO-III.

EPR spectroscopy is used to examine the presence of Cr³⁺ and Cr⁵⁺. Similar spectra were obtained on three samples. In Figure 3 we show the EPR spectrum of MgCrO-I. They are well resolved and exhibited a Lorentzian EPR signal with an average *g* value of 1.975 which is the typical value for Cr³⁺ [13]. The line width at peak-to-peak maximum (ΔH) is 410 G and 325 G for samples before and after oxidative dehydrogenation of ethanol, respectively. The concentration of Cr⁵⁺ if it is present is neglected.

The oxidation of ethanol over MgCrO catalysts calcined at 500°C is carried out at 260° and 280°C. The experimental data are collected in Table 2. The main oxidation product is acetaldehyde

with selectivity greater than 75%. CO and CO₂ are also obtained as minor products. CH₄, C₂H₄ or acetic acid are not detected under the reaction conditions used. The difference in conversion cannot be only attributed to difference in specific surface area. For MgCrO-III the specific activity (conversion per square meter) is higher and the combustion capacity is lower. Thus, at a same conversion level the selectivity to CO_x is 7% on MgCrO-III and 20.5% on MgCrO-II at 260°C. Then, it could be suggested a lower oxygen excess at the MgCrO-III surface. A lower intensity in the IR chromate bands (see Figure 2) could support this idea. However other characterization results, for example X-ray photoelectron spectroscopy (XPS), should be necessary to shed light on this matter. Although MgCrO catalysts are active in oxidative dehydrogenation of ethanol at higher reaction temperatures than those required on other catalytic systems such as VMgO [3] or supported V₂O₅ [5], the possibility to control the oxygen concentration at the surface becomes a promising catalytic system.

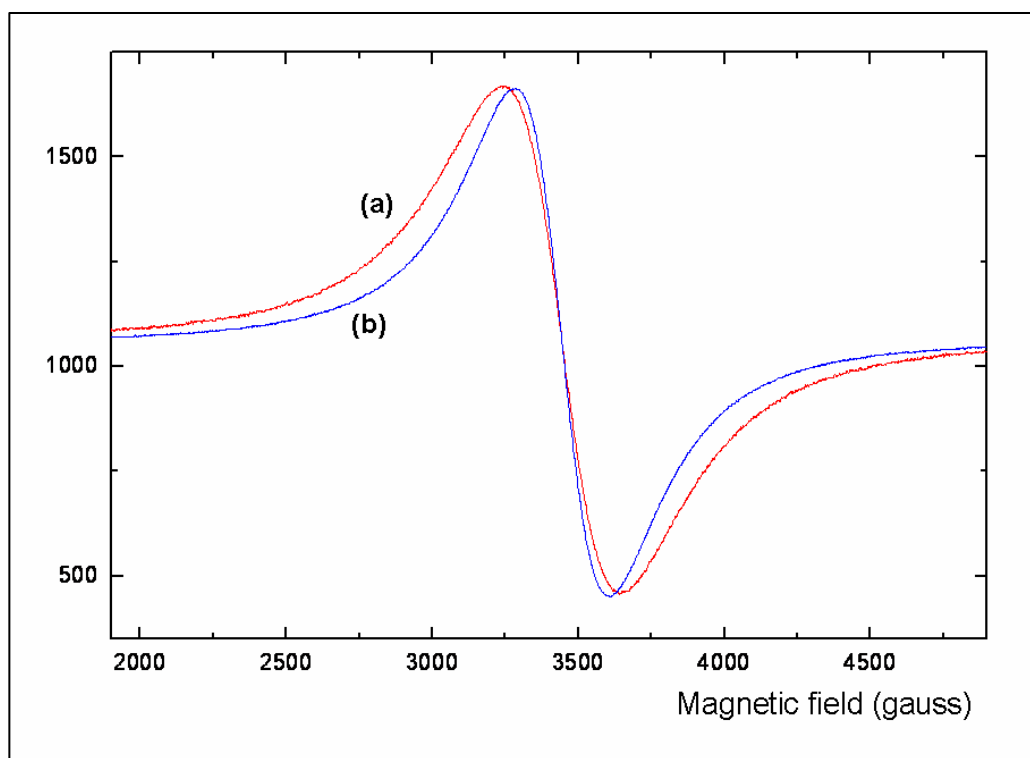


Figure 3. EPR spectrum of MgCrO-I calcined at 500°C (a) fresh catalysts; (b) used catalysts in the oxidative dehydrogenation of ethanol.

Table 2. Catalytic results in the oxidative dehydrogenation of ethanol.

	Reaction temperature, °C	Catalyst		
		MgCrO-I	MgCrO-II	MgCrO-III
X, %	260	39.5	31.6	32.4
	280	55.9	52.3	40.1
S _{AcH} , %	260	82.5	79.5	93.0
	280	76.9	77.5	88.8
S _{CO} , %	260	4.8	5.1	2.0
	280	7.0	6.3	3.0
S _{CO₂} , %	260	12.7	15.4	5.0
	280	16.1	16.2	8.2

W/F_{ethanol} = 59 g h (mol C₂H₅OH)⁻¹; Ethanol molar fraction = 0.062

Conclusions

Different preparation methods have been examined to develop MgCrO catalysts for oxidative dehydrogenation of ethanol to acetaldehyde. The characterization results reveal that a spinel highly organized, with a possible excess of oxygen at the surface, is obtained irrespective of preparation method. The initial crystallization temperature of spinel phase is around 450°C, lower than that required if the preparation is from oxides. The samples calcined at 500°C are active at 260° and 280°C with selectivity to acetaldehyde higher than 75%. The sample obtained by using citric acid leads to a relatively lower CO_x formation due likely to a lower oxygen excess at the surface.

Acknowledgments. Financial support is acknowledged to CONICET (Project PIP no. 6246), to Agencia Nacional de Promoción Científica y Tecnológica (ANPCYT) (Project PICT 25459) and to Universidad Nacional de San Luis (Project 7707). We are grateful to Dr. Ana M. Gennaro for EPR measurements. JCP is member of CONICET

References

- [1] S. Schmieg, B. Cho, H. Ah See, *Appl. Catal B: Environmental*. **2004**, *49*, 113.
- [2] J. McKetta, *Encyclopedia of Chemical Processing and Design*. Marcel Dekker, Inc. New York, 1988; *vol I*, p. 114.
- [3] M. Gomez, L. Arrua, M. C. Abello, *IE&C Research*. **1997**, *36*, 3468.
- [4] N. Quaranta, J. Soria, V. Cortés Corbarán, J.L.G. Fierro, *J. Catal.* **1997**, *171*, 1.
- [5] R. Tesser, V. Maradei, M. Di Seereio, E. Seanteacesaria, *IE&C Research*. **2004**, *43*, 1623.
- [6] E. Finocchio, G. Busca, V. Lorenzelli, R. J. Willey, *J. Catal.* **1995**, *151*, 204.
- [7] Y. Shimizu, S. Kusano, H. Kuwayama, K. Tanaka, M. Egashira, *J. Am. Ceram. Soc.* **1990**, *73*, 818.
- [8] A. Bielanski, J. Haber. *Oxygen in Catalysis*. Marcel Dekker Inc., New York, 1991.

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- [9] N. Yoshida, Y. Takano, M. Yoshinaka, K. Hirota, O. Yamaguchi, *J. Am. Ceram. Soc.* **1998**, *81*, 2213.
- [10] H. D. Lutz, B. Müller, H.J. Steiner, *Solid State Chem.* **1991**, *90*, 54.
- [11] S. D. Ross. *Inorganic Infrared and Raman Spectra*, McGraw-Hill, London, 1972.
- [12] E. Finocchio, G. Ramis, G. Busca, V. Lorenzelli, R. J. Willey, *Catal. Today.* **1996**, *28*, 381.
- [13] Ch. P. Poole, W. L. Kehl, D. S. MacIver, *J. Catal.* **1962**, *1*, 407.