

Cr₂O₃-Al₂O₃ mixed oxide material: synthesis, structure and catalytic behavior for C-H activation.

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Abstract. This work reports the synthesis of Cr₂O₃-Al₂O₃ mixed oxide material via the sol-gel process. The characterization techniques used are X-ray diffraction, Nitrogen adsorption, scanning Electron Microscopy, UV-visible and FT-IR spectroscopy. The results show the presence of the boehmite phase and it cannot be possible to identify crystalline phase of Cr₂O₃. The surface BET of Cr₂O₃-Al₂O₃ is about 130.5 m²/g. The catalytic behavior of the mesoporous material is evaluated for the liquid- phase oxidation of cyclohexane with hydrogen peroxide as oxidant. Cr₂O₃-Al₂O₃ was shown to be mild and efficient catalyst. The use of acetone as solvent presented an approximate 12.4% conversion with 89.66 % selectivity into cyclohexanol.

1 Introduction

Sol-gel processes have attracted the attention of many researchers in recent years [1-3]. In fact, the physical and chemical features of the materials obtained by these methods (e.g., particle sizes, surface areas and mechanical properties) can be changed according to the temperature, operating conditions, and to the used precursor. Nowadays, sol-gel methods are well established allowing the preparation of a board variety of supported metals, metal oxides, coating and composite materials with tailored properties. The obtained materials emerging from these processes can be used in selective heterogeneous catalysis, which represents an area of great economical interest.

Here we wish to report about the sol-gel synthesis and characterization of Cr₂O₃-Al₂O₃ mixed oxide. It was used then as heterogeneous catalyst for the oxidation of cyclohexane with hydrogen peroxyde. Cyclohexane oxidation is currently of considerable commercial significance [4-6].

2 Experimental

2.1 Synthesis of sample

The Cr₂O₃-Al₂O₃ material was prepared by the sol-gel method. An amount of Cr(NO₃)₃.9H₂O was dissolved in water; the resulting solution was stirred and then a mixture of aluminum butoxide and butanol was added into solution while stirring. The obtained green gel was aged for 1 day, then dried at 120 °C and finally calcined at 300 °C for 6 h under an air flow.

2.2 Catalyst characterization

The Cr₂O₃-Al₂O₃ material was characterized by X-ray powder diffraction (XRD) using a philips PW 3710 diffractometer with Cu K α radiation ($\lambda=1.54060$ Å) in the range of $2\theta=20^{\circ}$ - 80° .

The specific surface area was determined from N₂ adsorption isotherm at 77K using Nova 1000^e (Quantachrome) instrument.

The scanning Electron Microscopy (SEM) was realized on TM- 1000 HITACHI instrument.

The mixed oxide was also investigated by the UV-Vis and FT-IR spectroscopy using a Perkin Elmer and an AVARAR 320 Thermo-Nicolet FT-IR spectrometers.

2.3 Catalytic cyclohexane oxidation reactions

Cyclohexane oxidation reaction was carried out in a 250 ml three-necked flask. Typically, a mixture of 66.5 mmol cyclohexane, 66.5 mmol hydrogen peroxyde (H₂O₂), 25 ml solvent and 0.1g catalyst was magnetically stirred at 343 K for 6 h. The reaction mixture was analyzed by gas chromatography (GC), taking aliquots at different reaction times. A Schimadzu GC-14 B gas chromatograph equipped with Apiezon L column (10% on Chromosorb P UNDMCS) and flame ionization detector (FID) was used. Consumption of H₂O₂ was determinate by iodometric titration.

3 Results an discussion

3.1 Characterization

The X-ray pattern of Cr₂O₃-Al₂O₃ material (figure 1) exhibits diffraction lines of boehmite (JCPDS 21-1307) with well-defined peaks at $2\theta=14^{\circ}$, 28° , 38° , 46° and 64° which are assigned to (020), (120), (031), (131) and (231) planes, respectively [7, 8].

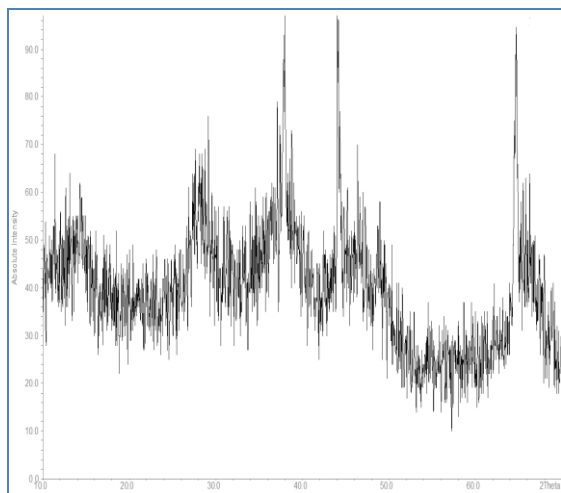


Fig. 1. X-ray diffractogram of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$

Nitrogen adsorption/desorption shows that the simple displayed isotherm of type IV according to IUPAC classification. This result is characteristic of mesoporous solid. The BET surface area of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ is about $130 \text{ m}^2/\text{g}$.

In figure 2, the SEM image of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ material is shown. Geometric grains coexisting with small grains lighter were observed.

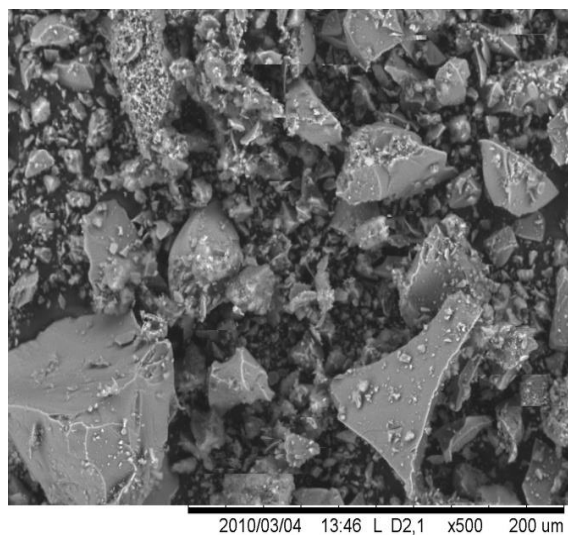


Fig 2. Scanning electron micrograph of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ material.

The diffuse reflectance UV-Vis spectrum of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (figure 3) exhibits a band around 267 nm characteristic of charge transfer transition from oxygen to Al^{3+} [9]. Two bands at 253 nm and 370 nm which are associated to charge transfer from oxygen to Cr (VI). The bands at 456 nm and 516 nm are attributed to Cr (III) in octahedral environment.

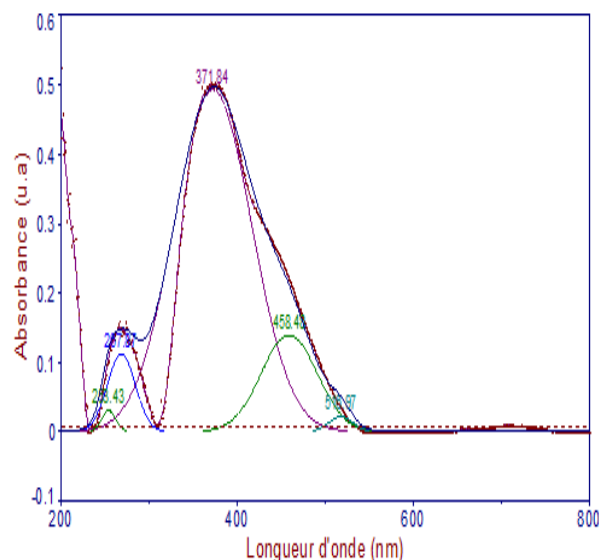


Fig 3. DR-UV-Vis spectrum of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ material.

Figure 4 shows IR spectrum of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide. The IR band at 3400 cm^{-1} is due to OH stretching mode of hydroxyl groups, both from the inter-layer water molecules and from Al-OH groups formed by hydrolysis of residual alkoxyde [11]. The band appearing 2300 cm^{-1} around is due to the C-H stretching. The deformation band of H_2O is situated at 1700 cm^{-1} . The bands appearing between $1500\text{-}1400 \text{ cm}^{-1}$ are attributed to the carbonate or carboxylate surface compounds formed due to adsorption of atmospheric CO_2 on the mixed oxide surface [12]. The IR band at 1050 cm^{-1} is assigned to Al-O-H bending vibration [12]. And band centered at 600 cm^{-1} can be due to Al-O stretching vibration [13]. We designated the absorption band at 480 cm^{-1} as Al-O bending vibration [13].

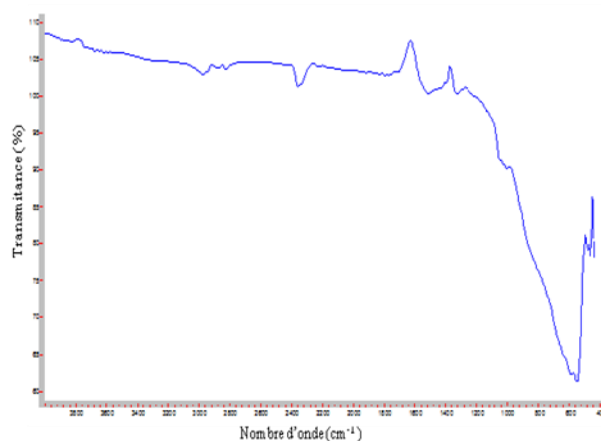


Fig 4. FT-IR spectrum of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ material.

3.2 Catalytic tests

Cyclohexane oxidation was carried out in presence of a little amount of cyclohexanol as initiator and in different solvents. It has been already shown that the cyclohexanol addition increased the catalytic activity [14].

Cyclohexane was first used as reagent and solvent, but no conversion was noticed for the control reaction after the addition of hydrogen peroxide (H_2O_2), in the complete absence of both catalyst and initiator. The sole addition of catalyst did not produce any change, thus showing that the oxidation of cyclohexane remains a hard reaction at 70 °C. However, the addition of cyclohexanol leads to 1.85 % conversion into cyclohexanol (Cy-OH) and cyclohexanone (Cy=O) products (table 1).

Table 1. Oxidation of cyclohexane by H_2O_2

Solvent	Cy-OH (mmol)	Cy=O (mmol)	conversion (%)
Cyclohexane	0.61	0.61	1.85
Ethanol	2.00	0.58	3.88
Acetone	7.37	0.85	12.36
Acetic acid	2.93	1.33	6.40

Reaction conditions: 66.5 mmol cyclohexane, 66.5 mmol H_2O_2 , 40 ml solvent, T= 343 K, t= 6h.

When oxidation reactions with H_2O_2 were carried out with ethanol, acetone or acetic acid as solvent, a considerable increase in cyclohexane conversion was observed. It has been shown that the presence of a polar solvent in this kind of catalytic reaction makes the catalyst more active. Efficient removal of the oxidation products from active sites of the catalyst by the polar solvent is assumed to explain this weak activity [15].

In the acetone 12.36 % conversion was obtained with 89.66 % selectivity into cyclohexanol product. This conversion can be rationalized, taking into account that acetone and hydroperoxydes can react with each other to form dimethyldioxirane (DMDO: $(CH_3)_2CO_2$) which is a powerful oxidizer for organic compounds [16].

4 Conclusion

The $Cr_2O_3-Al_2O_3$ mixed oxide can be prepared from aluminum butoxide and chromium nitrate by a simple sol-gel process. XRD analysis showed that this material presents a not well crystalline structure with the presence of only boehmite phase. BET analysis gives a surface area of about 130 m^2/g . The presence of Cr (III) and Cr (VI) was assigned by UV-Visible.

The mesoporous xerogel is a mild and efficient catalyst for the oxidation of cyclohexane into cyclohexanol and cyclohexanone products with H_2O_2 as oxidant and cyclohexanol as initiator. The presence of a polar solvent in this kind of reactions makes the catalyst more active. The use of acetone as solvent presented an approximate 12% conversion with 89.66% selectivity into cyclohexanol.

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