

# Preparation, Characterization and Catalytic Activity of CrSBA-15 for 2-Propanol Decomposition

M. Sánchez-Cruz<sup>1</sup>, R. Hernández-Huesca<sup>1</sup>, M. A. Pérez-Cruz<sup>1,\*</sup>, N. R. Silva-González<sup>2</sup>

<sup>1</sup>Faculty of Chemical Sciences, Autonomous University of Puebla, Puebla, Mexico

<sup>2</sup>Institute of Physics, Autonomous University of Puebla, Puebla, Mexico

## Email address:

maria.perezc@correo.buap.mx (M. A. Pérez-Cruz)

\*Corresponding author

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**Abstract:** The chromium mesoporous materials have been used in many catalytic reactions. Some studies have been devoted to determining the nature of chromium species and to characterizing the chemical structure. The different chromium species depend on synthetic methods and the support used. In this work we prepared mesoporous SBA-15 supported chromium materials referred to in this document as xCrSBA-15, was prepared by the incipient wetness impregnation method. The materials were characterized by X-ray diffraction (XRD), nitrogen (N<sub>2</sub>) adsorption-desorption isotherms, hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR), scanning electron microscopic (SEM), energy dispersive X-ray spectroscopy (EDS), diffuse reflectance ultraviolet-visible (UV-vis) and Fourier transform IR (FT-IR). Chromium in SBA-15 forms different types of chromates and Cr<sub>2</sub>O<sub>3</sub>, causing morphological and textural changes and generating different catalytic centers. The catalytic conversion of 2-propanol to xCrSBA-15 materials were carried out by in a quartz reactor with a loading of 30 mg of the material at 300°C. Before the catalytic test, the material was activated in two ways: with N<sub>2</sub> and reduced at a H<sub>2</sub>/Ar flow (MxCrSBA-15). The catalytic conversion of 2-propanol to xCrSBA-15 did not increase with reduction (MxCrSBA-15) but decreased deactivation. All the materials had an acidic behavior, which is related to the chromate species in the materials. These results suggest that the more acidic materials favor the formation of coke during the deactivation process, and coke reduces the Cr<sup>3+</sup> to Cr<sup>2+</sup> species, thus decreasing the acidity of the materials.

**Keywords:** Mesoporous Silica SBA-15, Chromates, Reduced Chromium, 2-Propanol Decomposition

## 1. Introduction

Porous materials have been intensively studied with regard to technical applications as catalysts and catalyst supports. However, micropore materials such as zeolites cause diffusion limitations when large reactant molecules are involved [1].

The pore size constraints of zeolite materials were addressed by developing mesoporous molecular sieves that have wider pore diameters in the range from 2 to 50 nm, a high surface area (1000-1500 m<sup>2</sup> g<sup>-1</sup>), uniform framework channels, an excellent sorption capacity (1 cm<sup>3</sup> g<sup>-1</sup>), etc. [2-4].

On the other hand, mesoporous materials such as SBA-15 possess a high surface area and a suitable wall thickness and

pore size for catalytic processes [5]. The most important advantage of these materials is their wall thickness, which is significantly thicker than those of the MCM-type silica [6]. However, these mesoporous materials exhibit a neutral framework, which limits their application in catalytic reactions [7].

Due to the neutral reactivity of the SBA-15 material, several researchers incorporate heteroatoms to its structure, such as Cr [7], Al [8], Fe [9] and Ti [10]. In addition, chromium-containing mesoporous molecular sieves have been studied because of their extensive use in many catalytic reactions [7]. In recent years, supported chromium oxide catalysts have been widely used in dehydrogenation of hydrocarbons [11, 12], selective catalytic reduction of nitrous oxide [13], organic compound oxidation [14, 15], ethylene polymerization, dehydrogenation catalysis [16, 17], hydrogen

production [18] and biodiesel production [19].

Several studies have been devoted to determining the nature of chromium species and to characterizing the chemical structure of the active sites on the catalyst [20]. One method to determine the type and strength of catalytic centers on the materials is the conversion of 2-propanol. This method is often used to test the acid-base properties of the material surface [21]. Two parallel reactions can occur during the process: dehydration to propene mainly on acid sites, and dehydrogenation to acetone on basic or redox sites [22].

Therefore, several studies of 2-propanol decomposition have been carried out in different chromium materials: chromium doped with non-trivalent cations [23],  $\text{Cr}_2\text{O}_3/\text{SiO}_2$  [24],  $\text{Cr}_2\text{O}_3$  powder [25] and  $\text{CrPO}_4/\text{AlPO}_4$  [26].

Recently, Cuesta Zapata *et al.* [20] reported that, when 2-propanol is decomposed on MCM-41 chromium/silica materials with different hydrothermal treatments, these treatments improved the chromium/silica interaction thorough chromasiloxane ring formation. These anchored  $\text{Cr}^{3+}$  species developed highly unsaturated Lewis acid sites responsible for the 2-propanol dehydration.

Tredja [27] reported a comparative study of the incorporation of chromium species via incipient wetness impregnation into mesoporous silica of MCM-41 type, SBA-3 and SBA-15, where they found that the formation of active centers on different silica supports strongly depends on the preparation conditions used in their synthesis.

Additionally, various synthetic methods are expected to result in different chromium species and the different chromium species may behave differently in catalytic reactions [28]. Thus, in this work, we have prepared SBA-15 and chromium-supported mesoporous SBA-15 (xCrSBA-15) by the wetness impregnation method. The type and strength of catalytic centers on materials were determined to the conversion of 2-propanol in the non-reduced and reduced materials with  $\text{H}_2$  before the reaction.

## 2. Experimental

### 2.1. Synthesis of the Materials

The mesoporous silica SBA-15 support was synthesized using sodium silicate as silica source as reported previously by Gómez-Cazalillas *et al.* [29]. The materials were prepared by the incipient wetness impregnation method with  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as chromium precursors. The impregnated support was dried at  $80^\circ\text{C}$  for 12 h and calcined at  $550^\circ\text{C}$  for 5 h, with a ramp of  $1^\circ\text{C min}^{-1}$ . These materials were assigned as xCrSBA-15, where x is the weight percentage of metal loading (2, 5 and 10 wt%).

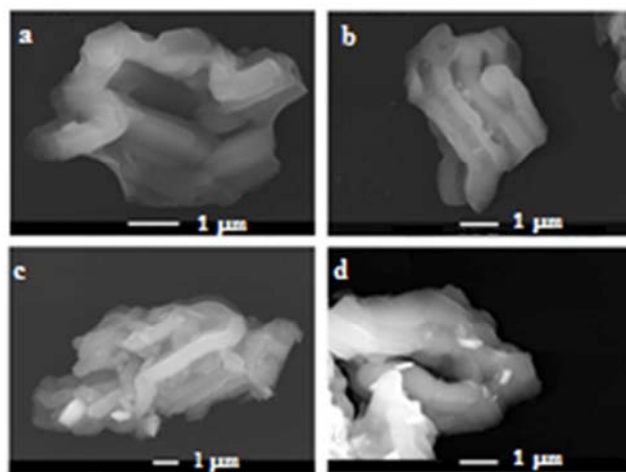
### 2.2. Characterization

The scanning electron microscopic (SEM) images and EDS analysis were recorded on a JEOL JSM-7800F microscope operated at 30 kV. X-ray powder diffraction patterns were recorded with CuK $\alpha$  radiation on a D8 Discover Bruker diffractometer, operated at 40 kV and 35 mA. XDR data were

recorded at a small angle from  $2\theta$  in the range from  $0.6$  to  $2^\circ$  and a wide-angle from  $20$  to  $80^\circ$ . Nitrogen adsorption isotherms of the materials were made with an Autosorb-1C-MS instrument after materials were outgassed at  $200^\circ\text{C}$  for 12 h in vacuum before measurements were made. The surface areas and pore size distribution were determined by BET and BJH methods, respectively. FTIR spectra were collected on a Varian Excalibur spectrometer in the range from  $4000$  to  $400\text{ cm}^{-1}$ , before and after measuring catalytic activity, using 1 mg of materials by 150 mg of KBr. UV-vis spectra of the materials in the range from  $200$  to  $1900\text{ nm}$  were obtained on a UV-vis spectrophotometer Varian-Cary 300 before and after measuring catalytic activity. The reducibility of the materials was determined by  $\text{H}_2$  temperature-programmed reduction ( $\text{H}_2$ -TPR) using 80 mg of the materials in  $\text{H}_2/\text{Ar}$  (10 vol% in Ar) with a heating rate of  $10^\circ\text{C min}^{-1}$  from  $25$  to  $600^\circ\text{C}$ . To carry out these measurements, the materials were previously treated with oxygen (flow rate =  $60\text{ cm}^3\text{ min}^{-1}$ ) at  $550^\circ\text{C}$  for 4 h.

### 2.3. Measuring the Catalytic Activity

The reaction of 2-propanol decomposition was carried out in a quartz reactor with a loading of 30 mg of the material. Before the catalytic test, the material was activated in two ways. In the first way, the xCrSBA-15 materials were activated at  $300^\circ\text{C}$  for 2 h under  $\text{N}_2$  with a flow rate of  $60\text{ cm}^3\text{ min}^{-1}$  to the materials. In the second way, the materials were reduced at a  $\text{H}_2/\text{Ar}$  flow rate of  $100\text{ cm}^3\text{ min}^{-1}$  for 2 h at  $600^\circ\text{C}$ . Then, the materials were cooled to  $300^\circ\text{C}$  under a  $\text{N}_2$  flow ( $60\text{ cm}^3\text{ min}^{-1}$ ) to the materials. These new materials were called MxCrSBA-15. In the catalytic test, 2-propanol was fed into the reactor through a saturator using  $\text{N}_2$  as a carrier gas with a flow rate of  $60\text{ cm}^3\text{ min}^{-1}$ . The partial pressure of 2-propanol used was 22.4 Torr, and the conversion was studied at  $300^\circ\text{C}$ . The products were identified with a Perkin Elmer Autosystem XL gas chromatographer with a flame ionization detector (FID) and a Porapak N column.



**Figure 1.** SEM micrographs of the materials: mesoporous silica support (a) SBA-15 and chromium-supported in mesoporous silica (b) 2CrSBA-15, (c) 5CrSBA-15 and (d) 10CrSBA-15.

### 3. Results and Discussion

#### 3.1. Characterization of the Materials

The materials obtained show different colors depending on the amount of chromium, that is, yellow for 2%, green for 5% and dark green for 10% of Cr loading. These colors indicate that there are different Cr species in the materials [30]. The 2CrSBA-15 coloring exhibits the presence of the  $\text{Cr}^{6+}$  species (chromate or polychromate), due to the rapid oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  in the nitrate salt solution before being impregnated [31], while the 5CrSBA-15 and 10CrSBA-15 colorings are green, which is a characteristic color indicating the presence of  $\text{Cr}^{3+}$  species, such as  $\text{Cr}_2\text{O}_3$  [20].

The estimated percentage of metal present in the xCrSBA-15 materials by an EDS analysis reveals that there is a minimal difference between the experimental concentration on the surface and the theoretical content of chromium (Table 1). These results demonstrate that the incipient wetness impregnation method is efficient in the preparation of these materials.

##### 3.1.1. xCrSBA-15 SEM

The external structure of the xCrSBA-15 materials characterized by SEM is presented in Figure 1. The SBA-15 support (Figure 1a) has a typical long-chain structure, between 200 and 600 nm in diameter, while the 2CrSBA-15 and 5CrSBA-15 materials (Figure 1b and 1c) have a chain-like structure that breaks into separate rod-like sub-units. The 10CrSBA-15 material (Figure 1d) displays the presence of a small rod-like structure that forms irregular spherical particles where pore formations can be observed [32, 33, 34]. The structural change of the xCrSBA-15 materials probably occurs due to a strong interaction between chromium nitrate and silica during the calcination of Cr precursor in oxygen at 550°C. According to Wang *et al.*, while chromium nitrate interacts with the Si—OH of the SBA-15 material to form Si—O—Cr and Cr—O—Cr linkages, these interactions result in the weakening of the Si—O—Si bonds and the breaking of long interconnected chains and the later formation of crystalline  $\alpha\text{-Cr}_2\text{O}_3$  at elevated chromium loadings [32]. As previously observed, the 5CrSBA-15 and 10CrSBA-15 materials (Figure 1c and 1d) contain needle-shaped and cube-shaped crystalline structures of  $\text{Cr}_2\text{O}_3$  [35]. This result was confirmed by an X-ray diffraction analysis.

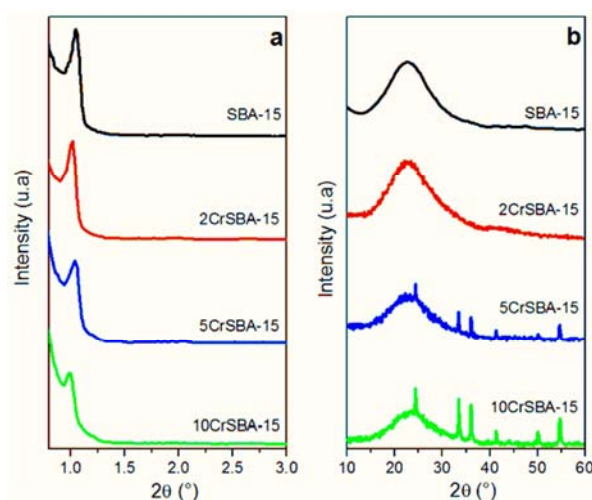
##### 3.1.2. X-ray Diffraction

Figure 2 depicts the patterns of the XRD support and catalytic materials. At the low angle range (Figure 2a), all the materials exhibit an intense diffraction peak at  $\sim 1^\circ$ , which can be indexed as the typical pattern of hexagonal structure attributed to the diffraction plane (1 0 0) [36]. With an increasing Cr content, the intensity of the (1 0 0) peak decreases as a result of a partial blocking of the SBA-15 mesopores and the deterioration of the ordered pore structure [32]. All the materials exhibit significant changes from the *d*-spacing of the (1 0 0) plane to lower values in relation to the SBA-15 material, implying dilation in the framework lattice [37]. It is important to take into consideration that there is a

decrease in the unit cell constant ( $a_0$ ) and the wall thickness ( $e$ ) in these materials (Table 1). A similar result has also been reported by Charan so the decrease in the  $a_0$  is attributed to a possible disruption in the inter-particle growth mechanisms at a macroscopic scale, which is in agreement with its structural change as it creates an ordered array of spheres [37]. Figure 2b depicts a broad peak at  $2\theta = 23.2^\circ$  attributed to  $\text{SiO}_2$  (the component of SBA-15) [38]. There are no diffraction peaks assignable to crystalline  $\text{Cr}_2\text{O}_3$  in the 2CrSBA-15 material. It may be deduced that the chromium species are highly dispersed on the surface of SBA-15 or that the particle size of chromium oxide may be small to be detected by XRD [35]. However, the 5CrSBA-15 and 10CrSBA-15 materials have the same peaks at  $2\theta = 24.5^\circ, 33.6^\circ, 36.2^\circ, 39.7^\circ, 41.5^\circ, 44.2^\circ, 50.2^\circ$  and  $54.8^\circ$ , attributable to the hexagonal phase of  $\text{Cr}_2\text{O}_3$  from the JCPDS powder diffraction file (PDF card 00-038-1479) [39]. The intensity of the  $\text{Cr}_2\text{O}_3$  peaks grows by increasing the chromium loading [40].

##### 3.1.3. $\text{N}_2$ Adsorption/Desorption Isotherms

The  $\text{N}_2$  adsorption-desorption isotherms of the SBA-15 support and the xCrSBA-15 materials are type IV with H1-type hysteresis (Figure 3a). This feature is typical of mesoporous materials with one-dimensional cylindrical channels [36]. The adsorption-desorption isotherms exhibit a hysteresis loop extended to very low relative pressures ( $P/P_0 < 0.3$ ). This low-pressure hysteresis may be the result of a change in the porous structure of the material, such as a swelling of a non-rigid structure [41, 42]. An X-ray diffraction analysis of the xCrSBA-15 materials confirms the change in the porous structure. The decline on the surface area and pore volume may be the result of the blocking by CrOx in the pores of the SBA-15 support (Table 1) [32]. Regarding the mesopore size distribution (Figure 3b), the support has pores between 30 and 50 Å with an average pore diameter of  $\sim 40.5$  Å. The materials impregnated with Cr (xCrSBA-15) exhibit a decrease in the intensity of the distribution peak with respect to the SBA-15 peak, which implies a blockage of pores.



**Figure 2.** (a) Low angle and (b) high-angle XRD patterns of the mesoporous silica support SBA-15 and the chromium-supported in mesoporous silica 2CrSBA-15, 5CrSBA-15 and 10CrSBA-15.



**Table 1.** Percentage of metals present in the materials estimated by an EDS analysis and the structural properties of the support and the xCrSBA-15 materials.

Materials	SBA-15	2CrSBA-15	5CrSBA-15	10CrSBA-15
Metal content (wt%) <sup>a</sup>	—	1.98	4.59	9.20
Planar distance $d_{100}$ (Å)	83.93	86.81	84.21	88.62
Lattice constant $a_0$ (Å) <sup>b</sup>	167.86	100.23	97.23	102.23
Wall thickness $e$ (Å) <sup>c</sup>	127.36	58.13	155.33	61.43, 66.83
Surface area ( $\text{m}^2 \text{g}^{-1}$ ) <sup>d</sup>	912.96	419.21	340.67	340.67
Pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>e</sup>	0.79	0.47	0.43	0.40
Average pore size (Å) <sup>f</sup>	40.5	42.1	41.9	40.8, 35.4

<sup>a</sup> Calculated by SEM  
<sup>b</sup>  $a_0 = 2 \times d_{100} / \sqrt{3}$   
<sup>c</sup> Calculated by  $e = a_0 - \text{pore size}$   
<sup>d</sup> Calculated by BET method  
<sup>e</sup> Mesopore volume by BJH  
<sup>f</sup> Calculated by BJH method

A slight shift towards larger pores occurs in the distribution peaks of the 2CrSBA-15 and 5CrSBA-15 materials, which may be attributed to a swelling of the mesopores caused by the impregnation of Cr in their walls ( $r_{\text{aq}}$  of  $\text{Cr}^{3+} = 0.6 \text{ Å}$  [43]). This distortion is also observed in the micropores as a consequence of low pressure hysteresis. On the other hand, the 10CrSBA-15 material exhibits a narrower pore distribution found within the SBA-15 distribution peak with two maximums at 40.8 Å and 35.4 Å. This result may be attributed to a change in structure by the presence of  $\text{Cr}_2\text{O}_3$  [33].

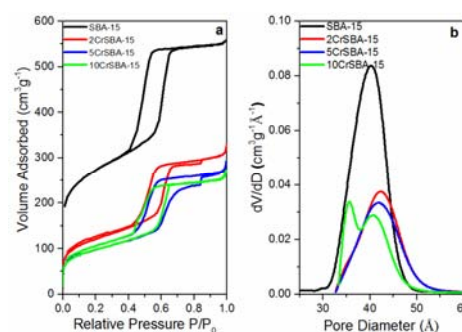
### 3.1.4. $\text{H}_2$ -TPR

Figure 4 depicts the  $\text{H}_2$ -TPR profiles of the materials supported with Cr (xCrSBA-15), where several  $\text{H}_2$  consumption peaks are observed, indicating the presence of various species of Cr in the materials. A poorly defined peak is observed at  $\sim 200^\circ\text{C}$ , which may be attributed to the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{5+}$ . Similarly, approximately at this temperature  $\text{CrO}_3$  is melted and decomposed by deoxygenation to form  $\text{Cr}_2\text{O}_3$  [44]. A second peak between 280 and  $300^\circ\text{C}$  is attributed to the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{4+}$  and  $\text{Cr}^{3+}$ , which was ascribed by Fouad [44] to the formation of  $\text{Cr}_2(\text{CrO}_4)_3$ , by thermal decomposition of  $\text{CrO}_3$ . A peak at  $\sim 390^\circ\text{C}$  is observed in the three xCrSBA-15 materials. This  $\text{H}_2$  consumption peak has been reported for materials impregnated with Cr by incipient wetness and is related to the reduction of  $\text{Cr}^{6+}$  species such as mono-, di-, tri- and tetrachromates isolated on the surface of the material. Shi associate this reduction to the presence of soluble  $\text{Cr}^{6+}$  as suggested by Cavani [12, 45]. Another  $\text{H}_2$  consumption peak at  $\sim 480^\circ\text{C}$  is observed in 10CrSBA-15, but it cannot be seen in 5CrSBA-15 and it only appears as a small shoulder in 2CrSBA-15, which is attributed to the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  to form  $\text{Cr}_2\text{O}_3$  [7, 12, 44]. Finally, a peak at  $\sim 543^\circ\text{C}$  is observed in 2CrSBA-15 and 5CrSBA-15 and it appears as a shoulder in 10Cr SBA-15. This peak has been reported for materials produced by adding Cr during the synthesis of the support and is associated to the reduction of ions from  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  grafted on the surface of the silica, making it difficult to reduce [12, 27]. Other authors have also attributed it to the reduction of  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$  during the reduction of  $\text{CrO}_3$  [44].

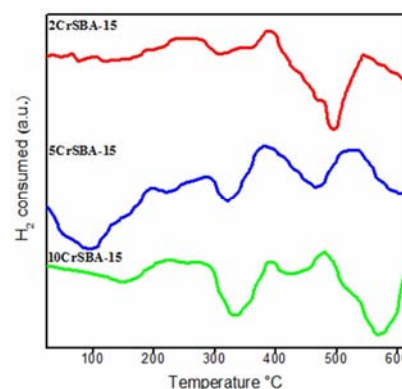
### 3.2. Conversion of 2-Propanol on xCrSBA-15 and MxCrSBA-15 Materials

Figure 5 compares the conversion of 2-propanol to propene

and acetone in the xCrSBA-15 (Figure 5a) and MxCrSBA-15 (Figure 5b) materials, where 5CrSBA-15 exhibits the highest conversion ability. It is observed that all the materials have a higher conversion ability towards propene formation, including the SBA-15 material that has a conversion to propene of less than 4%, but it does not present conversion to acetone. The 2CrSBA-15 material has the lowest conversion ability, whereas the 5CrSBA-15 and 10CrSBA-15 materials have a similar conversion ability to propene and acetone. The high  $\text{Cr}_2\text{O}_3$  content does not favor conversion. Apparently, the activity of the materials is related to the presence of soluble and grafted chromates [27]. On the other hand, the reduction of these materials (M5CrSBA-15 and M10CrSBA15) does not change the initial conversion, but it inhibits deactivation [46].



**Figure 3.** (a) Adsorption-desorption isotherms and (b) pore size distributions for the mesoporous silica support SBA-15 and the chromium-supported in mesoporous silica 2CrSBA-15, 5CrSBA-15 and 10CrSBA-15.



**Figure 4.**  $\text{H}_2$ -TPR profiles of chromium-supported in mesoporous silica 2CrSBA-15, 5CrSBA-15 and 10CrSBA-15.

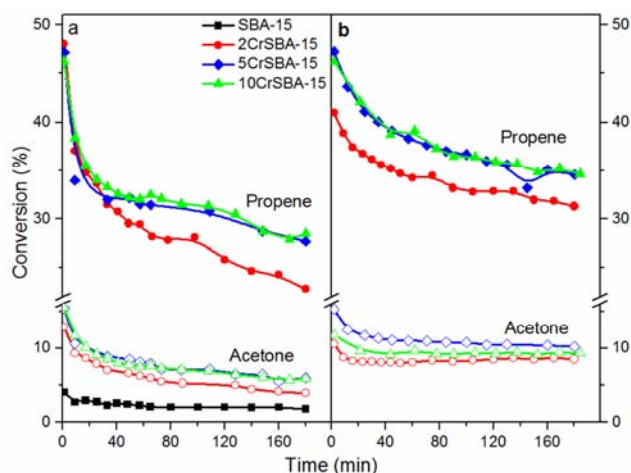
The xCrSBA-15 materials present a greater deactivation, thus a greater number of acidic species ( $\text{Cr}^{6+}$ ) or soluble chromates that dehydrate form  $\text{Cr}_2\text{O}_3$  determined by UV-vis (Figure 7), and they are also more susceptible to carbon poisoning or coke formation [47].

Regarding the selectivity of the materials (Figure 6), the xCrSBA-15 materials increase their selectivity to propene in relation to time (Figure 6a) and the reduced MxCrSBA-15 materials decrease their selectivity after a few minutes (Figure 6b). This phenomenon is the opposite in acetone. The selectivity towards dehydrogenation or dehydration of 2-propanol in the studied materials is explained by the relationship with the Cr species determined by IR and UV.

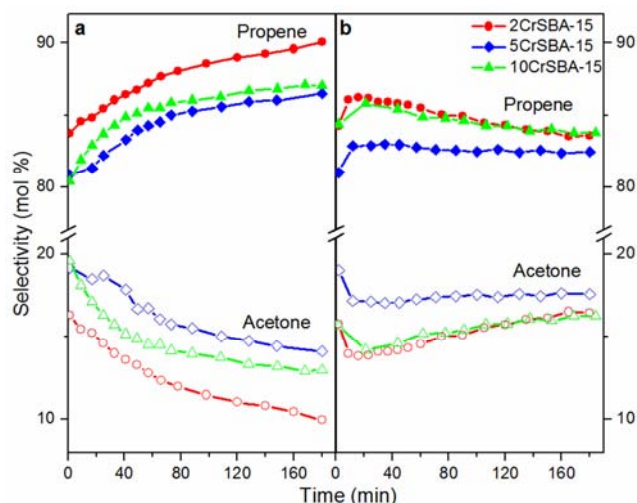
### 3.2.1. Uv-vis Spectroscopy of the CrSBA-15 Materials Before and After the 2-Propanol Conversion Reaction

The unused xCrSBA-15 materials have bands that correspond to the  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  species (Figure 7). The bands at 260 and 360 nm have been found in silica modified with Cr; they are typical of  $\text{Cr}^{6+}$  species caused by charge transfer of monochromate species [48].

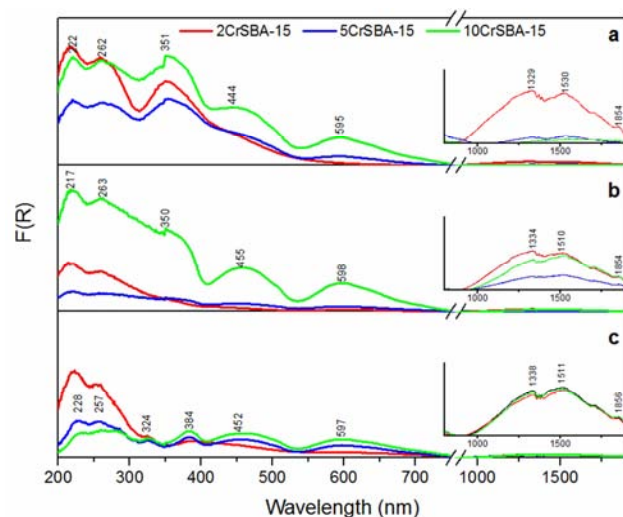
Another band that corresponds to the dichromate species is observed at 455 nm and increases its intensity with the chromium content due to an increase in the degree of polymerization of the  $\text{Cr}^{6+}$  species [48]. The band corresponding to the  $\text{Cr}^{3+}$  species appears at 600 nm and is attributed to the  $\text{Cr}^{3+}$  species in the  $\alpha\text{-Cr}_2\text{O}_3$  particles [49-51]. In the spectra of xCrSBA-15 (Figure 7c) and MxCrSBA-15 (Figure 7d) materials after the reaction, the charge transfer bands of the  $\text{Cr}^{6+}$  species located at 380 and 450 nm are more evidently observed. The band of the d-d transitions of the  $\text{Cr}^{3+}$  located at  $\sim 600$  nm increases its intensity, indicating the reduction of  $\text{CrO}_3$  to  $\text{Cr}_2\text{O}_3$  [52, 53]. Only in the MxCrSBA-15 materials is there a band at 324 nm corresponding to the transition from  $\text{O} \rightarrow \text{Cr}^{2+}$  in the silica [54]. There are also two other bands: the first at  $\sim 1000$  to  $1333$  nm, and the second at  $\sim 1428$  nm (insert) with very low response corresponding to  $\text{Cr}^{2+}$  pseudo-tetrahedral species. This band is more intense in the MxCrSBA-15 materials [53, 54].



**Figure 5.** Conversion of 2-propanol to propene (solid symbol) and acetone (open symbol) on chromium-supported in mesoporous silica materials: (a) non-reduced xCrSBA-15 and (b) reduced MxCrSBA-15 materials.



**Figure 6.** Selectivity to propene (solid symbol) and acetone (open symbol) on chromium-supported in mesoporous silica materials: (a) non-reduced xCrSBA-15 and (b) reduced MxCrSBA-15 materials.



**Figure 7.** Diffuse reflectance spectra of (a) the non-used xCrSBA-15, (b) the used non-reduced xCrSBA-15 and (c) the used reduced MxCrSBA-15 materials.

**Table 2.** Percentages of chromium species in the unused xCrSBA-15 materials and the used xCrSBA-15 and MxCrSBA-15 materials after decomposition of 2-propanol.

Materials	% species			
	Mono- chromate	Di- and polychromate	$\text{Cr}^{3+}$	$\text{Cr}^{2+}$
Unused				
2CrSBA-15	91.0	0.0	0.0	9.04
5CrSBA-15	69.6	21.5	8.1	0.77
10CrSBA-15	64.3	22.0	13.7	0.00
Used				
2CrSBA-15	58.6	11.9	8.1	21.43
5CrSBA-15	39.7	36.2	18.3	5.80
10CrSBA-15	46.4	35.8	15.2	2.51
M2CrSBA-15	44.8	26.5	10.0	18.74
M5CrSBA-15	25.7	36.9	21.5	15.93
M10CrSBA-15	18.8	39.9	26.7	14.70

Considering the area under the curve of the bands of the UV-vis spectra (Table 2), the percentage of the chromium species can be estimated. The results indicate that all the

xCrSBA-15 materials have high percentages of monochromate and dichromate species ( $\text{Cr}^{6+}$ ). However, a decrease in the percentage of  $\text{Cr}^{6+}$  species is observed in the used xCrSBA-15 and MxCrSBA-15 materials, whereas there is an increase in the percentage of  $\text{Cr}^{3+}$  and  $\text{Cr}^{2+}$  species due to the reduction process. The MxCrSBA-15 materials have higher percentages of  $\text{Cr}^{2+}$ .

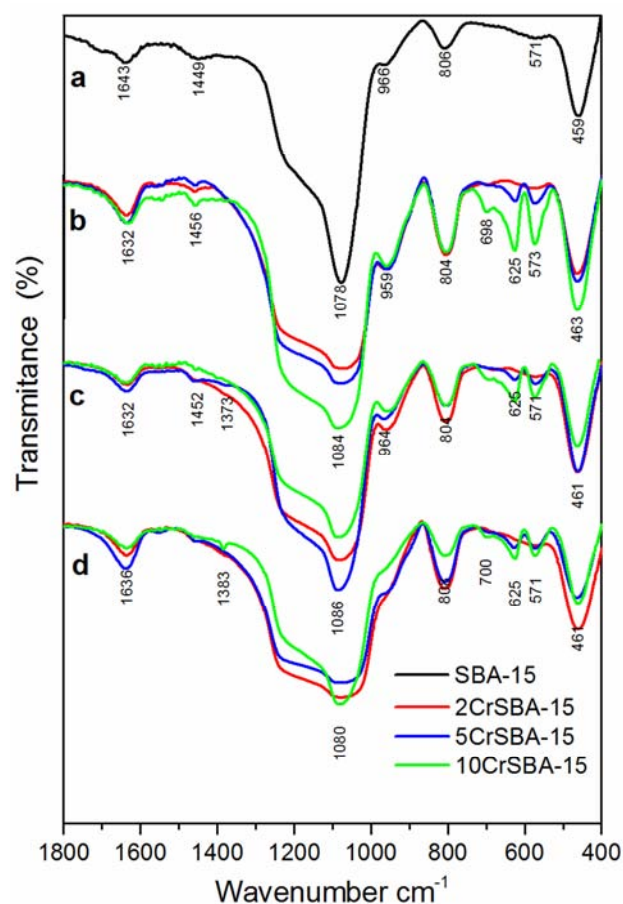
### 3.2.2. FTIR Spectroscopy of the CrSBA-15 Materials Before and After the 2-Propanol Conversion Reaction

In the FTIR spectra of the SBA-15 support and the xCrSBA-15 materials used and unused in the 2-propanol reaction, a band at  $\sim 3450\text{ cm}^{-1}$  (not presented here) is observed, which is attributed to the SiOH group on the surface of the SBA-15 support [55]. On the other hand, Figure 8 depicts the spectra of the SBA-15 support and the unused xCrSBA-15 materials. A band at  $1636\text{ cm}^{-1}$  is observed corresponding to the bending vibrations of the adsorbed water [57]. There is a slight increase with Cr loading in the band, indicating that Cr is bound to the surface of the silica and is hydrated. A band at  $1085\text{ cm}^{-1}$  and a shoulder at  $1200\text{ cm}^{-1}$  indicate  $\nu_{\text{as}}$  (Si—O—Si), where there is a decrease in their intensity with the impregnation of Cr [32], while a band at  $795\text{ cm}^{-1}$  corresponds to  $\nu_{\text{s}}$  (Si—O—Si), and a band at  $460\text{ cm}^{-1}$  corresponds to the bending group O—Si—O [56], where there is an increase in their intensity. There is a variation in the intensity of all these bands in comparison to the bands of the SBA-15 support. A band that appears at  $964\text{ cm}^{-1}$  has generally been assigned to Si—O vibration in Si—OH groups [57]. A shift of this band at  $959\text{ cm}^{-1}$  is recorded for the xCrSBA-15 materials, which could be attributed to defects in the Si—O—M stretching modes, where  $\text{M} = \text{Cr}$  [57], due to the presence of chromates on the surface. The bands at  $571$  and  $631\text{ cm}^{-1}$  appear in the spectra of the 5CrSBA-15 and 10CrSBA-15 materials, where the intensity is higher in the latter attributable to vibrations in hydrated  $\text{Cr}_2\text{O}_3$  on the surface of the pores, as reported by other authors [33, 57, 58]. The materials used in the 2-propanol conversion reaction exhibit a slight shift to higher wavenumbers of the shoulder at  $1200\text{ cm}^{-1}$ , which indicates the presence of C—O bonds, whose band appears at  $1260\text{--}1000\text{ cm}^{-1}$  [22, 55]. The band at  $958\text{ cm}^{-1}$  decreases in those materials used in the 2-propanol reaction and almost disappears in the previously reduced materials (MxCrSBA-15). This shift may be attributed to the  $\text{Cr}^{6+}$  bound as chromate that is reduced to form  $\text{Cr}_2\text{O}_3$ . Similarly, the bands at  $571$  and  $631\text{ cm}^{-1}$  decrease in intensity after the 2-propanol reaction. The change in these bands and the appearance of a small band at  $1380\text{ cm}^{-1}$  may be attributed to the formation of C—H bonds that inhibit the activity of the materials [22, 46].

## 4. Conclusion

Chromium materials of well-ordered mesoporous structure were generated using the incipient wetness impregnation method. These materials contain chromate and  $\text{Cr}_2\text{O}_3$  in their

structure. The results of the catalytic evaluation indicate a high selectivity to the formation of propene due to the presence of chromates on the surface of the materials, which is an evidence of their acidic behavior. Although the high content of chromium causes the formation of chromium oxide, its presence does not improve the catalytic activity of the xCrSBA-15 materials. The reduced materials (MxCrSBA-15) do not increase the conversion of 2-propanol to propene and acetone, but they do become deactivated in relation to time, whereas the non-reduced materials (xCrSBA-15) do increase their selectivity to propene in relation to time due to a self-reduction of chromate ions.



**Figure 8.** FTIR spectra of (a) the SBA-15, (b) the non-used xCrSBA-15, (c) the used non-reduced xCrSBA-15 and (d) the used reduced MxCrSBA-15 materials.

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