

# Synthesis, Characterization and Comparison of Cr-SBA-15 Materials Synthesized by Direct Hydrothermal Synthesis Method

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**ABSTRACT:** The chromium incorporated mesoporous SBA-15 materials (Cr-SBA-15) with the Cr content Si/Cr molar ratio 30 were synthesized by direct hydrothermal procedure and characterized by XRD (small and wide angle), FT-IR, ICP-OES and BET. Three samples were synthesized with Cr source addition and washing conditions differences in the same direct synthesis procedure. First one (Cr-SBA-15-30-1), Cr was added the synthesis gel overnight after the addition of TEOS and no washing (only centrifuge) after hydrothermal step. For the second sample (Cr-SBA-15-30-2), Cr was added 1 h after the addition of TEOS and no washing. The last one (Cr-SBA-15-30-3), Cr was added 1 h after the addition of TEOS and just one washing with de-ionize water after hydrothermal treatment. The materials were calcined at 540 °C for 6 h in dry air. The washing effect of materials were observed well in N<sub>2</sub> adsorption-desorption technique and ICP-OES analysis. When we had washed the sample (Cr-SBA-15-30-3), Cr content was decreased to % 0.23 contrast with the others.

**KEYWORDS:** Ordered mesoporous materials, Mesoporous silica SBA-15, Cr incorporated SBA-15, Direct hydrothermal synthesis, Surface characterization

## I. INTRODUCTION

Ordered mesoporous materials have attracted great interest for their potentially wide applications (i.e. in catalysis, adsorption, separation, and ion exchange) since the discovery of M41S family (MCM-41, MCM-48, MCM-50) in 1992 [1,2]. After this time, in 1998, Zhao et al. [3, 4] developed SBA-15 ordered mesoporous material in highly acidic conditions by using triblock copolymer P123 as structure-directing agent. SBA-15 usually possesses high surface area and uniform tubular channels with tuneable pore diameter in the range of 5–30 nm, significantly larger than that of MCM-41. Because of its thicker walls, SBA-15 shows much better thermal and hydrothermal stability than MCM-41 [3-6]. Therefore SBA-15 has become more interesting compared with MCM-41 [7].

Although highly ordered mesoporous materials have many advantages in the area of adsorption with their high surface area, large pore size, and large pore volume, they can have also the drawbacks in the area of catalyst due to the weak acidity of structure if they are used in pure form. With this reason heteroatoms may be incorporated into the framework of the mesostructured material in order to provide the acid sites and coordinating sites [8].

Transition metal oxides (MO<sub>x</sub>) are a kind of effective catalytic materials for many reactions but their catalytic performance is limited by the low-surface areas. Incorporating the M<sup>n+</sup> ions to a framework of mesoporous silica's with high surface areas or loading their oxides onto the surfaces of these porous materials is a logical way to eliminate this limitation [9]. M<sup>n+</sup> containing in the framework or MO<sub>x</sub> grafted of the surface of mesoporous silica provide high dispersion of metal ions. Consequently more active acid sites are ensured for the reactions which these metals used as catalysts. The incorporation of transition-metal elements such as Fe [7], Cr [8-14], Ti [15], Al [16], Au [16], Co [16-18], Pd [19], Mn [20, 21], Zr [22], or V [23] into the amorphous silica walls is mandatory for the formation of catalytically active sites in mesoporous molecular sieves. Depending on the type of transition- metal species, the coordination, and

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the number of metal species incorporated in the framework of silica walls, both the Bronsted and Lewis acid sites and their strength might be varied [14].

Chromium is a proper transition-metal element in the selective oxidation of light alkanes and exhibits high performance [10, 11]. Chromium supported on amorphous solids like silica and silica-alumina (the Phillips catalysts) are presently used to produce more than one third of all polyethylene sold all around the world. Therefore development of chromium supported silica materials has a great importance [12]. Chroma based mesoporous materials also can be used as catalyst in 1-hexene oligomerization [8].

Functionalization mesoporous materials with metals is a very common investigation area in the literature [7-18]. Sun et. al. synthesized Fe incorporated SBA-15 materials with changing prehydrolysis time of TEOS, the Fe/Si molar ratio and the Fe sources. When the prehydrolysis time of TEOS decreased, the specific surface area, pore volume and pore diameter of sample increased (Fe-SBA-15(1h)). They also denoted that the content of Fe-incorporation in the SBA-15 has a direct impact on the porous characters [7]. Grieken et. al. synthesized M-SBA-15 (M = Al, Fe, B, Cr) via direct synthesis method and investigated their catalytic activities in the 1-hexene oligomerization. Cr-SBA-15 samples were synthesized at different pH values (1,5, 3 and 5). Although all of the samples have lower Cr content, the highest one is Si/Cr = 240 at pH 5. According to UV measurements, chromium species formed after calcination were Cr(VI) for all the catalysts. Application to reaction showed that the highest conversion was obtained on Al-SBA-15. Despite the lower Cr content, Cr-SBA-15 exhibited also higher conversion [8].

There are two main procedure to synthesis metal containing SBA-15. One of them is direct synthesis, is most commonly used, and has many advantages such as uniform dispersion of active sites and larger surface area. But it has also a few drawbacks like lower metal content and hydrothermal statement. On the other hand post grafting method provides more hydrothermal statement and higher metal content on surface while causes lower dispersion of metal oxides and adsorption capacity due to blocking mesoporous by metal species. Zhang et. al. synthesized Cr-SBA-15 and CrO<sub>x</sub>/SBA-15 with direct synthesis method (i.e. one step synthesis) and incipient wetness impregnation method, respectively. They compare the structural properties of synthesized materials and emphasized that the reducibility of CrO<sub>x</sub>/SBA-15 is higher than Cr-SBA-15. Its reason that CrO<sub>x</sub>/SBA-15 has higher Cr surface density and accordingly more existed in +6 oxidation state (Cr<sup>+6</sup>, i.e. mono- and poly- chromate) than +3 oxidation state (Cr<sup>+3</sup>, i.e. Cr<sub>2</sub>O<sub>3</sub>) of Cr species [9]. Aguado et. al. used one-step synthesis procedure when they had synthesized chromium and aluminium containing SBA-15 materials. Their purpose was discover of new Philips catalysts for ethylene polymerization. The materials were synthesized both with direct and grafted-impregnated ways. The difference of their study was including synthesis of bifunctional SBA-15. That means they functionalized SBA-15 materials with Al and Cr at the same time. They found that the incorporation of chromium and aluminium into SBA-15 mesoporous structure increased pore size and pore volume. CrAlSBA-15 (prepared by directly) exhibited higher polymerization activity than Cr/AlSBA-15 (prepared by impregnation) [12]. Aguado et. al. also searched catalytic activity of Cr/SBA-15 and Cr/Al-SBA-15 in ethylene polymerization [13]. Selveraj et. al. is another research group that Synthesized Cr-SBA-15 with direct synthesis to investigate the best Cr source for synthesis and to obtain better hydrothermal stability [14].

Different metals can be supported SBA-15 meso structure. For example, Wan et. al. Produced Ti-SBA-15 for searching properties as a drug releaser [15]. Wua et. al. prepared Au-Co containing SBA-15 for testing catalytic activity of toluene combustion. As a results, they observed excellent catalytic activity [16]. Wang et. al. Synthesized ZnO/Al-SBA-15 by post-synthesis and immobilization method via microwave-assisted route. According to their opinion, they observed that ZnO/Al-SBA-15 could be an effective alternative to remove H<sub>2</sub>S from gaseous streams [17]. Cui et. al. produced Co substituted SBA-15 via pH adjusting method. The optimized preparation conditions for Co-SBA-15x were Si/Co ratio 10–20 and pH of synthesis system 7.2–8.0. Co-SBA-15x possessed excellent stability and recyclability (much higher than Co-MCM-41-TIE and Co/SBA-15.) in epoxidation of styrene with molecular oxygen [18].

The removal of the surfactant (EO20PO70EO20) by washing before final calcination is a critical step in the synthesis of silica SBA-15 [27]. In this work, they are reported that effects of metal addition time and washing conditions on the properties of mesoporous material SBA-15. For this aim they were synthesized three different materials, named as Cr-SBA-15-30-1, Cr-SBA-15-30-2 and Cr-SBA-15-30-3, each of them has different synthesis condition but generally with the same direct synthesis procedure, and was characterized by XRD (small angle), XRD (wide angle), ICP-OES, FT-IR, BET.

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## II. EXPERIMENTAL

Pluronic 123 triblock copolymer was used as surfactant and TEOS was used as silica source. According to the direct synthesis Cr source (Chromiumnitratnonahydrate,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was added directly synthesis gel before hydrothermal treatment. In direct synthesis of Cr-SBA-15 samples [14], 4.02 g of triblock copolymer  $\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$  (Pluronic 123, Aldrich) was dissolved in 25 ml of water at  $30^\circ\text{C}$ . After Pluronic had been dissolved completely, 70 ml of aqueous HCl at pH 0.8 were added to solution under stirring. The solution was heated up to  $35^\circ\text{C}$  after adding the aqueous HCl and maintaining at  $35^\circ\text{C}$  approximately 1h. 9 g of Tetraethylorthosilicate (TEOS, Aldrich %98) was added dropwise and the solution was stirred overnight (15 h) at  $35^\circ\text{C}$ . Calculated amount of chromiumnitratnonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) (for obtaining the desired molar ratio of  $\text{Si}/\text{Cr} = 30$ ) was added slowly and the solution was stirred 24 h at  $40^\circ\text{C}$ . Followed by aging at  $100^\circ\text{C}$  for 24 h under static conditions, and then the solid product was recovered by centrifuge (and no washing) and dried at  $100^\circ\text{C}$  overnight. The template was removed from the mesoporous material by calcination with dry air flow at  $540^\circ\text{C}$  for 6 h using a heating rate of  $1^\circ\text{Cmin}^{-1}$ . This sample was named as Cr-SBA-15-30-1.

All samples were prepared by the same way but with a few differences. During the preparation of Cr-SBA-15-30-2 metal source was added after 1 h of TEOS addition and wasn't washed after hydrothermal step like Cr-SBA-15-30-1. In the synthesis of Cr-SBA-15-30-3, metal source was added after 1 h of TEOS addition and the sample washed one time with deionize water after hydrothermal treatment.

## III. CHARACTERIZATION OF MATERIALS

The small and wide angle XRD patterns were determined on an X-ray diffractometer (XRD, Bruker/AXS D8 Advance) operating at 40 kV and 200 mA using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). The diffractograms were recorded in the  $2\theta$  range of  $0.4\text{-}10^\circ$  with a  $2\theta$  step size of  $0.04^\circ$ . The wide angle XRD patterns were determined on an X-ray diffractometer (XRD, Panalytical/Empryan) operating at 45 kV and 40mA using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15405 \text{ nm}$ ). The diffractograms were recorded in the  $2\theta$  range of  $0\text{-}80^\circ$  with a  $2\theta$  step size of  $0.02^\circ$ .

Fourier-transfer infrared spectroscopic (FT-IR) spectra of samples were recorded on a Perkin Elmer Spectrum 100 spectrometer ( $400\text{-}4000 \text{ cm}^{-1}$ , with a resolution of  $0.4 \text{ cm}^{-1}$  (ATR technique). Surface areas and pore size distributions as well as  $\text{N}_2$  adsorption-desorption isotherms of the samples were measured via  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  on a Micromeritics ASAP 2020 apparatus with all samples outgassed at  $250^\circ\text{C}$  for 180 min under vacuum before measurement. Surface areas and pore size distributions were calculated according to the BET and BJH (Barrett-Joyner-Halenda) method, respectively. Chromium content of the Cr-SBA-15-30 samples was measured by ICP-OES optical emission spectroscopy on a Varian Vista AX Axial CCD Simultaneous ICP-OES spectrometer. Previously, the sample was digested by acid treatment with  $\text{H}_2\text{SO}_4$  and HF.

For comparison, it was also given physical properties (BET surface area, Cr content %wt, pore size and pore volume) of Cr-SBA-15-30-x samples in Table 1.

## IV. EXPERIMENTAL RESULTS

Fig. 1 shows the small-angle XRD patterns of Cr-SBA-15-30 samples. It is observed from Fig. 1 that XRD features of all the samples are rather similar, with three diffraction peaks at  $2\theta = 0.888, 1.58,$  and  $1.88$  that can be indexed as (100), (110), and (200) reflections which associated with  $p6mm$  hexagonal symmetry [3], respectively. The intensity values of diffraction peaks are almost same for all samples. The wide-angle XRD patterns of Cr-SBA-15-30 samples were recorded in the  $2\theta$  range of  $10\text{-}80^\circ$  and are presented in Fig. 2. Peaks at  $2\theta = 24.5, 33.58, 36.22$  and  $54.84$  indicated that Chromium oxide ( $\text{Cr}_2\text{O}_3$ ) is existed crystal form in the structure of Cr-SBA-15-30-2 [9]. Peak at  $2\theta = 24.5$  was observed all of the samples which proved that the presence of crystal hexagonal  $\text{Cr}_2\text{O}_3$  in the structure [9]. Cr-SBA-15-30-2 (b) showed much more distinctive hexagonal crystal structure than the others. The small angle and wide-angle XRD patterns are consistent with the literature [8, 9, 14, 25, 26].

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Table 1  
Physical properties of Cr-SBA-15-30-x samples.

Sample	$A_{BET}$ ( $m^2/g$ )	Cr (wt %)	$d_p$ (nm)	$V_p$ ( $cm^3/g$ )
Cr-SBA-15-30-1	714.23	1.190	5.4	0.96
Cr-SBA-15-30-2	586.91	1.132	5.4	0.79
Cr-SBA-15-30-3	619.94	0.234	5.3	0.83

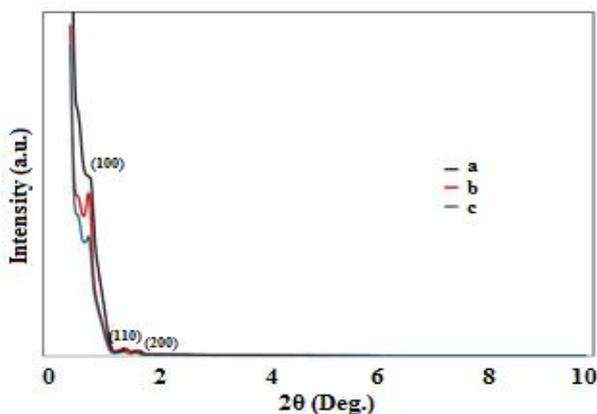


Fig. 1. Small-angle XRD patterns of Cr-SBA-15 (a) Cr-SBA-15-30-1 (b) Cr-SBA-15-30-2 (c) Cr-SBA-15-30-3.

The framework vibrations of Cr-SBA-15 materials were analysed by FT-IR spectroscopy and are presented in Fig. 3. Peak associated with Si-OH groups in the  $960-970\text{ cm}^{-1}$  range were observed for all samples. Raman band at  $970\text{ cm}^{-1}$  attributable to  $Cr^{6+}$  species [9]. The strong peak around  $1630\text{ cm}^{-1}$  might be attributed to the bending vibration of  $H_2O$  [24]. The samples showed absorbance peaks at  $1070-1060$ ,  $805-800$  and  $460-440\text{ cm}^{-1}$  which identified by typical of Si-O-Si bands that are associated with the formation of the silica networks [24].

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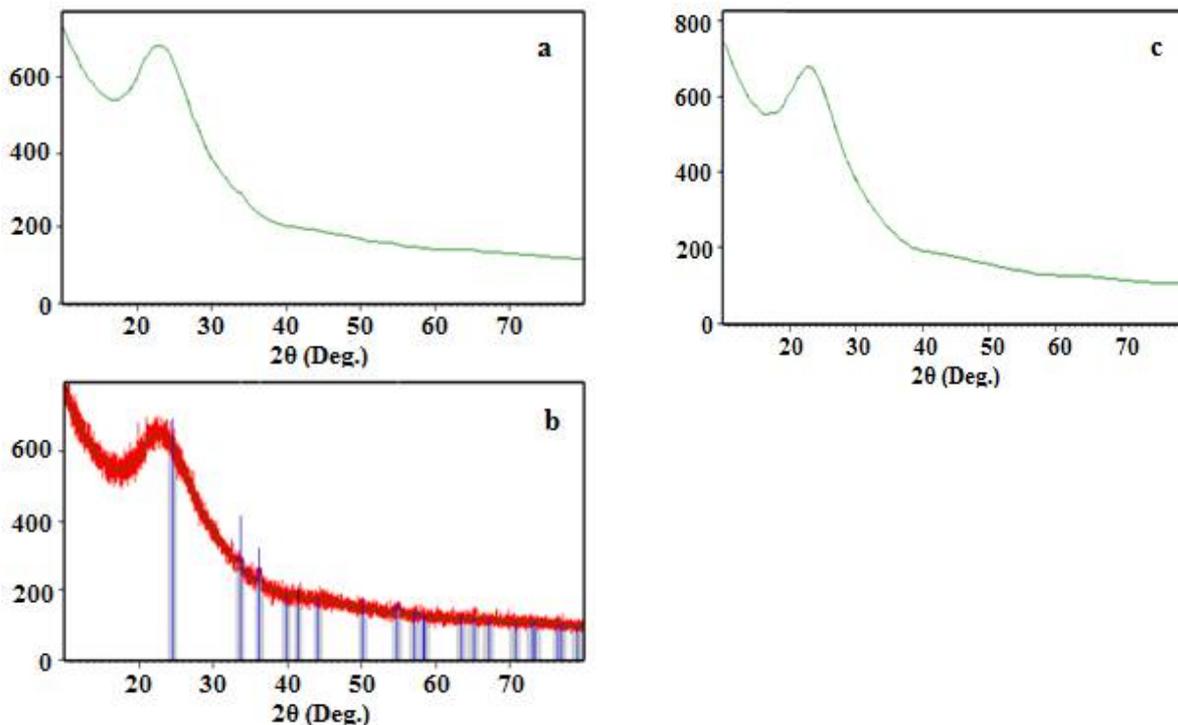
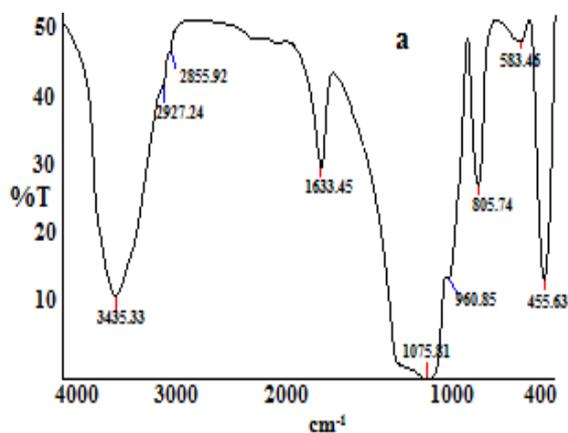


Fig. 2. Wide-angle XRD patterns of Cr-SBA-15  
(a) Cr-SBA-15-30-1 (b)Cr-SBA-15-30-2(c)Cr-SBA-15-30-3

According to ICP-OES measurements (Table 1) it is clear that Cr-SBA-15-30-1 has the highest Cr content with % 1.19 wt. Similarly Cr-SBA-15-30-2 has almost the same Cr with % 1.13 wt. The reason of this case may be no washing after hydrothermal treatment during these samples synthesis. The other one (Cr-SBA-15-30-3) has the lowest content of chromium (%0.234 wt.) because of washing effect. It is possible to understand that which one of them is more effective for specific reactions and can be atopic for following researches. Interestingly, Cr-SBA-15-30-1 has the highest BET surface area (714.23 m<sup>2</sup>/g). Actually it wasn't a predictable case because of washing conditions.



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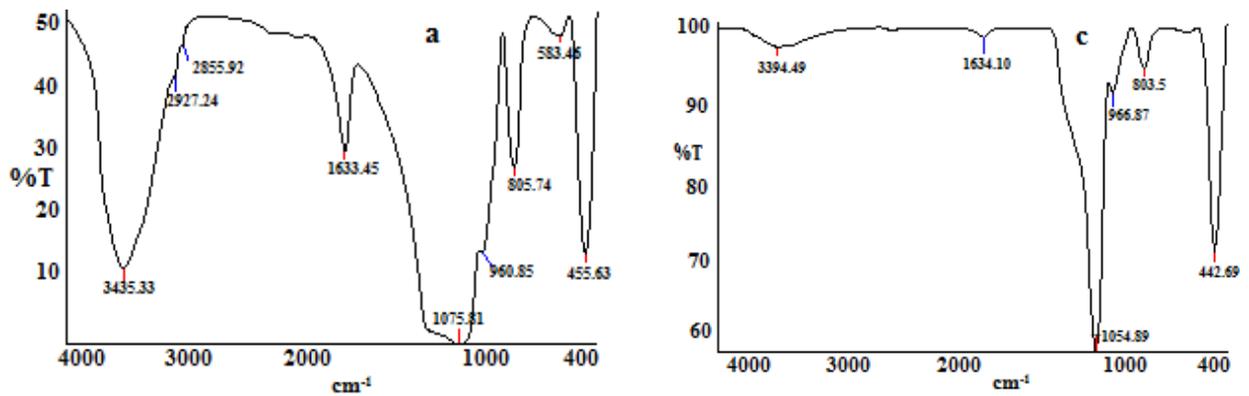


Fig. 3. FT-IR vibrations of Cr-SBA-15 (a) Cr-SBA-15-30-1 (b) Cr-SBA-15-30-2 (c) Cr-SBA-15-30-3.

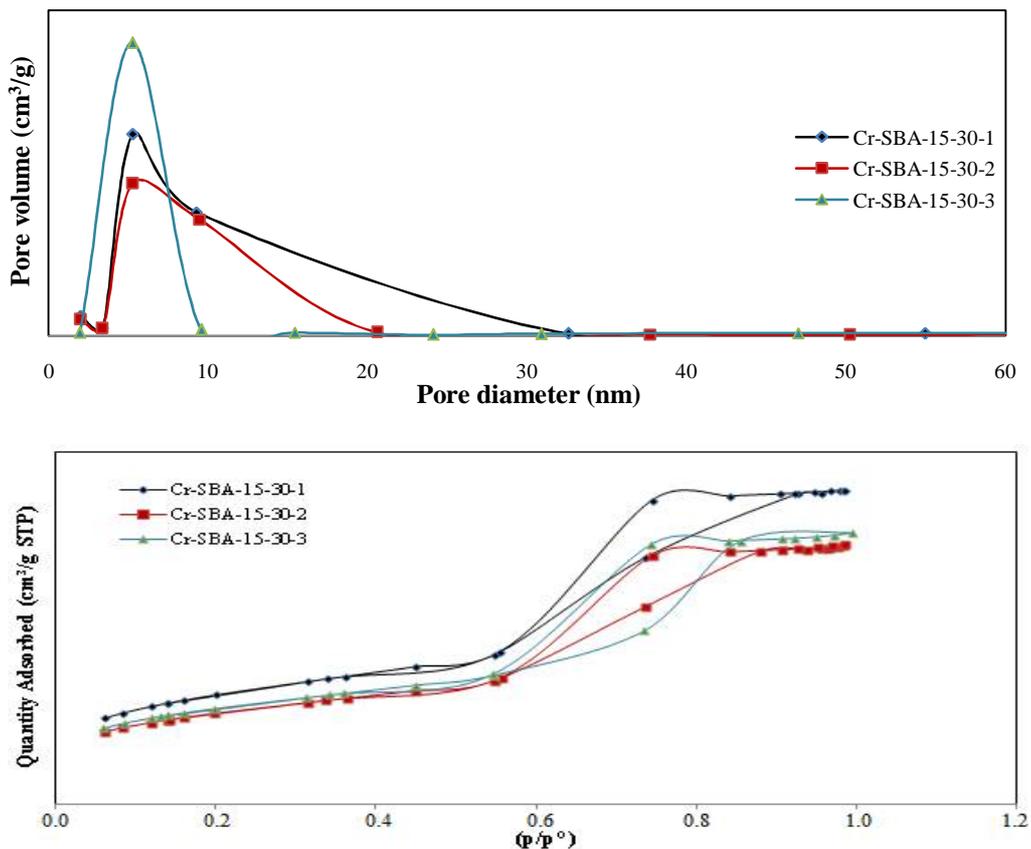


Fig. 4. N<sub>2</sub> adsorption–desorption isotherms (a) and pore size distributions (b) of samples.

The N<sub>2</sub> adsorption–desorption isotherms of Cr-SBA-15-30-x was presented in Fig.4.a. The results are similar. This means that the homogeneity and order of the hexagonal pores were not altered by washing [27]. In the  $p/p^0$  range of

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0.6–0.8, isotherms showed H1-type broad hysteresis. It is understood that they are type-IV isotherms which indicate presence of well-ordered pores with 2D-hexagonal structure [4, 9]. In contrast of Cr-SBA-15-30-1 and Cr-SBA-15-30-2 samples, Cr-SBA-15-30-3 has narrow pore sizedistribution. Insomuch that Cr-SBA-15-30-1 and Cr-SBA-15-30-2 exhibited pore size distributions which can be considered as wide range. (Fig.4b). Pore structure could be affected by washing of Cr-SBA-15-30-3 to remove the surfactant before calcination [27]. The highest BET surface area has been exhibited by Cr-SBA-15-30-1 (714.23 m<sup>2</sup>/g). It can be said that washing is a critical step for pore size distribution and surface area [27].

### V. CONCLUSION

In conclusion, the chromium incorporated mesoporous SBA-15 materials with the Cr content Si/Cr molar ratio 30 were synthesized by direct hydrothermal procedure. Three samples were synthesized with Cr source addition and washing conditions differences in the same direct synthesis procedure. The samples were examined by ICP-OES, FT-IR, N<sub>2</sub>-Adsorption-desorption, small and wide angle XRD methods.

These investigations indicate that a hexagonal mesoporous structure is retained for the Cr-SBA15-x materials. Also, the wide-angle XRD patterns of Cr-SBA15-30 samples present that chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) is existed crystal hexagonal form in the structure.

Surface properties are important in the anchoring of metal species, which is crucial for the catalytic activity.

All samples analysed by FT-IR showed type-IV isotherms which indicate presence of well-ordered pores with 2D hexagonal structure.

Results indicated that pore structure may be affected by washing of Cr-SBA15-30-x to remove surfactant before calcination. Also, the results obtained from characterization analysis showed that washing step and Cr addition are important steps for the surface properties and chromium incorporation of the framework. On the other hand, the same sample showed the best narrow pore size distribution as a consequence of washing effect. According to our investigation, it seems like logical that Cr should be added right after TEOS addition like Cr-SBA-15-30-1 and Cr-SBA-15-30-2.

### ACKNOWLEDGEMENTS

This work was supported by the Commission of Scientific Research Project of ESOGU (GR/201315049).

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