

# Synthesis and Characterization of Co-Pb/SBA-15 Mesoporous Catalysts

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Received 10.10.2005

## Abstract

Pure SBA-15 and Co and/or Pb incorporated SBA-15 have been prepared by direct synthesis. The synthesized samples were characterized by powder X-ray diffraction and N<sub>2</sub> adsorption isotherms. It is observed that the surface area of pure SBA-15 mesoporous structure slowly decreases by the addition of metal oxides. By the loading of 5, 10, 15 wt % Pb into SBA-15, no characteristic peaks of metal oxide observed in the large angle XRD pattern. But loading of 20 wt% Pb in SBA-15 shows more appreciable characteristic peaks, indicating small quantity of crystallites of metal oxide existing on the surface of silica. Low angle XRD patterns show that introduction of high amount of cobalt and lead oxides to SBA-15 result in the long range order. There are chemical interactions in between host SBA-15 and guest metal oxides and the strength of these interactions depend on the type of metal oxide and the amount of metal oxide loaded to SBA-15.

**Key Words:** Mesoporous materials; SBA-15; Lead; Cobalt; Catalyst.

## 1. Introduction

Mesoporous materials are a special type of nanomaterials with ordered arrays of uniform nanochannels. These materials have important applications in a wide variety of fields such as separation, catalysis, adsorption, advanced nanomaterials [1]. Pore size distribution, high surface area and pore volume make periodic mesoporous silicas promising supports for metal and oxide catalysts. Two most common types periodic silicas involve MCM-41 and SBA-15 materials. SBA-15 materials have been prepared in acidic conditions with poly (alkylene oxide) tri-block co-polymers. They usually have wider pores than MCM-41, with the reported SBA-15 pore diameters up to 300 Å. Both solids have periodically ordered structures, which consist of two dimensional hexagonal arrays of uniform mesoporous [2]. SBA-15 is by far the largest pore size mesoporous material with highly ordered hexagonally arranged mesochannels, with thick walls, adjustable pore size from 3 to 30 nm, and high hydrothermal and thermal stability [1]. SBA-15, which possesses larger pores, thicker walls and higher thermal stability as compared other mesoporous silicas may be used a promising catalyst support, particularly for reactions occurring at high temperatures [3]. The base mesoporous materials have

often been modified by adding noble metals or metal oxides in order to improve their physical and chemical properties [4].

Recently, there are various studies carried out by using SBA-15 as support. For example, SBA-15 supported  $\text{FePO}_4$  show higher  $\text{CH}_4$  conversion and HCHO selectivity than unsupported SBA-15 and MCM-41 supported one. The larger porous diameter and the ‘inertness’ of SBA-15 were probably responsible for the higher HCHO selectivity of the SBA-15 supported catalysts as compared with the MCM-41 supported ones particularly with low loading amount of  $\text{FePO}_4$  [3].

In another study, SBA-15 supported Iron (II)-Bisimine Pyridine Catalyst was synthesized for ethylene polymerization. In polymerization, the supported catalyst can successfully control the morphology of polyethylene and the supported catalyst has fairly high catalytic activity for ethylene polymerization [5].

Colloidal Pt particles of a narrow size distribution were impregnated on a mesoporous SBA-15 silica with 9-nm. Pt particles on Pt/SBA-15 showed excellent thermal stability. There was no agglomeration at low temperature (195 K) [6].

Another study is carried out in which Pt and Pd were introduced into mesoporous silica by impregnation method. While Pd is distributed as small clusters outside the mesoporous structure, leading to small catalytically active surface area (about  $15 \text{ m}^2/\text{g}$ ), Pt is preferentially distributed not only on the surface but also into the fine pores, resulting in large catalytically active area (up to  $800 \text{ m}^2/\text{g}$ ) [4].

As another example, impregnation of Co into MCM-41 and SBA-15 were implemented. It is observed that catalysts supported by SBA-15 are 5-10 times more active than supported by MCM-41. While MCM-41 structure collapsed after impregnation and BET-surface area decreased with adding much amount of Co impregnation, SBA-15 structure led to no destruction of ordered structure [6].

The Zr-incorporated SBA-15 was shown to have good catalytic activities in selective oxidation reactions. With the Zr content up to 0.1 Zr/Si atomic ratios and of well ordered pore structure high surface area and narrow pore size distribution was developed [7].

Co and Pb based mixed oxide catalysts were effectively used as soot oxidation catalysts in previous studies in our laboratory. Soot oxidation tests revealed that the oxidation took place by using the lattice oxygen of the catalysts. Better performances were obtained in the presence of Pt. The role of the Pt was to assist the oxygen transfer from the gas phase to the lattice. The catalyst has demonstrated very good soot oxidation performance both in laboratory tests [8] and in engine tests [9]. Equilibrium thermodynamics of the oxide to nitride conversion was investigated theoretically for both components (Pb and Co) of the mixed oxide. The performances of these oxides were not as good as BaO, known for its  $\text{NO}_x$  storage capability, but still good enough for temperatures attainable in Diesel exhausts, 300-400 °C.

An alternative solution proposed by Delphi Technologies Inc. is to use an on board fuel reforming system to generate syngas from Diesel fuel for igniting the engine, therefore reducing the cold start emissions. Delphi technology involves fast start-up fueling strategy. Preheating is executed with stoichiometric gasoline combustion and fuel shut off occurs to quench combustion. The reformer can be used as hydrogen generator in hybrid vehicles, or the syngas generated can be used for  $\text{NO}_x$  reduction afterwards.

With the Delphi technology in mind, a mixed oxide catalyst formerly developed in our labs for soot oxidation is being improved in terms of material design and will be tested for its soot oxidation ability and hydrogen generation properties. The mixed oxide catalyst is prepared in a mesoporous framework of SBA-15 to improve the surface area and to stabilize a low melting point component [10].

Preliminary tests in our laboratory on catalytic partial oxidation of LPG over Pb-CoO/ $\text{Al}_2\text{O}_3$ , Pb-CoO/ $\text{TiO}_2$  catalysts revealed promising results under time interrupted reaction conditions.

## 2. Experimental

In this work, SBA-15 and cobalt or lead incorporated mesoporous silica materials are synthesized by Pluronic 123 nonionic triblock co-polymer. Pluronic 123 is used as a template to obtain high surface area

and large pore sizes. The synthesized catalysts were characterized by chemical techniques, such as X-ray diffraction (XRD), BET surface analysis.

## 2.1. Synthesis of mesoporous SBA-15 silica

Silica SBA-15 was prepared according to the method reported in the literature [11]. 4 g Pluronic 123 (triblock co-polymer,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Aldrich) is dissolved in 150 ml HCl (37% , Riedel-de Haen) (1.6 M) with stirring at room temperature for 1 hour. Afterwards, 8.8. g TEOS ( $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ , Merck) was added to the solution with stirring at 35-40 °C for 20 hours. The mixture was aged at 95-100°C for 24 hours. The white powder was obtained through filtration. The product was calcined at 500°C for 8 hours. The final calcined material had a surface area 772.5 m<sup>2</sup>/g.

## 2.2. Synthesis of Co/ SBA-15, Pb/SBA-15 and Co/Pb/SBA-15

4 g Pluronic 123 (triblock co-polymer,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Aldrich) is dissolved in 150 ml HCl (1.6 M) with stirring at room temperature for 1 hour. Afterwards, appropriate amount of TEOS was added regarding the percent of added  $(\text{CH}_3\text{COO})_2\text{Pb}\cdot 3\text{H}_2\text{O}$  (Merck) as Pb source or  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (Riedel-de Haen) as Co source with stirring at 35-40 °C for 20 hours. The mixture was aged at 95-100 °C for 24 hours. The powder was obtained through filtration. The product was calcined at 500°C for 8 hours.

## 2.3. Catalyst Characterization

### 2.3.1. X-Ray Diffraction Analysis

XRD patterns were measured on a Rigaku-Miniflex diffractometer using Cu  $K\alpha$ -ray radiation ( $\lambda=1.5405 \text{ \AA}$ ) operating at 30 kV and 15mA. XRD patterns were recorded between  $2\theta = 1.0\text{--}3.0^\circ$  with  $0.005^\circ$  intervals,  $0.2^\circ$  data collection velocity in one minute; and  $2\theta = 5.0\text{--}75.0^\circ$  with  $0.05^\circ$  intervals,  $1^\circ$  data collection velocity in one minute.

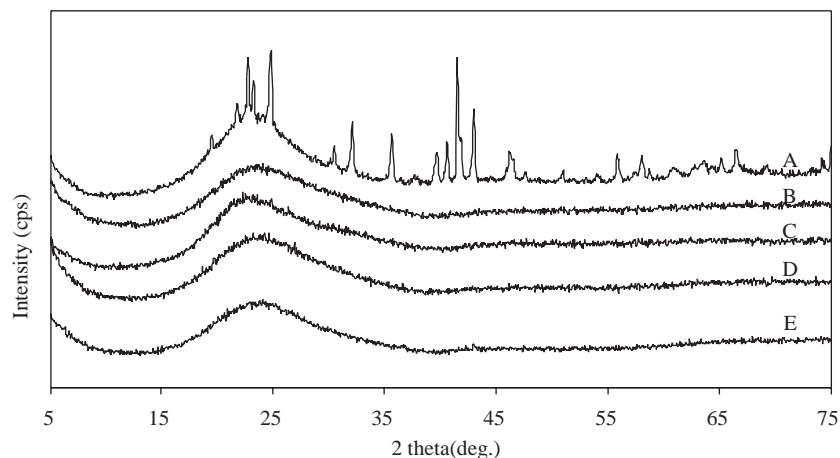
### 2.3.2. BET Surface Analysis

$\text{N}_2$  adsorption-desorption were measured at 77 K on a micromeritics ASAP 2000 volumetric system, with the samples outgassed for 8 h at 363K in vacuum prior to the nitrogen adsorption measurements at 77 K.

## 3. Results and Discussion

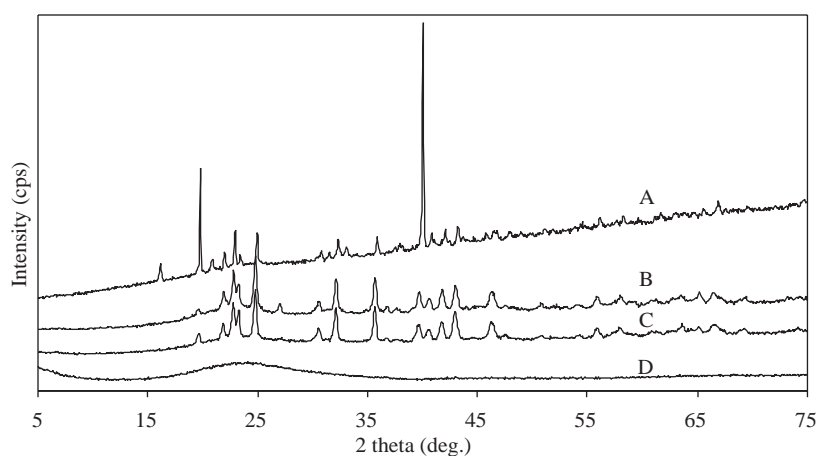
### 3.1. X-ray Diffraction Analysis

The XRD patterns of pure SBA-15 and Pb/SBA-15, which consist of different loading amount of Pb samples, are shown in Figure 1. According to the large angle XRD pattern ( $2\theta=5\text{--}75^\circ$ ), no characteristic peaks of metal oxide observed in 5, 10, 15 wt % Pb loading in SBA-15 sample, indicating that Pb finely dispersed on the surface of the sample or incorporated in the pore wall of the sample. However, more appreciable characteristic peaks are observed for the sample of 20 wt% Pb loading in SBA-15, indicating small quantity of crystallinities of metal oxide existing on the surface of silica.



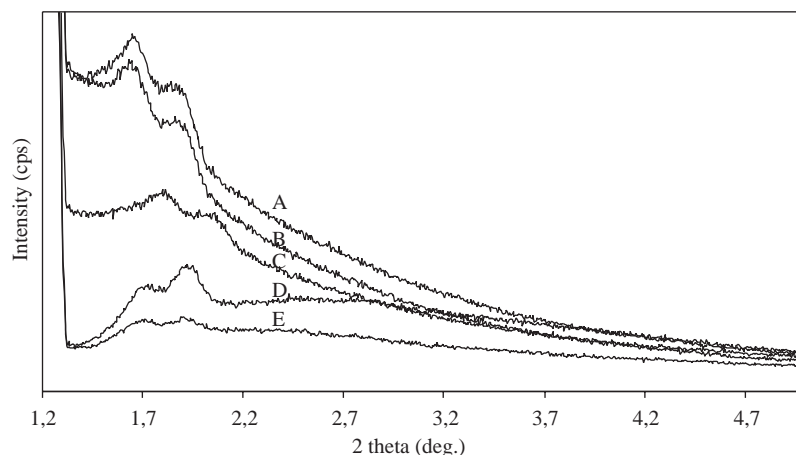
**Figure 1.** Wide angle XRD patterns of Pb/SBA-15 (A) 20% Pb 55% Si, (B) 15% Pb 55% Si, (C) 10% Pb 55% Si, (D) 5% Pb 55% Si, (E) SBA-15.

As shown in Figure 2, the XRD patterns at high diffraction angles were obtained by incorporating different weight percentages of Pb and Co into SBA-15. The presence of highly intense characteristic peaks of Co and Pb in the pattern indicates that the formation of crystallites increased by the addition of smaller amount of cobalt chloride than lead acetate to the silica.



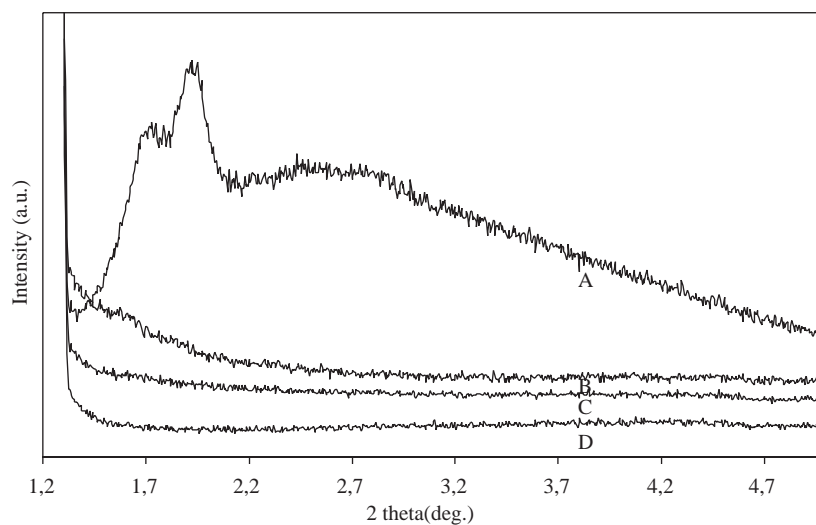
**Figure 2.** Wide angle XRD patterns of Co-Pb/SBA-15 (A) 17% Pb 40% Co 15% Si, (B) 25% Pb 10% Co 40% Si, (C) 30% Pb 10% Co 40% Si, (D) SBA-15.

Two characteristic peaks of SBA-15 ( $2\theta=1.6, 1.8^\circ$ ) structure were observed in the low-angle X-ray patterns, which are shown in Figure 3. For all samples the hexagonal structure of SBA-15 was confirmed by a typical XRD pattern consisting of weak two peaks (at  $2\theta$  around  $1.6$  and  $1.8^\circ$ ), the strong peak at  $2\theta$  around  $0.8^\circ$  could not be observed due to the instrumental limitation. Higher intensity of peaks in the XRD pattern of pure SBA-15 than loaded samples shows the decrease in the long-range order of pores by the addition metal oxides. Higher amount of Pb loading causes the shift of peaks to the higher  $2\theta$  angles means the decrease in the d spacing. This is probably due to the shrinkage of the surfactant micelles arising from the weakening in the interaction between the silica and surfactant in the high addition of metal oxide during the hydrothermal process, which should be confirmed by further studies.



**Figure 3.** Low-angle XRD patterns of Pb/SBA-15 (A) 5% Pb 55% Si, (B) 15% Pb 55% Si, (C) 20% Pb 55% Si, (D) SBA-15, (E) 10% Pb 55% Si

The long range order was lost in the high amount of metal loading to SBA-15 which is observed in Figure 4, the low angle powder XRD pattern of SBA-15 loaded with cobalt and lead oxides. It can be concluded that there are chemical interactions between host SBA-15 and the guest metal oxides and the strength of these interactions are changing by the type and the amount of metal oxides loaded to samples.



**Figure 4.** Low-angle XRD patterns of Co-Pb/SBA-15 (A) SBA-15, (B) 17% Pb 40% Co 15% Si, (C) 25% Pb 10% Co 40% Si, (D) 30% Pb 10% Co 40% Si.

### 3.2. Nitrogen Adsorption

Figure 5 shows nitrogen adsorption/desorption isotherms for siliceous SBA-15, Co/ SBA-15, Pb/ SBA-15 samples. All of the nitrogen adsorption/desorption isotherms showed hysteresis loop which is typical of mesoporous solids. The estimated textural parameters such BET surface area, adsorption average pore diameter, cumulative adsorption pore volume for various samples are shown in Table 1.

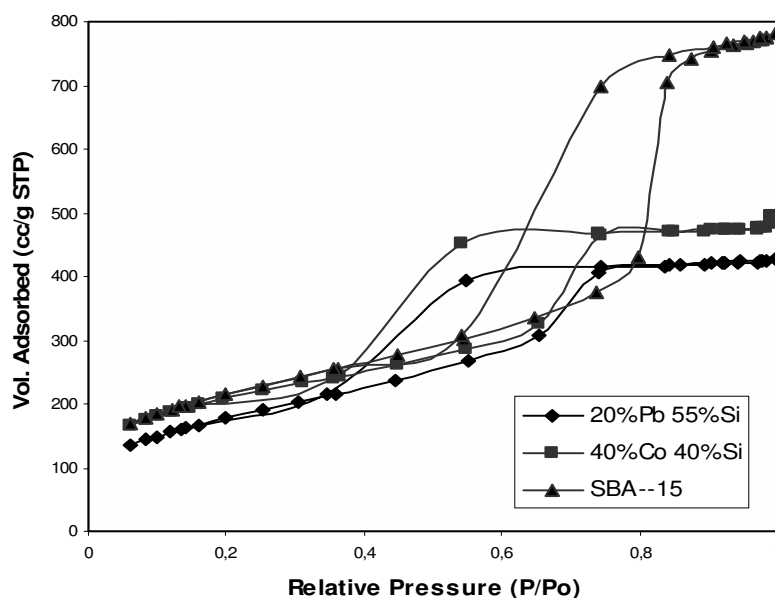


Figure 5. Nitrogen adsorption-desorption isotherms for the mesoporous silica.

Table 1. The mixed oxide catalyst compositions and surface areas

Sample	Si wt %	Co wt%	Pb wt%	Oxygen wt %	BET surface area (m <sup>2</sup> /g)	D <sub>B<sub>JH</sub></sub> (Å)	V <sub>B<sub>JH</sub></sub> (cm <sup>3</sup> /g)
SBA-15	56	-	-	44	772.5	71.2018	1.188868
Co/SBA-15	40	40	-	20	747.5	46.7766	0.698352
Pb/SBA-15	55	-	20	25	648.9	44.3254	0.718421

Incorporation of Co and Pb into mesoporous SBA-15 slowly decreased the surface area of pure SBA-15 leading to nearly no destruction of the ordered structure.

## 4. Conclusion

Co and Pb incorporated SBA-15 mesoporous materials were synthesized by direct synthesis method by using cobalt chloride as cobalt source and lead acetate as lead source. The loading of 20 wt% Pb led to the formation of crystallites of Pb over SBA-15 structure. The surface area of pure SBA-15 is slowly decreased with the addition of 40wt% Co and 20wt% Pb. No characteristic peaks of metal oxide were observed in 5, 10, 15 wt % Pb loading in SBA-15 sample regarding large angle XRD pattern ( $2\theta = 5-75^\circ$ ). It can be concluded that Pb is finely dispersed on the surface of the sample or incorporated in the pore wall of the sample. Incorporation of 20 wt% Pb into SBA-15 indicated more appreciable characteristic peaks. This can be explained that a small quantity of crystallites of metal oxide exist on the surface of silica. The hexagonal structure of SBA-15 was observed for all samples via the small angle XRD pattern consisting of two weak peaks at  $2\theta$  around  $1.6$  and  $1.8^\circ$ . In the XRD pattern, higher intensity of peaks of pure SBA-15 than loaded samples indicates the decrease in the long-range order of pores by the addition of metal oxides. In the high amount of cobalt and lead oxides loading to SBA-15 as metal oxides leads the long range order to disappear. It can be concluded that there are chemical interactions between host SBA-15 and the guest metal oxides.

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