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## Synthesis and Characterization of Co-SBA-15 via Rapid Ultrasonic Technique and Their Catalytic Properties

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The rapid preparation of SBA-15 with cobalt (Co) introduction was performed via the ultrasonic irradiation in combination with "pH-adjusting" method. The catalytic properties of the synthesized Co-SBA-15 were investigated by examining the oxidation of styrene with hydrogen peroxide. The effect of pH values on the textural properties were extensively investigated using small-angle X-ray Diffraction (XRD), N<sub>2</sub> adsorption–desorption isotherms and Transmission Electron Microscipy (TEM). The characterization results showed that the incorporation of Co by ultrasonic method did not destroy the mesoporous structure of SBA-15. The Co-SBA-15 catalyst with Co/Si (the molar ratio of 0.03) at pH of 7.5 exhibited a well-ordered hexagonal mesoporous structure with higher surface area and pore volume. This catalyst had excellent styrene conversion and selectivity to benzaldehyde of 21.8% and 92.3%, respectively. The physicochemical properties and catalytic activity of the Co-SBA-15 catalysts via ultrasonic technique possessed the comparable characteristics as those prepared via conventional hydrothermal method.

Keywords: Ultrasonic, pH Adjustment, Incorporation, Co-SBA-15, Styrene.

## **1. INTRODUCTION**

Mesoporous materials have attained considerable attention in the recent years because of their desirable features (e.g., high surface areas, uniform mesopore size and easily controlled pore size).<sup>1–6</sup> Mesoporous silica of Santa Barbara Amorphous (SBA) type material, SBA-15 with high specific surface area (up to 1160 m<sup>2</sup>/g), high hydrothermal stability, well-ordered two-dimensional hexagonal structure with tunable pore size (47–300 Å), thick wall (31–64 Å) and large pore volume (up to 2.5 cm<sup>3</sup>/g),<sup>7</sup> has numerous potential applications in catalysis,<sup>8</sup> gas sensor,<sup>9</sup> separation and material science.<sup>10</sup> However, pure silica mesoporous materials lack sufficient intrinsic activities for chemical reactions.<sup>11</sup>

In order to create the active sites and generate the catalytic activity, SBA-15 has been modified with a wide diversity of metal ions, transition metal oxides.<sup>12–14</sup> and organic functional groups.<sup>15</sup> Many efforts have been made to incorporate heteroatoms into the framework of SBA-15, by post-synthesis grafting,<sup>16</sup> direct synthesis,<sup>17</sup>

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"two solvents" method.<sup>18</sup> and "pH-adjusting" method.<sup>19,20</sup> Compared with these approaches, "pH adjusting" method appears to be an effective and convenient method to obtain high contents of metal species in SBA-15, because metal species exist only in the cationic form and can not be introduced into the mesoporous walls via a condensation process.<sup>19</sup> However, in the "pH-adjusting" method, the heteroatom source was added into the initial reaction mixture in strongly acidic media (pH < 0); when the mesostructure was basically formed, the pH value of the system was adjusted from a strong acid (pH < 0) to neutral (pH  $\approx$  7.5).<sup>19</sup> Several feasible research protocols have been developed to incorporate Al,<sup>21</sup> Co,<sup>22</sup> Fe<sup>23</sup> or Ag<sup>24</sup> heteroatoms by "pH-adjusting" methods. Hydrothermal synthesis, chemical reactions carried out in heated aqueous solution, is widely applied to produce different kinds of nanomaterials.<sup>25</sup> The aforementioned heteroatoms were incorporated into the silica matrix unexceptionally by hydrothermal method under static conditions for a few days (more than 48 hrs). It has been reported that by "pHadjusting" method, it usually required a long time more than 96 hrs to incorporate Al atoms into the framework

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of SBA-15.<sup>21</sup> Therefore, much attention has been paid to reduce the synthesis time for economic benefit without sacrificing the quality of the products.

Ultrasound irradiation has emerged as a powerful technique for the preparation of novel nanostructure materials.<sup>26, 27</sup> The acoustic cavitation effect from the ultrasound irradiation can produce high temperatures, promoting the rates of chemical reactions. The ultrasonic technique has been applied in the synthesis of silica MCM-41.<sup>28</sup> and SBA-15,<sup>29</sup> as well as in the incorporation of MnO<sub>2</sub><sup>30</sup> or ruthenium<sup>31</sup> in the pore structure of SBA-15.

This study targeted the challenge of a rapid and feasible preparation strategy to synthesize the metal-containing SBA-15 for the oxidation of styrene with higher styrene conversion and benzaldehyde selectivity using hydrogen peroxide as oxidant. Hydrogen peroxide is the most desirable oxidant for the oxidation of alkenes with respect to environmental and economic considerations. Cobalt ion and complexes are well-known catalysts for the selective oxidation of alkanes and alkylbenzenes.32, 33 The incorporation of cobalt (Co) into the framework of SBA-15 was carried out by the ultrasonic irradiation in combination with "pH-adjusting" method. The effect of pH values during the preparation process on the textural properties were extensively investigated using small-angle X-ray diffraction (XRD), N<sub>2</sub> adsorption–desorption isotherms and Transmission Electron Microscopy (TEM). The catalytic properties of synthesized Co-SBA-15 were further evaluated by examining the oxidation of styrene. In addition, the physicochemical properties and catalytic activity of the synthesized catalysts were compared with those prepared by conventional hydrothermal method.

## 2. EXPERIMENTAL DETAILS

### 2.1. Catalysts Preparation

Cobalt (Co)-substituted SBA-15 was synthesized via ultrasonic technique with the modified pH-adjusting method.<sup>34</sup> Triblock copolymer Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, molecular weight 5800, Aldrich) was used as the template and tetraethylorthosilicate (TEOS) as the silica source. 2 g Pluronic P123 was dispersed in 100 g 2 M HCl under vigorous stirring for 2 hrs to obtain a homogeneous solution. 4 g TEOS was added into the solution dropwise and stirred for another 1 hr. A requisite amount of  $Co(NO_3)_2 \cdot 6H_2O$  was then added to the solution. The mixture was immediately subjected to sonication at room temperature irradiated by an ultrasonic generator (Numerical control ultrasonic cleaning machine, KH3200DE, KunShanHeChang ultrasonic instrument Co., Ltd.) with the ultrasonic waves (40 kHz) at the output power of 150 W. After 1 hr of irradiation, the pH of the mixture was adjusted by adding the concentrated ammonia, and the mixture was then sonicated for 1 hr. The synthesized product was thoroughly filtered and extensively washed with distilled water to remove the weakly adsorbed ions, and then dried overnight at 110 °C in an oven at static condition. Finally, the product was calcined at 550 °C for 6 hrs to remove the surfactants at a heating rate of 2 °C/min. The obtained product was denoted as xCo-SBA-15<sub>*a*</sub>, where "*x*" is the Co/Si (molar ratio) in the initial gel and "*a*" is the adjusted pH value. Catalysts containing various metel ions M-SBA-15 (M = Nd, Ni, Ce, Y) were synthesized through the same procedure under pH = 7.5, using the corresponding nitrate salts. SBA-15 was synthesized via the same procedure under ultrasonic irritation for 1 hr without pH adjusting. The sample obtained was referred to SBA-15-ultra.

Another series of Co-substituted SBA-15 were synthesized using the conventional hydrothermal method. The preparation and calcination procedures were similar with those of xCo-SBA-15<sub>a</sub>, but the difference was the long preparation time. After the addition of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, the mixture was transferred to an autoclave for crystallization at 100 °C for 24 hrs. Then the pH was adjusted by adding ammonia. The mixture was then crystallized at 100 °C for another 24 hrs. The obtained powder was denoted as xCo-SBA-15<sup>*H*</sup><sub>*a*</sub>, where "x" is the Co/Si (molar ratio) in the initial gel and "a" is the adjusted pH value.

#### 2.2. Characterization Methods

The actual element compositions were determined by an inductively coupled plasma (ICP) spectrophotometer (Spectro Ciros, Germany). The calcined solid samples were dissolved by acidic digestion.

The crystalline phases of the catalysts were measured by X-ray diffraction (XRD) with a CuK $\alpha$  ( $\lambda = 0.154$  nm) radiation source (D8 Advance, Bruker, Germany). The tests were operated at 40 kV and 40 mA over the scattering angle of  $2\theta$  from 0.6° to 5° with a step size of 0.02° and a step time of 0.4 s.

The textural properties of the samples were derived from N<sub>2</sub> adsorption/desorption measurement at 77 K on Micromeritics TriStar II 3020. Prior to the measurement, the samples were outgassed at 200 °C to a residual pressure below  $1 \times 10^{-4}$  Torr for 5 hrs. The pore-size distribution was measured from the desorption branch using the Barrett–Joyner–Halenda (BJH) method.

Surface morphology of the samples was examined by transmission electron microscopy (TEM) (JEM-2100HR, JEOL) equipped with a lanthanum hexaboride electron gun and operated at an accelerating voltage of 200 kV. The samples were dispersed ultrasonically in ethanol and then deposited a TEM copper grid before the measurement.

### 2.3. Catalytic Activity Measurements

The catalytic reaction was carried out in a 50 ml twonecked round-bottomed glass flask connected to a reflux condenser and a thermometer. The temperature of the reaction vessel was maintained using a water bath. Hydrogen peroxide (aqueous solution 30 wt%) was used as

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the oxygen-donor and acetonitrile as the solvent. In a typical oxidation reaction, 0.05 g catalyst was mixed with 10 ml acetonitrile solvent, 10 mmol styrene and 10 mmol 30 wt%  $H_2O_2$ . The mixture was heated with stirring under reflux at 70 °C for 6 hrs. After the reaction, the catalyst was removed by hydrophobic membrane. The organic compounds were analyzed quantitatively by gas chromatograph, equipped with a 5% diphenyl-95% dimethylpolysiloxane benzyl siloxane capillary column, and a flame ionization detector (FID). The products identification was achieved from the retention time of the pure compound. Quantitative analyses were performed by taking into account the FID response factors for each compound.

### 3. RESULTS AND DISCUSSION

### 3.1. Catalytic Performance Over

#### Various Metal Species Catalysts

The results showed that different heterogeneous catalysts had significant effects on the catalytic performance in the oxidation of styrene with  $H_2O_2$ . The catalytic performance in terms of the styrene conversion and selectivity was summarized in Table I, which was obtained by using several metal element-containing SBA-15 catalysts prepared by ultrasonic waves at the pH of 7.5 during the preparation process. Except for La-SBA-15, the main product was benzaldehyde for other catalysts, resulting from the nucleophilic attack of  $H_2O_2$  to styrene oxide followed by a cleavage of the intermediate hydroxy-hydroperoxystyrene and also from the direct oxidative cleavage of the styrene side chain double bond.35,36 Using different metal elements doped SBA-15 mesoporous materials, the obtained styrene conversions varied substantially. Compared with the Ni-, Nd-, Ce-, Y- and La-containing SBA-15, the Co-SBA-15 converted 22% of styrene and exhibited higher styrene conversion, thus leading to the greatest quantity of benzaldehyde in the products. Other metal species were not as good as Co catalyst for the reaction. The different catalytic performance of M-SBA-15 mesoporous materials was caused either by the different nature of metal element

Table I. Catalytic performance of M-SBA-15 catalysts with various metal species in the oxidation of styrene with  $H_2O_2$ .

	Styrene conversion (%) <sup>b</sup>	Selectivity (%)				
Catalyst <sup>a</sup>		Benzaldehyde	Styrene epoxide	Hyacinthin		
Ni-SBA-15	6.4	72.7	26.4	1.0		
Nd-SBA-15	7.5	80.2	18.8	1.0		
Ce-SBA-15	5.1	88.1	11.3	0.7		
Y-SBA-15	6.1	76.5	22.4	1.2		
La-SBA-15	4.3	47.8	51.6	0.5		
Co-SBA-15	21.8	92.3	7.1	0.6		

*Notes*: <sup>*a*</sup>M/Si molar ratio: 0.03; adjusted pH value: 7.5; <sup>*b*</sup>Reaction condition: styrene, 10 mmol;  $H_2O_2$ , 10 mmol; acetonitrile, 10 ml; catalyst, 0.05 g; temperature, 70°C; reaction time, 6 hrs.

Table II. Oxidation of styrene with  $H_2O_2$  catalyzed by different cobaltbase catalysts.

	Selectivity (%)				
Styrene conversion (%) <sup>a</sup>	Benzaldehyde	Styrene epoxide	Hyacinthin		
3.3	16.0	84.0	0.0		
4.7	77.4	21.7	0.9		
4.7	76.5	22.6	0.9		
18.3	84.5	15.2	0.3		
21.8	92.3	7.1	0.6		
25.6	86.9	12.3	0.8		
12.8	83.0	16.4	0.5		
	Styrene conversion (%) <sup><i>a</i></sup> 3.3 4.7 4.7 18.3 21.8 25.6 12.8	Styrene conversion (%) <sup>a</sup> Sele           3.3         16.0           4.7         77.4           4.7         76.5           18.3         84.5           21.8         92.3           25.6         86.9           12.8         83.0	Styrene conversion (%) <sup>a</sup> Selectivity (%           3.3         16.0         Styrene epoxide           3.3         16.0         84.0           4.7         77.4         21.7           4.7         76.5         22.6           18.3         84.5         15.2           21.8         92.3         7.1           25.6         86.9         12.3           12.8         83.0         16.4		

*Notes*: <sup>*a*</sup>Reaction condition: styrene, 10 mmol; H<sub>2</sub>O<sub>2</sub>, 10 mmol; acetonitrile, 10 ml; catalyst, 0.05 g; temperature, 70 °C; reaction time, 6 hrs; <sup>*b*</sup>Synthesized without pH adjustment; <sup>*c*</sup>Prepared by conventional impregnation method with Co/Si (molar ratio) of 0.03. SBA-15 was synthesized by ultrasonic technique.

doped in the framework of SBA-15<sup>37</sup> or by the coordination of the solvent to  $Co^{2+}$  which affects the ability of  $H_2O_2$  to bind the metal ions.<sup>38</sup>

# **3.2.** Effect of pH During the Preparation Process on the Oxidation of Styrene with H<sub>2</sub>O<sub>2</sub>

The catalytic performance of various Co-based catalysts prepared under different pH value was shown in Table II. A blank test was performed in the identical reaction condition for comparison, and the conversion of styrene was only 3.3%. Pure siliceous SBA-15 gave a similar conversion. It should be addressed that if the pH was not adjusted during the preparation process (pH < 0 in the parent solution), the 0.03 Co-SAB-15 catalyst displayed negligible catalytic activity that was nearly the same as that of the blank, which means that there was no active cobalt sites in the catalyst.

Interestingly, the styrene conversion was significantly affected by pH values. It substantially increased to 25.6% when pH was adjusted to 9.0. The cobalt contents in the solid product increased with the pH values (Table III). This implies that the higher pH condition favored the incorporation of metal ions. The highest selectivity to benzaldehyde (92.3%) was obtained at the pH of 7.5. It is probably that the excess  $OH^-$  (pH = 9.0) reacted with  $Co^{2+}$  to form Co(OH)<sub>2</sub> precipitation, which prevented the

 Table III.
 Textural properties of cobalt catalysts prepared under different pH conditions.

	Co/Si (molar ratio)						
Materials	Initial gel	Product	<i>d</i> <sub>100</sub> (nm)	<i>a</i> <sub>0</sub> (nm)	$S_{\rm BET} \ (m^2/g)$	$V_p$ $(cm^3/g)^a$	Pore size (nm) <sup>b</sup>
SBA-15-ultra	_	_	9.3	10.7	501	0.61	4.58
Co-SBA-1560	0.03	0.006	10.0	11.5	465	0.89	7.44
Co-SBA-1575	0.03	0.007	10.0	11.5	488	0.97	7.13
Co-SBA-15 <sub>9.0</sub>	0.03	0.014	9.7	11.2	336	0.88	9.25

*Notes*: <sup>a</sup>Total pore volume; <sup>b</sup>Average pore diameter by the desorption branch of the isotherm calculated by BJH method.

attacking of  $H_2O_2$  to styrene oxide and resulted in a lower benzaldehyde selectivity.<sup>22</sup> Therefore in the following experiments, the pH of 7.5 was chosen as the optimal condition. The quantum calculation on the cobalt growth mechanism under the alkaline condition is currently carried out to fully understand the influence of the pH on this reaction system.

Different synthetic methods lead to different location of the active species. The Co<sub>3</sub>O<sub>4</sub>/SBA-15 catalyst, synthesized using impregnation with an equivalent cobalt loading, was compared with the catalysts prepared by ultrasonic technique at the pH of 7.5. For the impregnation method, the conversion of styrene was 12.8% (Table II), which was much lower than that of the 0.03Co-SBA- $15_{75}$ . The oxidation of styrene with hydrogen peroxide mainly occurred on the internal surface of mesoporous pores when the metal active sites are incorporated inside the framework.<sup>34</sup> The  $Co_3O_4$  particles outside the framework of SBA-15 were obviously inactive for the conversion of styrene. The results in this study demonstrated the feasibility of the introduction of Co<sup>2+</sup> into the mesoporous pores of SBA-15 via rapid ultrasonic technique and pH adjustment.

## 3.3. Catalytic Performance versus Reaction Time Over 0.03Co-SBA-15<sub>7.5</sub> Catalyst

The conversion of styrene and the selectivity to benzalde-ology hyde as well as styrene epoxide versus reaction time catalyzed by 0.03Co-SBA-15<sub>7.5</sub> was shown in Figure 1. The styrene conversion increased with the prolonging of reaction time,<sup>39</sup> with 12% in 1 hr to 38% in 10 hrs. The reaction was fast at the initial period, because the total amount of reactants was added in one batch at the beginning of the reaction. The selectivity of benzaldehyde reached a maximum at 92% in 6 hrs and remained constant for up to 10 hrs. The selectivity of styrene oxide gradually



decreased from 20% to 7%, which is attributed to the formation of benzaldehyde via the further oxidation of the epoxide.<sup>40</sup> The optimal reaction time was 6 hrs in our experiments, in which the highest benzaldehyde selectivity was reached.

### 3.4. Structure and Morphology of Various Cobalt Catalysts Prepared via Ultrasonic Method

Structure and morphology were studied using XRD, nitrogen-physisorption analyses and TEM. The smallangle XRD patterns of 0.03Co-SBA-15 catalysts prepared by ultrasonic irradiation at different pH values were shown in Figure 2(A). An intense main diffraction peak and two small peaks were well-resolved in the  $2\theta$  range of 0.7° to 2°, corresponding to the (1 0 0), (1 1 0) and (2 0 0) planes, which were the characteristics of the hexagonal pore mesostructure of the synthesized materials.<sup>41</sup> This suggested that all the materials had a well-ordered 2D hexagonal mesoporous structure (p6 mm) and the introduction



**Figure 1.** Effect of reaction time on oxidation of styrene with  $H_2O_2$  over 0.03Co-SBA-15<sub>7.5</sub>. ( $\blacktriangle$ ) styrene conversion, ( $\bigstar$ ) benzaldehyde selectivity, ( $\Delta$ ) styrene epoxide selectivity. Reaction condition: styrene, 10 mmol;  $H_2O_2$ , 10 mmol; acetonitrile, 10 ml; catalyst, 0.05 g; temperature, 70 °C.

**Figure 2.** (A) Small-angle XRD patterns of (a) SBA-15-ultra, (b) 0.03Co-SBA- $15_{9,0}$ , (c) 0.03Co-SBA- $15_{7,5}$ , (d) 0.03Co-SBA- $15_{6,0}$ . (B) Large-angle XRD patterns of (a1) Co<sub>3</sub>O<sub>4</sub>/SBA-15, (a) SBA-15-ultra, (b) 0.03Co-SBA- $15_{9,0}$ , (c) 0.03Co-SBA- $15_{7,5}$ , (d) 0.03Co-SBA- $15_{6,0}$ .

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of Co via rapid ultrasonic method did not destroy the original mesoporous structure of SBA-15-ultra. In addition, the 0.03Co-SBA-15<sub>6.0</sub> presented the weak reflection peaks of (1 1 0) and (2 0 0) planes, indicating the slight loss of long-range ordering at lower pH condition. This was the possible for its lower catalytic performance than 0.03Co-SBA-15<sub>9.0</sub> and 0.03Co-SBA-15<sub>7.5</sub> in the oxidation of styrene (as indicated in Table II).

According to the wide-angle XRD patterns (Fig. 2(B)), xCo-SBA-15<sub>*a*</sub> showed only a broad peak of the amorphous feature of SBA-15 and no peaks of Co<sub>3</sub>O<sub>4</sub> were observed. However, the diffraction of 2 $\theta$  at 31.4°, 38.7°, 45.0°, 59.6° and 65.5° attributed to the crystalline Co<sub>3</sub>O<sub>4</sub> (JCPDS 65-3103) were observed over Co<sub>3</sub>O<sub>4</sub>/SBA-15 catalyst (Fig. 2(B)-a1). The lack of Co<sub>3</sub>O<sub>4</sub> phase in xCo-SBA-15<sub>*a*</sub> catalysts indicates that cobalt ions introduced by ultrasonic technique have been incorporated into the framework of SBA-15.

The incorporation of cobalt into the framework of SBA-15 affected the position of the diffraction peak in XRD patterns (Fig. 2(A)). All the peaks for cobaltcontaining catalysts shifted towards lower-angle direction, which represented an increase in the lattice parameter  $(d_{100})$  values. Through the calculation from the peak with hkl = 100 using the equation  $a_0 = 2d_{100}/\sqrt{3}$ , the  $(d_{100})$  values were obtained along with the corresponding unit cell parameter  $(a_0)$  of different SBA-15 samples (Table III). The increase of the *d*-values and  $a_0$  indicated the presence of Co atoms in the framework, which could be explained by the structure expansion caused by the larger atomic radius of Co<sup>2+</sup> (Pauling radius: 72 pm) than Si<sup>4+</sup> (Pauling radius: 41 pm). Previous studies showed different metal elements incorporated into molecular sieves.<sup>42,43</sup> The results in this study suggested that the  $Co^{2+}$  cations could be easily incorporated into the mesoporous framework of SBA-15 to replace Si<sup>4+</sup> via rapid ultrasonic technique, which substantially saved time compared with conventional methods.

The pH adjustment under ultrasonic condition obviously changed the textural properties, including surface area, pore volume and pore size of the catalysts. Compared with pure silica SBA-15-ultra, the pH-adjusted catalysts had lower BET surface area (Table III), however, their pore volume and average pore diameters increased. The decrease in surface area can be attributed to the blocking of the support porosity by the cobalt species that made them inaccessible for nitrogen adsorption.44 This effect was also observed on the mesoporous matrix filled with La.<sup>45</sup> The increase in pore volumes was in accordance with XRD results and confirmed the expansion of the mesopores on the introduction of the Co(+2) in the Si framework.<sup>46</sup> The increase in pore size with cobalt incorporation was due to the longer bond length of Co-O than that of Si-O.<sup>22,43</sup> The N<sub>2</sub> adsorption results well corresponded with the XRD results and clearly showed the incorporation of Co<sup>2+</sup> into the mesoporous framework of SBA-15 via



**Figure 3.** TEM images of SBA-15-ultra (A) and 0.03Co-SBA-15<sub>7.5</sub> (B) viewed down the direction parallel to pore.

rapid ultrasonic method. It should be addressed that among three Co-containing catalysts, Co-SBA- $15_{7.5}$  showed the highest pore volume with the similar surface area to the parent SBA-15-ultra, which indicated the effective and higher cobalt introduction without sacrificing its high surface area. This is in favor of its higher catalytic activity in the oxidation of styrene.

Transmission electron microscopy (TEM) observation clearly showed the well-ordered channels over the SBA-15 catalysts prepared via rapid ultrasonic method (Fig. 3(A)). Moreover, the representative TEM images (Fig. 3(B)) of  $0.03\text{Co-SBA-15}_{7.5}$  confirmed that the highly ordered channel was retained when cobalt was introduced. No  $\text{Co}_3\text{O}_4$ particles were observed for  $0.03\text{Co-SBA-15}_{7.5}$  sample, indicating that cobalt species were homogenously incorporated into the framework of SBA-15.<sup>47</sup> These TEM results indicated the use of ultrasonic waves does not damage the ordered structure of SBA-15.

## 3.5. Comparison of the Catalysts Prepared by Rapid Ultrasonic and Conventional Hydrothermal Methods

## 3.5.1. Catalytic Performance During the Oxidation of Styrene

Hydrothermal procedure is a common and effective method for the synthesis of ordered metal elementcontaining mesoporous silicas, however it usually takes 1–4 days for the crystallization. The comparison of the catalytic activity and the textural properties for the catalysts (xCo-SBA-15<sub>7.5</sub> and xCo-SBA-15<sup>H</sup><sub>7.5</sub>) prepared by rapid ultrasonic and hydrothermal methods were extensively investigated (Fig. 4).

The Co content in *x*Co-SBA-15<sub>7.5</sub> and *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> clearly affected the catalytic performance. At the Co/Si ratio of 0.03, the selectivity to benzaldehyde and the conversion of styrene increased remarkably. It should be noted that *x*Co-SBA-15<sub>7.5</sub> catalysts exhibited excellent benzaldehyde selectivity, comparable with the conventional synthesis method, although the latter presented a slight higher conversion of styrene. When the Co/Si ratio increased to 0.06, the conversion of styrene kept nearly unchanged, but the selectivity to benzaldehyde decreased. The results

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**Figure 4.** Effect of cobalt contents on oxidation of styrene with  $H_2O_2$  over *x*Co-SBA-15<sub>7.5</sub> (solid line) and *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> (dotted line). ( $\blacktriangle$ ) styrene conversion, ( $\bigcirc$ ) benzaldehyde selectivity. Reaction condition: styrene, 10 mmol;  $H_2O_2$ , 10 mmol; acetonitrile, 10 ml; catalyst, 0.05 g; temperature, 70 °C; reaction time, 6 h.

indicate that *x*Co-SBA-15<sub>7.5</sub> catalysts exhibit the comparable catalytic performance with *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> products. When the Co/Si molar ratio was further increased to 0.10, *x*Co-SBA-15<sub>7.5</sub> showed 25% of styrene conversion, higher than *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> catalyst prepared by hydrothermal method. This suggested that the ultrasonic method is beneficial when the metal species are introduced in large amount.

### 3.5.2. Textural Characteristics

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The comparable structural patterns of *x*Co-SBA-15<sub>7.5</sub> with that of *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> were observed (Fig. 5). For all *x*Co-SBA-15<sub>7.5</sub> catalysts, three XRD diffraction peaks were detected in the region of  $2\theta = 0.85-2^{\circ}$ , which was indexed to the (100), (110) and (200) diffractions typical of the hexagonal lattice for the ordered mesoporous silica. The results indicated that the structural integrity were retained after the incorporation of Co under sonication. At higher Co loadings, the three XRD peaks had lower intensity and



Figure 5. Small-angel XRD pattern of xCo-SBA-15 and xCo-SBA-15<sup>H</sup> catalysts.

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the peaks were shifted to the lower  $2\theta$  values. The changes in peak intensity and low angle shift suggest that cobalt was present on the internal pore wall of SBA-15.<sup>48</sup>

The advantage in the higher metal content incorporation (Co/Si = 0.10) by the ultrasonic method was observed using XRD method (Fig. 5). For the xCo-SBA-15<sub>7.5</sub> (x =0.10), a highly ordered mesostruction was observed, which was proved by the three well-resolved peaks. On the other hand, for the *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> (x = 0.10), the diffraction peaks of (1 1 0) and (2 0 0) were relatively weak and broad, implying a decrease in the framework order by the higher content of Co<sup>2+</sup>.<sup>34</sup> This was a clear indication that although the ordered mesoporous structure was retained at the Co/Si molar ratio up to 0.10, higher cobalt content caused a distortion of hexagonal ordering structure to some extents. The reason for this phenomenon was that when the system was adjusted to the neutral condition, the metal ions transformed to the oxo form and condensed with adjacent silanols.<sup>19</sup> As a consequence, more metal ions in interstitial regions probably affected the interaction of silica and organic template during the crystallization procedure, and resulted in the disordered structure.<sup>49</sup> This disordered structure led to an inferior styrene conversion in the oxidation of styrene to the equivalent catalyst (in terms of Co content) synthesized by the ultrasonic method, (as indicated in Fig. 4 when Co/Si molar ration was 0.10) kin University Library

The different preparation method for Co incorporation into the framework of SBA-15 had a significant influence on the pore size distribution. The nitrogen adsorptiondesorption isotherms and the corresponding pore size distribution for xCo-SBA-15<sub>7.5</sub> and xCo-SBA-15<sup>H</sup><sub>7.5</sub> were found to be type IV in nature and exhibited a type-H1 hysteresis loop (Fig. 6), which was typical of the mesoporous SBA-15 with one-dimensional cylindrical channels according to the IUPAC (International Union of Pure and Applied Chemistry) classification.<sup>50</sup> For xCo-SBA- $15_{75}$  catalysts, the adsorption branch of each isotherm showed a sharp inflection at  $p/p_o = 0.6-0.7$ , which indicated the capillary condensation within uniform pores.51-53 The capillary condensation step suggested a relatively narrow and sharp pore size distribution centered in the range of 7.1–7.3 nm. On the other hand, in the case of xCo-SBA-15 $_{7.5}^{H}$  catalysts, the inflection point appeared at higher  $p/p_o = 0.8$ , compared with that of xCo-SBA-15<sub>7.5</sub> catalysts, indicating a relatively wider pore size distribution with maximum in the range of 7.9-10.2 nm. The broad hysteresis loop extending to  $p/p_o = 1.0$  was caused by the presence of long mesopores connected by smaller micropores.<sup>54</sup> Moreover, the sharpness of the inflection step decreased with an increasing in cobalt loadings, and the pore size distribution was slightly shifted toward wide regions, which indicated the larger pore diameter in the xCo-SBA-15<sup> $H_{75}$ </sup> catalysts prepared by the conventional method.



Figure 6. N<sub>2</sub> adsorption–desorption isotherms of xCo-SBA-15<sub>7.5</sub> (left) and xCo-SBA-15<sup>H</sup><sub>7.5</sub> (right). The pore size distribution curve for each isotherm is shown as insert.

## 4. CONCLUSION

Cobalt incorporated within the framework of SBA-15, xCo-SBA-15 (x: Co/Si molar ratio ranging from 0.01–0.10) was successfully synthesized by the rapid ultrasonic irradiation in combination with "pH-adjusting" method in this study. Their catalytic properties were extensively investigated in the oxidation of styrene with hydrogen peroxide, and compared with the catalysts prepared by conventional methods. There were four major conclusions drawn:

First, the highly ordered hexagonal structure was wellretained after the incorporation of cobalt via ultrasonic technique. The rapid preparation strategy appeared to be feasible and effective for the grafting of various metal species to mesoporous silica materials. This route can be potentially expanded to the incorporation of other heteroatoms into porous materials to modify their catalytic properties.

Second, pH value and Co/Si molar ratio affected the surface area, pore volume and ordering structure. The xCo-SBA-15 with Co/Si of 0.03 obtained at pH 7.5 exhibited well-ordered hexagonal mesoporous structure with higher surface area and pore volume, giving excellent styrene conversion and selectivity to benzaldehyde.

Third, *x*Co-SBA-15<sub>7.5</sub> catalysts have relatively uniform narrow pore size distribution and exhibited the comparable catalytic performance with *x*Co-SBA-15<sup>*H*</sup><sub>7.5</sub> products.

Forth, the catalytic performance in the oxidation of styrene with  $H_2O_2$  was strongly dependent on the metal species. Compared with the Ni-, Nd-, Ce-, Y- and

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La-containing SBA-15, Co-SBA-15 converted 22% of styrene and achieved the highest benzaldehyde selectivity.

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