Steam Reforming of Ethanol over CoMg/SBA-15 Catalysts

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ABSTRACT

Hydrogen production through steam reforming of ethanol (SRE) over Mg modified Co-based catalysts supported on mesoporous SBA-15 was studied herein to evaluate the catalytic activity and the behavior of coke deposition. The Co⁹Mgᵪ/SBA-15 catalysts are obtained according to the steps of consecutive impregnation of Mg (x = 5 and 10 wt%) to be incorporated on SBA-15 and then follow the loading of Co (y = 10 and 20 wt%) using the incipient wetness impregnation method. The catalysts are characterized by using X-ray diffraction (XRD), temperature programmed reduction (TPR), transmission electron microscopy (TEM) and BET techniques. Also, the spent catalysts are further characterized by using XRD and TEM. The catalytic activity of the SRE is evaluated in a fixed-bed reactor under 22,000 h⁻¹ GHSV and with an H₂O/EtOH molar ratio of 13. All the Co⁹Mgᵪ/SBA-15 catalysts present a mesoporous structure, even after the SRE reaction. The optimum catalyst of Co₂⁰Mg⁵/SBA-15-H₆₅₀ comes from the high loading of Co and high reduction temperature pretreatment, which show a high catalytic activity and stability at 550°C with a hydrogen yield (YH₂) up to 5.78 and CO selectivity around 3.10%.

Keywords: SBA-15; Steam Reforming of Ethanol; Cobalt; Magnesium

1. Introduction

Hydrogen generation from biomass-derived alcohols has been the activity of choice recently. Ethanol is more attractive because it is non-toxic, has higher hydrogen content, is renewable energy and has an easy-to-handle nature when compared to methanol [1,2]. The main catalytic reaction using ethanol to produce hydrogen by steam reforming is shown in Equation (1), where only hydrogen and non-renewable CO₂ are produced, providing 6 moles of H₂ per mole of ethanol stoichiometrically [3].

\[ C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \] (1)

Several metallic active phases have been used as catalysts for the steam reforming of ethanol (SRE) to produce hydrogen. Since Co-based catalysts, mainly metal exhibiting appreciable activity for C-C bond broken and water-gas shift (WGS) reactions, generate a low temperature and few by-products, they are efficient when used in SRE. The early stage of SRE research has focused on Co-based catalysts. Haga et al. [4] found that the properties of cobalt catalysts were greatly influenced by the supports, where the hydrogen production decreased in the order of: Co/Al₂O₃ > Co/ZrO₂ > Co/MgO > Co/SiO₂ > Co/C. The Co/Al₂O₃ catalyst showed high hydrogen selectivity for SRE by suppressing CO methanation and ethanol decomposition. Supported cobalt catalysts showed a significant improvement in catalytic performance on the SRE compared with corresponding supports reported by Llorca et al. [5], a variety of oxides involving acidic/basic and redox properties. Batista et al. [6] studied the high efficiency SRE over Co/Al₂O₃ and Co/SiO₂ catalysts with little Co content (%8) in which the Co/SiO₂ catalyst showed better CO removal. Llorca et al. [7] reported CO-free hydrogen produced from SRE over the Co/ZnO catalyst at low temperatures, where the highly stable catalyst was prepared by using Co₂(CO)₈ as a precursor.

The technique of doping extra components, such as alkali (Li, Na and K) [8], alkaline earth (Mg and Ca) [9, 10] and lanthanide (La and Ce) [10] to modify the original property and improve the performance of a catalyst is interesting. Pigos et al. [8] reported that the addition of Na and K significantly improved the formate decomposi-
tion rate on a WGS reaction over Pt/ZrO\textsubscript{2} catalysts. Wang et al. [9] reported that the addition of Na improved the catalytic performance of a PtRu/ZrO\textsubscript{2} catalyst on the oxidative steam reformation of ethanol, where the Na not only enhanced the WGS reaction at a low temperature, but also reduced coke deposition. Cheng et al. [10] also reported the promotional effect of doping alkaline earth oxides or lanthanide oxides on a Ni/Al\textsubscript{2}O\textsubscript{3} catalyst for CO\textsubscript{2} reforming of CH\textsubscript{4}.

Besides the selection of an active metal or promoter for the supported catalysts, the choice of a support with a high surface area to disperse the metal phase over their surface is a main consideration to enhance catalytic performance. Support material, such as γ-Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, ZSM-5 [11], MCM-41 [12] and SBA-15 [13], have been widely used in recent years as catalyst supports for catalytic reactions occurring at high temperatures, based on the support material’s larger pores, thicker walls and higher thermal stability. Of considerable interest in this regard are mesoporous materials as a support that will provide an improvement on hydrogen production via steam reforming reaction [14-19]. The promoter effect of alkaline earth metals (Mg and Ca) over Cu-Ni/SBA-15 [16] and Cu-Ni/SiO\textsubscript{2} [18] catalysts has been studied; both of them improved the dispersion of the metallic phase and strengthened the metal-support interaction. High hydrogen selectivity was obtained with Mg and reduced deposited carbon with the incorporation of Ca. A promoter made up of a Ce\textsubscript{3}Zr\textsubscript{1-x}O\textsubscript{2} layer pre-coated on SBA-15 changes the redox properties and enhances the catalytic activity on steam reformation of methane over a Ni-based catalyst, as reported by Wang et al. [19].

It is well known that Co-based catalysts suffer from deactivation by carbon deposition at high reaction temperatures [20]. This is obviously an important point to consider in SRE reactions related to Co-based catalysts. The SBA-15 supported Co catalysts with high surface area and modified by an Mg promoter were prepared in this work. The catalytic performance and coking behavior of hydrogen production via SRE over mesoporous structure catalysts were also considered.

2. Experimental

2.1. Catalyst Preparation

SBA-15 was prepared according to the method described in the literature [13]. Briefly, a triblock copolymer P123 (8 g, Strem) was dissolved in 250 mL HCl (1.9 M). The solution was stirred at 40°C for 2 h, and 16 g of tetraethyl orthosilicate (TEOS) were then slowly added to the mixture and stirred vigorously at 40°C for 22 h. The solution was transferred into a Teflon bottle and aged at 100°C for 24 h. The solid product was filtered, washed with deionized water and then dried at room temperature for 24 h, followed by calcination in air at 500°C for 6 h with a heating rate of 7°C/min.

Catalysts promoted with alkaline are much more sensitive to the preparation order for catalytic performance, and the promoting effect is more significant when the support is impregnated with the promoter oxides before the incorporation of the active phase [10]. For this reason, Mg-modified Co/SBA-15 catalysts are prepared by consecutive impregnation with Mg and then Co. Mg\textsubscript{x}/SBA-15 samples were prepared from the aqueous solution of Mg(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O (Mg loading, x = 5 and 10 wt%, Showa) incorporating SBA-15 by the impregnation method. Co\textsubscript{y}Mg\textsubscript{x}/SBA-15 samples were prepared by the incipient wetness impregnation method using Mg\textsubscript{x}/SBA-15 with aqueous Co(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O (Co loading, y = 10 and 20 wt%, Showa). All samples were dried at 100°C overnight and then calcined at 300°C for 3 h.

2.2. Catalyst Characterization

The metal loading of catalysts was determined by the atomic-emission technique (ICP-AES) using a Perkin Elmer Optima 3000 DV. The BET surface area and pore size distribution were measured by N\textsubscript{2} adsorption at a liquid nitrogen temperature using a Micromeritics ASAP 2010 analyzer. X-ray diffraction (XRD) measurement was performed using a Siemens D5000 diffractometer with Cu K\textsubscript{α1} radiation (λ = 1.5406 Å) at 40 kV and 30 mA. The microstructure and particle size of the samples were observed by using transmission electron microscopy (TEM) with a JEOL JEM-2010 microscope equipped with a field emission electron source and operated at 200 kV. Reduction behavior of Co\textsubscript{y}Mg\textsubscript{x}/SBA-15 catalysts was studied by temperature-programmed reduction (TPR). About 50 mg of the sample were heated in a flow of 10% H\textsubscript{2}/N\textsubscript{2} gas at a flow rate of 10 ml·min\textsuperscript{-1}. During TPR, the temperature was increased by 7°C·min\textsuperscript{-1} from room temperature to 900°C.

2.3. Activity Tests

Catalytic activity of Co\textsubscript{y}Mg\textsubscript{x}/SBA-15 catalysts in an SRE reaction was determined at atmospheric pressure in a fixed-bed flow reactor. 100 mg of the catalyst were placed in a 4 mm i.d. quartz tubular reactor and held by glass-wool plugs. The temperature of the reactor was controlled by heating tape and measured by a thermocouple (1.2 mm i.d.) at the center of the reactor bed. The feed of the reactants was comprised of a gaseous mixture of ethanol (EtOH), H\textsubscript{2}O and Ar (purity 99.9995%, supplied by a mass flow controller). The composition of the reactant mixture (H\textsubscript{2}O/ EtOH/Ar = 37/3/60 vol%) was controlled by the Ar flow stream (22 ml/min) through a saturator (maintained at 120°C) containing EtOH and H\textsubscript{2}O. The gas hourly space velocity (GHSV) was main-
tained at 22,000 h\(^{-1}\) and the H\(_2\)/EtOH molar ratio was 13 (H\(_2\)/EtOH = 80:20 by volume). Prior to reactivity measurement, the catalyst was reduced in 10% H\(_2\) in N\(_2\) for 2 h at 400\(^\circ\)C. The SRE activity was tested stepwise, increasing the temperature from 350\(^\circ\)C to 550\(^\circ\)C. The reaction was carried out online by gas chromatography (GC) with columns of Porapak Q (for CO\(_2\), H\(_2\)O, C\(_2\)H\(_4\), CH\(_3\)CHO, CH\(_3\)OCH\(_3\) and EtOH) and using a Molecular Sieve 5 Å (for H\(_2\), CH\(_4\) and CO) for separation. It was also quantitatively analyzed by two sets of thermal conductivity detectors (TCD) on line. Response factors for all products were obtained, and the system was calibrated with appropriate standards before each catalytic test. Activity evaluation of all samples depended on the conversion of ethanol (X\(_{\text{EtOH}}\)), the distribution of products (mol %) and the yield of hydrogen (Y\(_{\text{H2}}\), mol H\(_2\)/mol EtOH) according to the following equations.

\[
X_{\text{EtOH}} = \left( \frac{n_{\text{EtOH, reacted}}}{n_{\text{EtOH, fed}}} \right) \times 100\% \tag{2}
\]

\[
Y_{\text{H2}} = \frac{n_{\text{H2, out}}}{n_{\text{EtOH, reacted}}} \tag{3}
\]

\[
S_i = \left( \frac{n_i}{\Sigma n_i} \right) \times 100\% \tag{4}
\]

where \(n_i\) was a mole of products and included H\(_2\).

3. Results and Discussion

3.1. Characterization of Supports and Catalysts

The XRD patterns at small angles of SBA-15, Mg\(_x\)/SBA-15 and Co\(_y\)Mg\(_x\)/SBA-15 (x = 5 and 10; y = 10 and 20) samples are shown in Figure 1. The SBA-15 support (Figure 1(a)) shows a pattern with three well-resolved peaks observed at 2\(\theta\) values of 0.92\(^\circ\), 1.54\(^\circ\) and 1.77\(^\circ\) that correspond to the diffraction of (100), (110) and (200) planes, respectively, indicating their ordered 2D hexagonal structure with space group \(p6mm\) [13]. The \(d\)-spacing of this structure, calculated from \(n\lambda = 2\sin\theta\) is 9.6 nm, which is also in the mesoporous range. Both Mg\(_x\)/SBA-15 samples (x = 5 and 10) are presented in Figures 1(b) and (c), respectively. The intensity of the diffraction peaks of the hexagonal mesostructure decreases gradually with the increase of x from 5 to 10. Moreover, a similar trend can be observed with the decrease in \(d\)-spacing where the \(d\)-spacing for x = 5 and 10 are 9.3 and 9.0 nm, respectively. The intensity of diffraction peaks for the Co\(_y\)Mg\(_x\)/SBA-15 (y = 10 and 20) catalysts (Figures 1(d)-(h)) decreases with the increase of x and y, and weakens more than the Mg\(_x\)/SBA-15 samples. Furthermore, the material composed of a high surface area, larger pores and thicker walls seems to disintegrate with increasing metal loading, raising doubt about the structural integrity.

The N\(_2\) adsorption-desorption analysis of the Co\(_y\)Mg\(_x\)/SBA-15 catalysts is shown in Figure 2. All of the samples exhibit a Type IV isotherm with a clear H1-type hysteresis loop, with metal loading or not (SBA-15 and Mg\(_x\)/SBA-15 samples are not shown), which is typical for mesoporous materials. Even though the XRD analysis showed the destruction of the hexagonal structure with impregnation of cobalt, the SBA-15 supported catalysts still maintained the mesoporous structure. Table 1 summarizes the physical characterization of Co\(_y\)Mg\(_x\)/SBA-15 catalysts, which includes the metal loading, surface area and phase composition. The surface area decreases with the increase of the (x + y) value, where the surface areas are 359, 313, 234 and 130 m\(^2\)/g, respectively for the values of 15, 20, 25 and 30. The decrease of surface area indicates that the mesoporous structure may be blocked by large amounts of Mg and Co loading.

The wide-angle XRD patterns of the Co\(_y\)Mg\(_x\)/SBA-15 catalysts are shown in Figure 3. The broad and wide
Table 1. Physical characterization of the Co$_y$Mgx/SBA-15 catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loading (wt %)$^a$</th>
<th>Co/Mg ratio (%)</th>
<th>Surface area$^b$ (m$^2$/g)</th>
<th>Phase$^c$</th>
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<tr>
<td>Co$_{10}$Mg$_5$/SBA-15</td>
<td>8.68</td>
<td>4.18</td>
<td>67</td>
<td>359 Co$_3$O$_4$, (Co, Mg)O</td>
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<td>Co$<em>{10}$Mg$</em>{10}$/SBA-15</td>
<td>9.12</td>
<td>8.24</td>
<td>50</td>
<td>313 Co$_3$O$_4$, (Co, Mg)O</td>
</tr>
<tr>
<td>Co$_{20}$Mg$_5$/SBA-15</td>
<td>19.0</td>
<td>8.16</td>
<td>67</td>
<td>130 Co$_3$O$_4$, MgCo$_2$O$_4$, (Co, Mg)O</td>
</tr>
<tr>
<td>Co$_{20}$Mg$_5$/SBA-15-H650</td>
<td>18.4</td>
<td>4.81</td>
<td>80</td>
<td>234 Co$_3$O$_4$, MgCo$_2$O$_4$, (Co, Mg)O</td>
</tr>
<tr>
<td>Co$_{20}$Mg$_5$/SBA-15</td>
<td>18.4</td>
<td>4.81</td>
<td>80</td>
<td>220 MgCo$_2$</td>
</tr>
</tbody>
</table>

$^a$ICP-AES measurement. $^b$BET measurement. $^c$The phase was identified by the XRD and TPR analysis.

peak at 2$\theta$ around 15° - 30° is characteristic of amorphous silica. The peak related to MgO (2$\theta$ ≈ 43°) is unobservable in the XRD patterns for Co$_y$Mgx/SBA-15 catalysts, which indicate the Mg shows highly dispersed on SBA-15 or becomes the nickel-magnesia solid solution oxides (Co, Mg)O [21,22]. Both the Co10Mg5/SBA-15 and Co10Mg10/SBA-15 catalysts (Figure 3(a) and (b)) show the characteristic diffraction peaks corresponding to the (220), (311), (511) and (440) planes at 31.3°, 36.8°, 59.0° and 64.8°, respectively. These are related to the cubic phase of Co$_3$O$_4$ (JCPDS No: 76-1802). The spinel structure of magnesium cobaltite MgCo$_2$O$_4$ [23,24] (JCPDS No: 81-0671) shows the corresponding planes of (111), (220), (311), (400), (511) and (440) at 18.9°, 31.1°, 36.6°, 44.5°, 58.9° and 64.7°, respectively. These are obtained on the high Co loading catalysts of Co20Mg5/SBA-15 and Co20Mg10/SBA-15 (Figures 3(c) and (d)). Otherwise, the higher Co loading would show the stronger diffraction signal. In here, both the Co$_3$O$_4$ and MgCo$_2$O$_4$ phases are not able to give clear assignment, because their diffraction peaks are overlapped. Choudhary et al. [25] reported that the MgCo$_2$O$_4$ phase was only observed in the case of catalysts with high Co loadings, such as over 20%, which was supported by our results when $y = 20$. Therefore, the Co$_y$Mgx/SBA-15 catalysts may contain two phases of Co$_3$O$_4$ and MgCo$_2$O$_4$, and further investigation will be discussed on TPR analysis.

Figure 4 shows the TPR profiles of the Co$_y$Mgx/SBA-15 catalysts. There are two continuous reduction peaks around 180°C to 350°C and broad peak around 500°C to 700°C, respectively. While the lower temperature peaks may be related to the two-steps reduction of Co$_3$O$_4$ [26] and the higher temperature peak is assigned the reduction of MgCo$_2$O$_4$ [25]. Besides, a faint peak over 800°C may be attributed to the reduction of cobalt-magnesia solid solution oxides (Co, Mg)O formed on the catalysts [27]. Further, the reduction signal of Co$_3$O$_4$ would be raised by increasing the Co loading. These results are confirmed to the XRD study, the Co$_3$O$_4$ and MgCo$_2$O$_4$ phases are coexisting in Co$_y$Mgx/SBA-15 catalysts. Particularly, the lower Mg loading will produce the less amount of MgCo$_2$O$_4$ phase.
3.2. Catalytic Performance

Catalytic performance of ethanol conversion ($X_{\text{EtOH}}$), products distribution and hydrogen yield ($Y_{\text{H}_2}$) for the Co$_{10}$Mg$_5$/SBA-15 catalysts are summarized in Table 2. The $X_{\text{EtOH}}$ reaches completion for Co$_{10}$Mg$_5$/SBA-15, Co$_{10}$Mg$_{10}$/SBA-15 and Co$_{20}$Mg$_{10}$/SBA-15 catalysts as the reaction temperature ($T_R$) approaches 475°C; while the $Y_{\text{H}_2}$ only approaches less than 2.0 at 550°C. Otherwise, both the Co$_{20}$Mg$_5$/SBA-15 and Co$_{20}$Mg$_{10}$/SBA-15 catalysts show that the $Y_{\text{H}_2}$ increases with $T_R$ and up to 5.02 and 5.78, respectively at 550°C.

Table 2. Products distribution of SRE reaction over Co$_y$Mg$_x$/SBA-15 catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_R$ (°C)</th>
<th>$X_{\text{EtOH}}$ (%)</th>
<th>Products distribution (%)</th>
<th>$Y_{\text{H}_2}$</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$H_2$</td>
<td>$CH_4$</td>
</tr>
<tr>
<td>Co$_{10}$Mg$_5$/SBA-15</td>
<td>400</td>
<td>44.4</td>
<td>44.2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>425</td>
<td>52.6</td>
<td>44.9</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>90.0</td>
<td>45.6</td>
<td>0.42</td>
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<td>475</td>
<td></td>
<td>46.1</td>
<td>0.79</td>
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<td>500</td>
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<td>1.75</td>
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<td>74.3</td>
<td>3.15</td>
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*Water is not included.*
Based on the phase diagram of the Mg-Co system [28], there is an equilibrium phase for MgCo$_2$ when Co loading is over 67%. Two conditions are required to obtain MgCo$_2$: a high Co loading over 20 wt% [25] and a Co/Mg ratio over 67% [28]. In regard to the pretreatment with reduction temperature effects for the sample with a Co/Mg ratio over 67%, a ε-Co structure is the major type for a reduction temperature below 422°C. Otherwise, an α-Co structure shows for a reduction temperature over 422°C [28]. Compared to the pretreatment of temperature effects, a Co$_{20}$Mg$_5$/SBA-15 catalyst is reduced by H$_2$ at 650°C for 2 h (denoted as Co$_{20}$Mg$_5$/SBA-15-H$_{650}$). The XRD characterization is shown in Figure 3(e) and the TPR analysis is shown in Figure 4(e). The XRD of Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ catalyst presents only a diffraction peak around 45°C that can be identified and assigned to the (400) plane of the MgCo$_2$ phase (JCPDS No. 29-0486). Since the Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample is stored in atmosphere, the oxidation of sample may be occurred. A TPR profile of Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ shows a weak peak below 350°C which relates to the reduction of Co$_3$O$_4$.

In order to understand the variation in the Co/Mg ratio over 67% and pretreatment with the reduction temperature effect, both the Co$_{20}$Mg$_5$/SBA-15 and Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ samples are further discussed. Temperature profiles of catalytic performance on the SRE reaction over the Co$_{20}$Mg$_5$/SBA-15 and Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ samples are described in Figures 5 and 6. There are significant differences in catalytic activity and products distribution due to the high temperature reduction. The Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample is better than the Co$_{20}$Mg$_5$/SBA-15 sample. The results indicate that the X$_{1EOH}$ approaches completion around 425°C for Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ samples while requiring 450°C for Co$_{20}$Mg$_5$/SBA-15 samples to complete the conversion. The Y$_{H_2}$ increases up to 5.78 and S$_{CO}$ is 3.10% for the Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample, while the Y$_{H_2}$ approaches 5.02 and S$_{CO}$ is 3.88% for the Co$_{20}$Mg$_5$/SBA-15 sample at 550°C. Dehydration especially from ethanol to ethylene is a dominant reaction for all samples that are not pretreated under high temperature reduction, where the selectivity of C$_2$H$_4$ is over 10%.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$  \hspace{1cm} (5)

The main reaction is the dehydrogenation of ethanol to acetaldehyde at low temperature. As the temperature raised, a major reaction proceeded the decomposition of acetaldehyde into methane and CO for Co$_{20}$Mg$_5$/SBA-15 and Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ samples.

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$  \hspace{1cm} (6)

$$CH_3CHO \rightarrow CH_4 + CO$$  \hspace{1cm} (7)

Comparing the temperature effect on the decomposi-

Figure 5. Catalytic performance of SRE reaction over Co$_{20}$Mg$_5$/SBA-15 catalyst.

Figure 6. Catalytic performance of SRE reaction over Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ catalyst.

The distribution of CO is minor when the T$_R$ is above 425°C for a Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample. At 525°C, the selectivity of CH$_4$, CO and CO$_2$ arrive at 3.20%, 3.05% and 19.5%, respectively, for a Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample. The D$_T$ of a Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample is lower than 400°C, while it is above 450°C for a Co$_{20}$Mg$_5$/SBA-15 sample.

The distribution of CO is minor when the T$_R$ is above 425°C for a Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample. This demonstrates that the water-gas shift reaction (WGSR) is an important side-reaction in the SRE reaction producing H$_2$ and CO$_2$.

$$CO + H_2O \rightarrow CO_2 + H_2$$  \hspace{1cm} (8)

At 525°C, the selectivity of CH$_4$, CO and CO$_2$ arrive at 3.20%, 3.05% and 19.5%, respectively, for a Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ sample. The hydrogen selectivity is close to its stoichiometric value (75%), whereas an increase of up to 74% is obtained at over 450°C. Unlike the Co$_{20}$Mg$_5$/SBA-15 and Co$_{20}$Mg$_5$/SBA-15-H$_{650}$ samples, other Co$_y$Mg$_x$/SBA-15 catalysts show poor catalytic performance in an SRE reaction. The low H$_2$ yields (<1.9)
and CO₂ selectivity are produced by the ethanol dehydration to ethylene followed by steam reforming, where C₂H₄ is up to 20% at 450°C. However, the formation of carbon through C₂H₄ is a possible route, which leads to catalyst deactivation.

\[ \text{C}_2\text{H}_4 \rightarrow \text{polymer} \rightarrow \text{coke} \quad (9) \]

### 3.3. Characterization of Used Catalyst

XRD and TEM analysis are used to characterize the CoₓMgₓ/SBA-15 catalysts after the SRE reaction. XRD patterns reveal MgO (JCDPS No. 4-829) and CoO (JCDPS No. 78-0431) diffraction patterns on Co₁₀Mg₁₀/SBA-15, Co₁₀Mg₁₀/SBA-15 and Co₂₀Mg₁₀/SBA-15 samples (Figures 7(a), (b) and (e)). Only the Co₂₀Mg₁₀/SBA-15 and Co₂₀Mg₁₀/SBA-15-H650 samples show metallic Co (JCDPS No. 89-4307) reflections of (111) and (200) planes (Figures 7(c) and (d)). These results are in good agreement, helping to convince researchers that the Co₂₀Mg₁₀/SBA-15 and Co₂₀Mg₁₀/SBA-15-H650 samples show the better catalytic activity than others in an SRE reaction, exhibiting an active site of metallic Co. The metallic Co usually generated via the reduction of Co₃O₄, which was easily sintered if the interaction with the support was absent [27]. However, the Co₂₀Mg₁₀/SBA-15 and Co₂₀Mg₁₀/SBA-15-H650 samples could form MgCo₂O₄ or MgCo₂ phases and formatted well-dispersed Co clusters, which are more resistant to sintering due to a stronger interaction between MgO and the support [25]. Based on previous reports [27,29], coke formation would not be stimulated on well-dispersed Co clusters to deactivate the catalyst.

The TEM images (Figure 8) show that carbon deposited as large filaments and tubes emerged with the catalyst particles and/or as an amorphous coating carbon on the catalyst particles. The filaments and tubes carbon is shown in the Co₂₀Mg₁₀/SBA-15 and Co₂₀Mg₁₀/SBA-15-H650 samples (Figures 8(c) and (d)), and amorphous carbon is presented in the Co₁₀Mg₁₀/SBA-15, Co₁₀Mg₁₀/SBA-15 and Co₂₀Mg₁₀/SBA-15 catalysts (Figures 8(a), (b) and (e)). According to the deactivation with the deposited carbon, the coating carbon could shorten the lifetime of a catalyst rather than filaments carbon [30], which agreed with our results. Moreover, all the samples maintain a mesoporous structure of SBA-15 after the SRE reaction. A good thermal stability is presented.

### 4. Conclusion

Steam reforming of ethanol was studied over SBA-15 supported catalysts with a Mg promoter and a cobalt loading of 10 and 20 wt%. The Co/Mg ratio and pretreatment of catalysts play a major role on the catalytic performance regarding the structural properties. A high catalytic performance and hydrogen yield were obtained on the high loading of Co, where the Co/Mg ratio was 0.8. According to the phase diagram of an Mg-Co system,
a reduction temperature of 650°C would form MgCO$_3$ as the main phase convinced by XRD, which leads to the active site to enhance the catalytic performance. The Y$_{H2}$ approaches 5.78 and the S$_{CO}$ is 3.10% for CO$_{2}$Mg$/$/SBA-15-H650 sample as the T$_R$ approaches 550°C.

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