

## Removal of Coke during Steam Reforming of Ethanol over La-CoO<sub>x</sub> Catalyst

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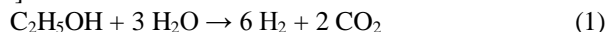
**ABSTRACT :** An active La-CoO<sub>x</sub> catalyst with 10 wt% lanthanum (assigned as 10La-Co) was prepared by an impregnation method. The 10La-Co sample was further calcined under 300, 500 and 700 °C for 3 h (assigned as C300, C500 and C700, respectively). Catalytic activities toward the steam reforming of ethanol (SRE) were tested in a self-designed fixed-bed reactor. Prior to the reaction, the sample was activated by reduction with hydrogen at 200 °C for 3 h. The SRE tests indicated that both the 10La-Co and C300 samples possessed better activity than the C500 and C700 samples. The time-on-stream of the 10La-Co catalyst could persist 60 h and no coke accumulated on the surface of the catalyst. According to the products of CO<sub>2</sub> and CO distribution in the SRE reaction and the XRD characterization of used catalyst, we suggested that the formation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> came from the interaction of La<sub>2</sub>O<sub>3</sub> with CO<sub>2</sub> product. Under reforming reaction conditions, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species can further react with the deposited carbon on an active metal surface; the accumulated carbon from the reforming process can therefore be effectively removed and prolonged the lifetime of catalyst.

**KEYWORDS:** Deposited carbon, Lanthanum oxycarbonate, Production of hydrogen, Removal of coke, Steam reforming of ethanol.

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### I. INTRODUCTION

Hydrogen is a clean fuel often used to generate electricity through its reaction with oxygen in a fuel cell. Hydrogen may effectively help to reduce the emission of green house gases due to the fact that it has much higher energy conversion efficiency as compared to fossil fuels. Currently, hydrogen is produced mainly from fossil oils. Because it is stored and distributed in gas cylinder or gas tank, the cost of transportation is relatively high. The cost might be lowered if hydrogen could be produced on site through a simple chemical reaction of an organic material having high energy density. Ethanol may represent a potential source for hydrogen production and the steam reforming of ethanol (SRE) could make the use of hydrogen viable while at the same time solving problems related to storage and distribution. Moreover a high yield of hydrogen can be obtained from this reaction [1-4]:



The SRE is a catalytic process for generating hydrogen from an ethanol solution at high temperature. Direct production of hydrogen through the SRE reaction over oxide catalysts such as MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO, V<sub>2</sub>O<sub>5</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub> has been reported [5], in which the MgO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub> showed poor ethanol conversion (< 38 %) even with the reaction temperature up to 450 °C. Otherwise, the SRE reaction over supported catalysts can improve their catalytic ability; the cobalt metal was especially effective in exhibiting catalytic ability. Llorca et al. [6, 7] reported that Co/ZnO was the preferential catalyst for producing CO-free hydrogen through the SRE reaction. Also, Haga et al. [8] reported that Co/Al<sub>2</sub>O<sub>3</sub> catalyst showed high H<sub>2</sub> selectivity for the SRE reaction by suppressing the methanation of CO and the decomposition of ethanol. The supported-cobalt catalysts showed good activity and fewer by-products; however, the accumulated coke during the SRE catalytic reaction at a high temperature would be deactivated and shorten the lifetime of catalyst. Although the efficiency of ethanol conversion by the SRE reaction may be satisfactory, the cost of the raw material [i.e. cobalt carbonyl, Co<sub>2</sub>(CO)<sub>8</sub>, as precursor] is too expensive to render such a method practical in terms of commercial value. An improved method using cobalt nitrate [Co(NO<sub>3</sub>)<sub>2</sub>] as the starting material for the preparation of a cobalt oxide catalyst is therefore suggested as a practical hydrogen producing process [9, 10] as well as for oxidation reaction [11-13]. Furthermore, cobalt oxides can be prepared by the citrate method [9, 11] and the precipitation-oxidation method [10, 12-14].

Among the compounds of cobalt oxide, we recognize that both the CoO and Co<sub>3</sub>O<sub>4</sub> are more stable and active, whereas the Co<sub>3</sub>O<sub>4</sub> would be reduced to CoO and further metallic cobalt under high temperature SRE reaction. Although La<sub>2</sub>O<sub>3</sub> is not suitable for the SRE reaction, it exhibits excellent stability and can therefore be considered as a support or promoter to modify the catalyst. The reaction of carbon dioxide reforming and steam reforming of ethanol were studied by employing a Ni/La<sub>2</sub>O<sub>3</sub> catalyst and showed good activity and stability for both reactions [15-18]. In addition, lanthanum oxide may react with carbon dioxide to form a stable compound, lanthanum oxycarbonate (La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>) [17]. Under reforming reaction conditions, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species can react with carbon on an active metal surface; the accumulated carbon from the reforming process can therefore be effectively reduced and the lifetime of the catalysts should be prolonged. In our previous work [10], the as-prepared cobalt oxide catalyst showed high activity under low temperature, where Y<sub>H<sub>2</sub></sub> reached 5.72 and minor by-products of CO and CH<sub>4</sub> were detected. These results also showed that the deactivation of reforming catalysts was caused by the deposited carbon and phase transformation of cobalt oxides. Therefore, we would like to induce lanthanum into the cobalt oxide catalyst to remove the deposited carbon. The study will carry out the SRE reaction over lanthanum-modified CoO<sub>x</sub> catalyst with or without calcined treatment.

## II. EXPERIMENTAL

### 2.1 CATALYSTS PREPARATION

A high valence cobalt oxide support, CoO<sub>x</sub>, was synthesized by the precipitation-oxidation method described earlier in detail [12]. A lanthanum-based catalyst was prepared through an impregnation method. Lanthanum nitrate solution (10 wt%) was added drop-by-drop into the dispersed cobalt oxide suspension solution, and the mixture was stirred continuously for 24 h to ensure that the lanthanum ions were well dispersed within the as-prepared cobalt oxide. The resulting solution was dried in an oven at 110 °C for 24 h to remove moisture, and the obtained as-prepared lanthanum-modified cobalt oxide catalyst was labeled as 10La-Co. The as-prepared sample was further calcined for 3 h under 300, 500 and 700 °C (labeled as C300, C500 and C700), respectively.

### 2.2 CATALYSTS CHARACTERIZATION

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu K<sub>α1</sub> radiation ( $\lambda = 1.5405 \text{ \AA}$ ) at 40 kV and 30 mA. The diffraction patterns were recorded in the  $2\theta$  value range of 10 – 80° with a step size of 0.01° and 1 s per step. The crystallite sizes of cobalt oxides were estimated using the Scherrer equation. The microstructure and particle distribution of 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 cobalt oxides was studied by temperature-programmed reduction (TPR). About 50 mg sample was heated in a flowing 10% H<sub>2</sub>/N<sub>2</sub> gas (10 ml·min<sup>-1</sup>) with a heating rate 7 °C·min<sup>-1</sup> from room temperature to 800 °C. Hydrogen consumption was detected by a thermal conductivity detector (TCD).

### 2.3 CATALYTIC ACTIVITY MEASUREMENT

Catalytic activities toward the SRE reaction were performed at atmospheric pressure in a fixed-bed flow reactor. A catalyst amount of 100 mg was placed in a 4 mm i.d. quartz tubular reactor, held by glass-wool plugs. The temperature of the reactor was controlled by heating tape, and measured by a thermocouple at the center of the reactor bed. The feed of the reactants was comprised of a gaseous mixture of ethanol (EtOH), H<sub>2</sub>O and Ar (purity 99.9995%, supplied by a mass flow controller). The composition of the reactant mixture (H<sub>2</sub>O/EtOH/Ar = 37/3/60 vol.%) was controlled by a flow of Ar streamed through a saturator (maintained at 130 °C) containing EtOH and H<sub>2</sub>O. The gas hourly space velocity (GHSV) was maintained at 23,000 h<sup>-1</sup> and the H<sub>2</sub>O/EtOH molar ratio was 13 (H<sub>2</sub>O:EtOH = 80:20 by volume). Prior to the reaction, the sample was activated by reduction with hydrogen at 200 °C for 3 h. The SRE activity was tested in increments, while increasing the temperature from 350 to 475 °C. A 5 h reaction time was maintained for each measured temperature. The analysis of the reactant and all of the products was carried out online by gas chromatography, with columns of Porapak Q and Molecular Sieve 5A for separation. The evaluation of SRE activity for all samples is dependent on the conversion of ethanol (X<sub>EtOH</sub>), the distribution of products (mol%) and the yield of hydrogen (Y<sub>H<sub>2</sub></sub>). Both the X<sub>EtOH</sub> and Y<sub>H<sub>2</sub></sub> in the SRE reactions were calculated according to the following equations:

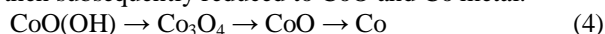
$$X_{\text{EtOH}} = (n_{\text{EtOH-in}} - n_{\text{EtOH-out}}) / n_{\text{EtOH-in}} \times 100\% \quad (2)$$

$$Y_{\text{H}_2} = n_{\text{H}_2\text{-out}} / (n_{\text{EtOH-in}} - n_{\text{EtOH-out}}) \quad (3)$$

### III. RESULTS AND DISCUSSION

#### 3.1 CHARACTERIZATION OF 10La-Co SERIES CATALYSTS

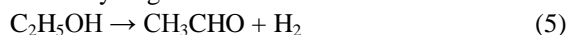
The structural distinction can be judged from the XRD. Figure 1 shows the XRD profiles of 10La-Co series catalysts, which indicates that the patterns of the 10La-Co sample [Fig. 1(a)] match the JCPDS 14-0673 file identifying cobalt oxyhydroxide, CoO(OH), with a hexagonal structure and a particle size around 10 nm. As increasing the calcined temperature [Figs. 1(b) and 1(c)], whose positions and relative intensities are indicative of pure Co<sub>3</sub>O<sub>4</sub> for C300 and C500 samples with particle size 7 and 14 nm, respectively. As the calcined temperature is raised to 700 °C [Fig. 1(d)], in addition to the Co<sub>3</sub>O<sub>4</sub> phase (the particle size is 17 nm), a new component, LaCoO<sub>3</sub> perovskite is formed which matches the JCPDS 86-1662 file. According to this observation, we can control both the phase and particle size of 10La-Co catalysts by tuning the calcined temperature. Figure 2 shows the TPR profiles of a series of 10La-Co series catalysts. The as-prepared 10La-Co sample [Fig. 2(a)] presents a continuous reduction which occurs at 228 (T<sub>r1</sub>), 250 (T<sub>r2</sub>), and 359 °C (T<sub>r3</sub>), respectively. According to our previous results [10, 13, 14], the reduction of CoO(OH) is a three-step process: it is initially reduced to Co<sub>3</sub>O<sub>4</sub>, and then subsequently reduced to CoO and Co metal.



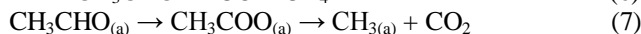
For C300 and C500 samples [Figs. 2(b) and 2(c)], the reduction temperatures of 190 and 198 °C, respectively, are derived from the residue of nitrate species which is difficult to remove even by heating up to 500 °C. The other two reduction signals above 250 °C in C300 (275 and 447 °C) and C500 (330 and 460 °C) samples result from the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO; furthermore, CoO is reduced to Co. Each step in the reduction shifting to higher temperature may be due to the stronger interaction of lanthanum with cobalt oxide. As the calcined temperature rises to 700 °C, the addition of lanthanum can enhance the interaction with cobalt oxide to form a new component of LaCoO<sub>3</sub> perovskite. In addition to the reduction of Co<sub>3</sub>O<sub>4</sub> (356 and 396 °C), a signal for the reduction of LaCoO<sub>3</sub> was observed at 546 °C [Fig. 2(d)], and confirmed with XRD analysis [Fig. 1(d)].

#### 3.2 CATALYTIC PERFORMANCE ON THE SRE REACTION

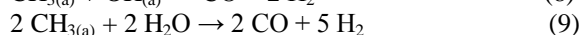
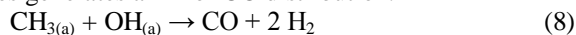
The SRE reaction was studied between 350 and 475 °C at atmospheric pressure. The catalytic performance of 10La-Co series catalysts at different temperatures (T<sub>R</sub>) is summarized in Table 1 and Figs. 3, 4. Performance is described in terms of ethanol conversion and products distribution (water excluded) for each test temperature. Catalytic performance of SRE reaction over the as-prepared 10La-Co and C500 samples are shown in Table 1. In looking at the distribution of products (only H<sub>2</sub>, CO<sub>2</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, CO and CH<sub>4</sub>) at different temperatures, some side-reactions have been excluded in SRE over 10La-Co series catalysts: ethanol dehydration to ethylene and ethanol decomposition to CO, CH<sub>4</sub> and H<sub>2</sub> (since only minor CO and CH<sub>4</sub> is detected at all temperature ranges). The conversion of ethanol increased with T<sub>R</sub> and completed at 425 °C for the 10La-Co sample and 450 °C for the C500 sample. Large amounts of CH<sub>3</sub>CHO obtained in the lower T<sub>R</sub> (< 400 °C) and further decreased by increasing T<sub>R</sub> accompanied with H<sub>2</sub> production. The formation of acetaldehyde suggests that the dehydrogenation of ethanol occurs first at 350 °C.



Further, the acetaldehyde could be transformed in different ways: decomposed to methane and carbon monoxide or, on the surface of cobalt oxide, it could be oxidized to acetate and the further decomposed into methyl group and CO<sub>2</sub>:



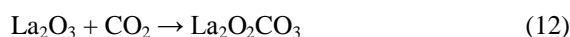
From the minor distribution of CO and CH<sub>4</sub> at all temperature ranges for 10La-Co series catalysts, pathways of (8) and (9) are plausible [19]. Also, accompanying the water gas shift (WGS) reaction with CO oxidation on cobalt oxides generates a minor CO distribution.



By increasing temperature, the formation of acetone was detected and the overall reaction could be described by the following reaction [20]:



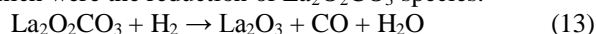
Moreover, the selectivity of H<sub>2</sub> and CO<sub>2</sub> were up to 80 and 13%, respectively, and the CH<sub>3</sub>CHO was neglected at 425 °C for the 10La-Co sample. The lower CO<sub>2</sub> came from the La<sub>2</sub>O<sub>3</sub> reacting with CO<sub>2</sub> to form La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species [17]. Incidentally, the H<sub>2</sub> selectively rose to 74% for the C500 sample and negligible CH<sub>3</sub>CHO was obtained at 450 °C.



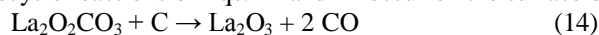
Figures 3 and 4 summarize the effects of temperature on  $X_{\text{EtOH}}$  and  $Y_{\text{H}_2}$  of the 10La-Co series catalysts. The results show that the activity of the 10La-Co sample was better than that of the C300, C500 and C700 samples, with a lower  $T_{\text{R}}$  and a higher  $Y_{\text{H}_2}$ . Under  $\text{H}_2\text{O}/\text{EtOH}$  molar ratio of 13 and  $23,000 \text{ h}^{-1}$  GHSV for the as-prepared 10La-Co catalyst, the  $Y_{\text{H}_2}$  reaches 5.9 under  $425^\circ\text{C}$ . Otherwise, the catalytic activity of calcined samples were shown in the order of C300 (7 nm) > C500 (14 nm) > C700 (17 nm), results accompanied by increases in calcined temperature. It was found that the small particle size of the C300 sample possessed better catalytic activity and selectivity of hydrogen at a lower temperature during the SRE reaction.

#### CHARACTERIZATION OF USED CATALYSTS

The XRD patterns of used catalysts of the 10La-Co series are shown in Fig. 5, and TPR profiles are shown in Fig. 6. The  $\text{Co}_3\text{O}_4$  and the major component of CoO could be assigned in as-prepared 10La-Co sample; in C300 sample only the CoO diffractions were observed. These results showed that the most of the cobalt oxides had been reduced by the produced hydrogen to form CoO in the SRE condition. Besides the CoO and the metallic cobalt signals, the lanthanum compound signals also could be assigned. Both the C500 and C700 samples include the  $\text{La}_2\text{O}_3$  and  $\text{LaCoO}_3$  phases. The used 10La-Co sample had two reduction temperatures at  $298$  and  $354^\circ\text{C}$  related to the reduction of  $\text{Co}_3\text{O}_4$  species and can be confirmed by the XRD pattern. According to the XRD and TPR characterization of used catalyst and products ( $\text{CO}_2$  and CO) distribution from the SRE reaction, we suggest that the formation of  $\text{La}_2\text{O}_2\text{CO}_3$  came from the reaction of  $\text{La}_2\text{O}_3$  with  $\text{CO}_2$  [17]. The sensitive TPR profiles showed the additional reduction signal around  $600^\circ\text{C}$  for 10La-Co, C300 and C500 samples, which were the reduction of  $\text{La}_2\text{O}_2\text{CO}_3$  species.



Furthermore, the deposited carbon on the catalyst could also be removed by the  $\text{La}_2\text{O}_2\text{CO}_3$  species via reaction (Eq. 14) to prolong the lifetime of catalyst. The TEM micrographs of fresh and used (no shown in this manuscript) 10La-Co samples indicate that the addition of lanthanum could inhibit the sinter of cobalt oxide, and differ from those of our previous study [10] of cobalt oxide. A comparison between the fresh and used sample indicated no apparent deposited coke on the used 10La-Co sample after the SRE reaction. Scheme 1 displays a schematic diagram to describe the decarbonation that deposits on the peripheral of cobalt oxide. Within it, recycle reactions of Eqs. 12 and 14 occur on the surface of La-modified cobalt oxide.



The durability of the 10La-Co and C300 samples had been tested 60 h without any coke being accumulated on the surface of catalyst.

#### IV. CONCLUSION

The preferential cobalt-based catalyst has been designed with modification of lanthanum. Effect of calcination temperature indicates that both the C500 and C700 samples would form the unactivated  $\text{LaCoO}_3$  species. Furthermore, the formation of special species " $\text{La}_2\text{O}_2\text{CO}_3$ " on both the 10La-Co and C300 samples were able to remove the peripheral deposited coke to prolong the lifetime of catalysts. Over 10La-Co sample in a SRE reaction at  $425^\circ\text{C}$ , up to 5.9 mol of  $\text{H}_2$  produced per mole of ethanol, few byproducts and a longer catalyst lifetime up to 60 h were obtained.

#### V. ACKNOWLEDGEMENTS

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Table 1. Catalytic performance in the steam reforming of ethanol over 10La-Co catalysts

Catalysts	$T_R$ (°C)	t (h)	Conversion (%)	Products distribution (%) <sup>a</sup>						$\text{H}_2/\text{EtOH}$ (mol/mol)
				$\text{H}_2$	$\text{CH}_4$	CO	$\text{CO}_2$	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_3\text{H}_6\text{O}$	
10La-Co	350	6	40.9	39.9	—	—	35.5	23.8	0.8	1.0
	375	10	62.2	58.8	0.2	2.1	23.6	11.8	3.5	2.0
	400	18	83.3	76.7	0.1	1.7	17.9	—	3.6	4.9
	425	60	100	81.2	0.1	1.4	15.7	—	1.6	5.9
C300	350	6	40.5	34.5	—	—	48.2	17.3	—	0.9
	375	10	54.5	68.6	—	1.5	22.1	3.5	4.3	3.1
	400	24	76.9	75.3	—	1.9	15.9	3.3	3.6	4.3
	425	60	100	80.8	0.1	0.7	15.4	—	3.0	5.6
C500	375	12	40.8	63.5	—	—	20.2	9.8	6.5	2.2
	400	20	67.7	68.4	—	—	16.9	6.8	7.9	2.6
	425	36	90.5	70.3	0.2	2.6	17.0	2.7	7.2	2.8
	450	60	100	74.5	0.1	1.2	17.2	—	7.0	3.8
C700	400	12	39.3	47.8	—	—	21.1	31.1	—	1.2
	425	16	63.7	66.4	0.1	2.0	16.6	14.9	—	2.7
	450	24	100	64.2	0.1	1.7	18.1	8.7	7.2	2.2
	475	48	100	64.0	0.2	3.4	18.4	7.2	6.8	2.3

<sup>a</sup> Water not included.

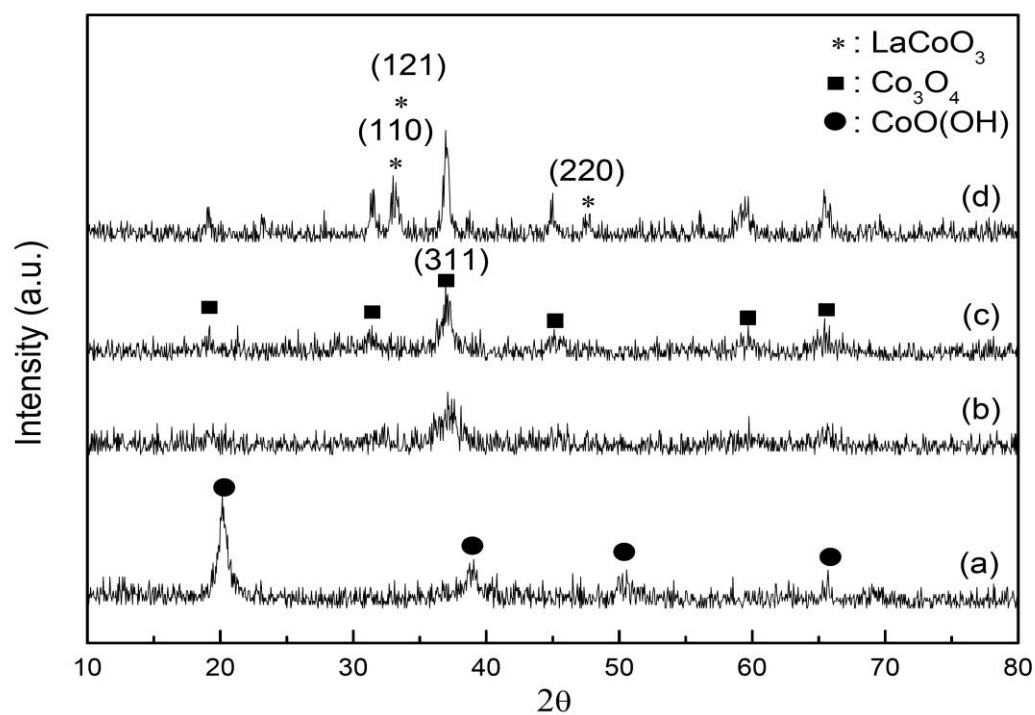


Fig. 1 XRD patterns of 10La-Co catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700

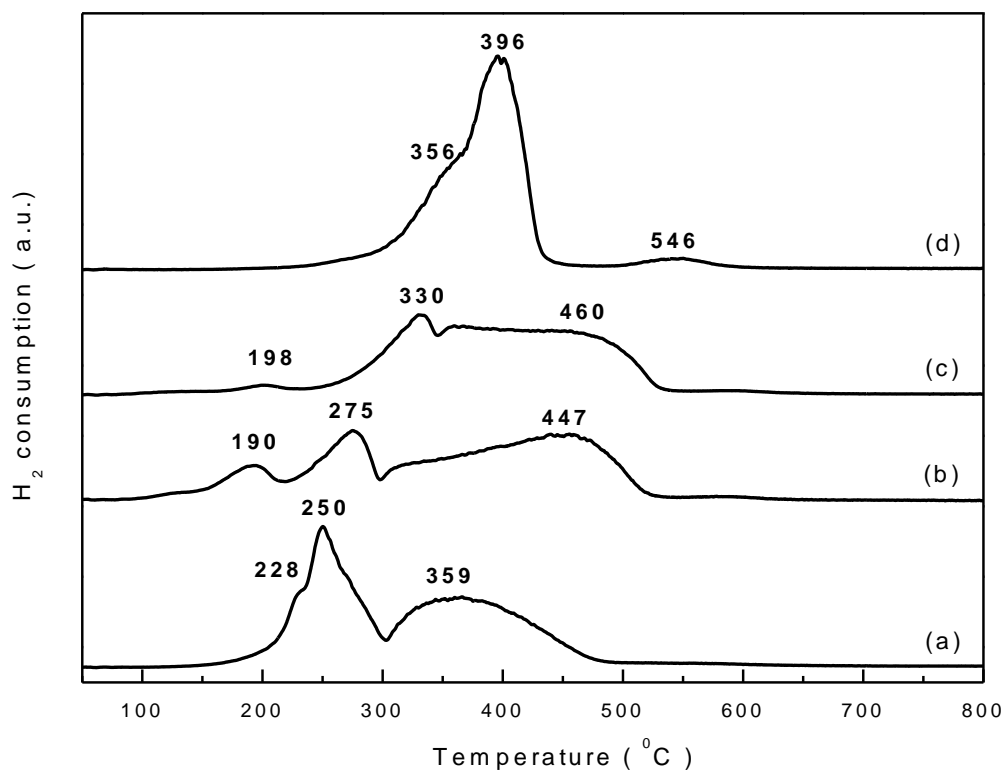


Fig. 2 TPR profiles of 10La-Co catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700

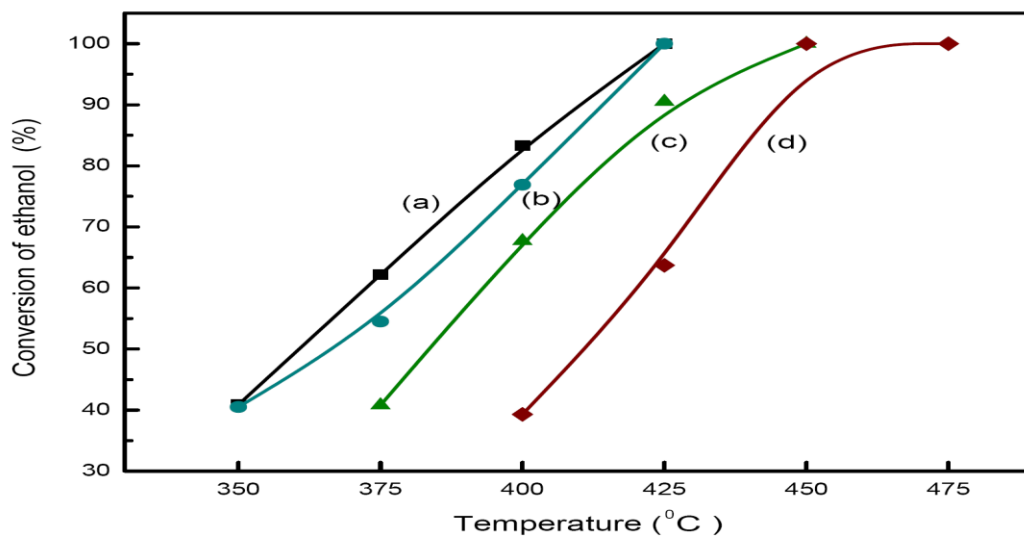


Fig. 3 Effects of reaction temperature for the ethanol conversion toward SRE reaction over 10-La catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700

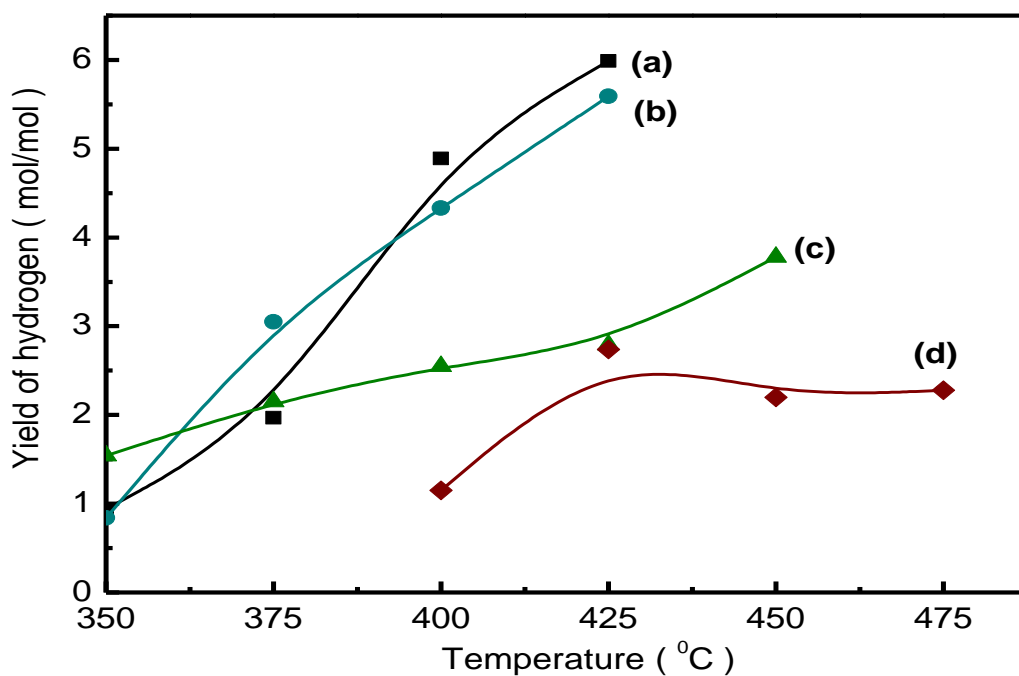


Fig. 4 Effects of reaction temperature for the yield of hydrogen toward SRE reaction over 10La-Cocatalyst: (a) 10La-Co (b) C300 (c) C500 (d) C700

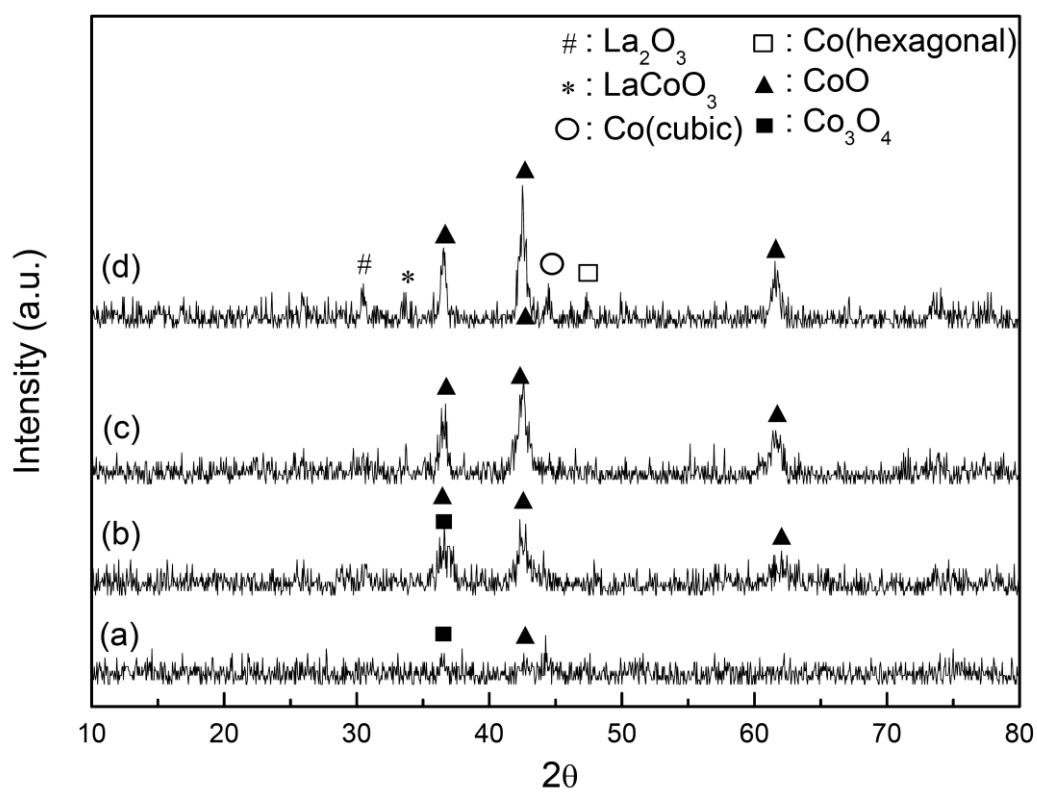


Fig. 5 XRD patterns of used catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700

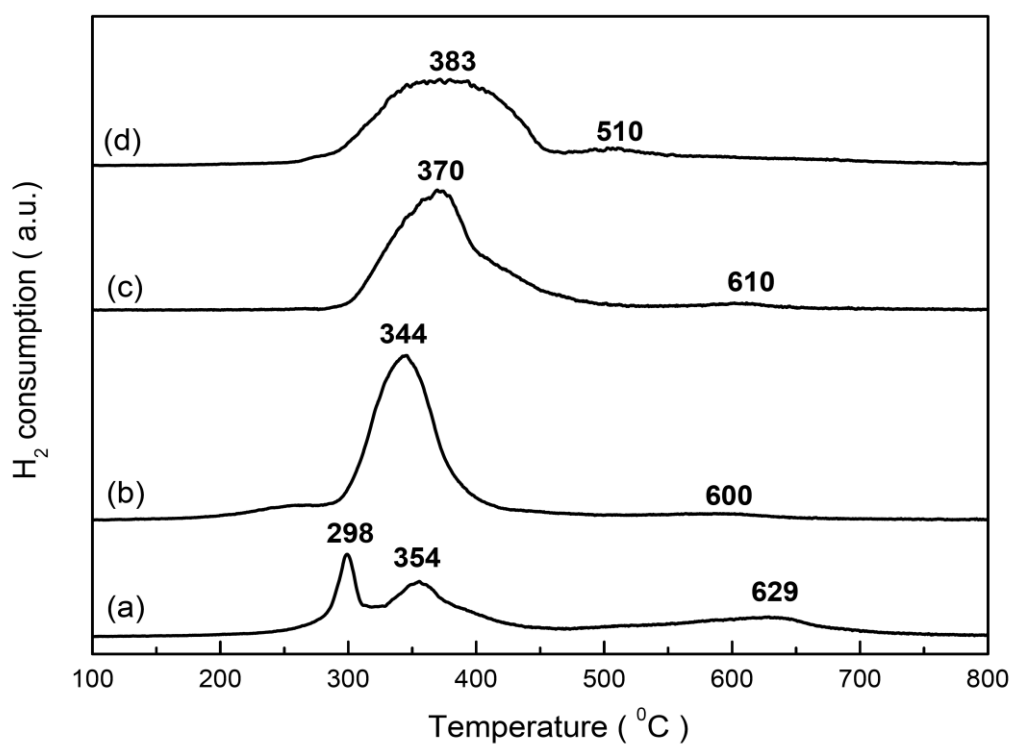
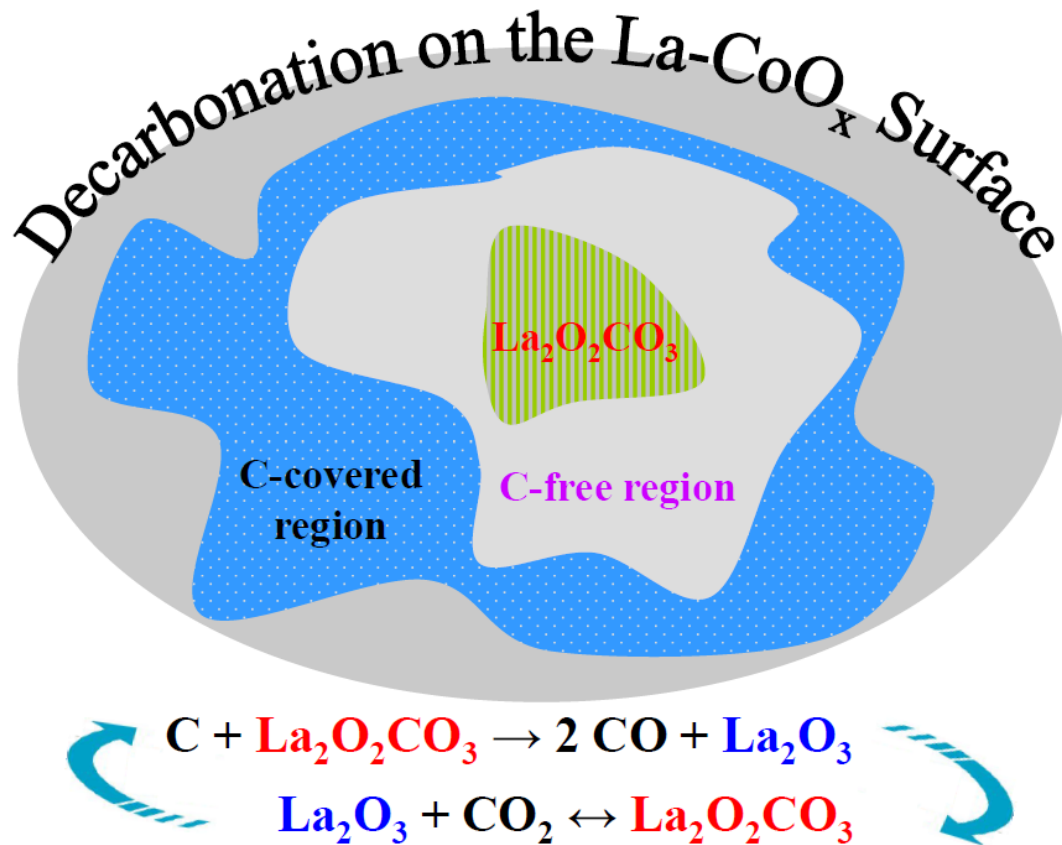


Fig. 6 TPR profiles of used catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700





Scheme 1 Model proposed for the decarbonation on the peripheral of 10La-Co series catalysts.