出國報告（出國類別：國際研討會）

出席 2012 年國際產氫會議心得報告

服務機關：國防大學理工學院化學及材料工程學系
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摘要

ICH2P-2012 會議是由韓國能源技術研究院主辦，大會地點為首爾萬麗酒店，為燃料電池及氫能產業界重要的國際會議之一。參加人員來自世界各地，包括加拿大、美國、韓國、德國、日本、中國、台灣、土耳其、波蘭、希臘、法國和英國等多國之專家學者，此研討會投稿論文分口頭報告及壁報展示，共計 300 餘篇。在會議中聆聽各國學者之學術演講，其中以土耳其學者 Ugur Cakir 針對由有機材料產氫之研究做一完整的回顧性報導；波蘭學者 Andrzej Krzton 探討 Ni/CeZrO$_2$ 觸媒用於碳氫化合物分解產氫之研究對我們現階段的研發受益最大。大會所討論之範圍很廣，包含能源、燃料電池之創新科技及燃料電池之應用、產氫技術等。世界各國學者齊聚一堂討論不同領域的研究成果與應用。本次會議提供個相當好的知識交流平台，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，真是獲益匪淺。此外，藉由參與大會各國專家學者之交換研究心得及吸取他人寶貴之研究經驗，將可做為本實驗室日後研究之參考。

筆者此次感謝獲國科會研究計畫之補助成行，發表題目共計二篇："Removal of Coke during Steam Reforming of Ethanol over La-CoO$_x$ Catalyst"，"Catalytic Performance and Coking Behavior of Platinum-Promoted Cobalt-Based Catalysts for Ethanol Steam Reforming"，達到與各國學者切磋交流的機會，並試乘了價值昂貴的氫能燃料電池汽車，真是獲益匪淺。

目次

壹、 會議目的

　　ICH2P-2012 會議是由韓國能源技術研究院主辦，為二年舉辦一次之國際學術會議。其會議宗旨在於結合世界各國有關氫能與燃料電池技術研究領域之學者專家，就專長領域進行一系列學術研究成果發表及新知討論，以便交流最新進展和技術信息，歷年來所主辦之學術研究年會、研討會及專題討論會，皆對該學術領域有深遠的影響及貢獻。因此，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，並與各國專家學者交換研究心得及吸取他人寶貴研究經驗，將可做為日後研究之參考。

貳、 會議過程

　　(一)本會議屬於國際型研討會，參加人員為來自世界各國之民間機構、專家學者及研究人員參與為期三天之學術論文發表及討論會。ICH2P-2012會議是由韓國能源技術研究院主辦，於2012年6月25日至6月27日在首爾萬麗酒店舉行。此為產氫技術與燃料電池領域非常重要的研討會之一，與會者多為各國在該領域學有專精之教授與學者，本次台灣參與之人員多達十餘人(元智、國防大學、中興、逢甲、明志、宜蘭大學、陸軍專科學校等)以上。於此與各國學者相互交流之下獲益良多。

　　(二)本次研討會每天安排於不同研討會議地點同時舉行不同議題發表，與會者可在會議期間自行選擇有興趣的場次參與研討過程，其研究領域與大會流程如后。

June 25, 2012: 1. Hydrogen infrastructure (HIN)/General (GEN)

　　　　　　　2. Hydrogen production by electrolysis (HPE)/Fuel cells (FCE)

　　　　　　　3. Photochemical hydrogen production (PHP)

　　　　　　　4. Hydrogen storage (HST)

　　　　　　　5. Fuel cells (FCE)

　　　　　　　6. Biological hydrogen production (BHP)

　　　　　　　7. Hydrogen production by reforming (HPR)

　　　　　　　8. Thermochemical hydrogen production (THP)

June 26, 2012: 1. Thermochemical hydrogen production (THP)

2. Conventional hydrogen production (CHP)

3. Fuel cells (FCE)

4. Biological hydrogen production (BHP)

5. Hydrogen separation (HSE)/Miscellaneous (MIS)

6. Photochemical hydrogen production (PHP)

7. Hydrogen production by reforming (HPR)

8. Hydrogen infrastructure (HIN)/Hydrogen in vehicles (HIV)

9. Hydrogen storage (HST)

June 27, 2012: 1. Hydrogen production by reforming (HPR)

2. Hydrogen production by electrolysis (HPE)/Fuel cells (FCE)

3. Biological hydrogen production (BHP)

4. Thermochemical hydrogen production (THP)

5. Photochemical hydrogen production (PHP)

6. Hydrogen storage (HST)

參、 會議心得

　　本研討會以產氫技術與燃料電池技術研究領域為主軸，會議是由韓國能源技術研究院主辦，為該領域中相當重要之研討會。參加人員為世界各國之專家學者，此研討會投稿論文分口頭報告及壁報展示，共計300餘篇。大會所討論之範圍很廣，包含能源、燃料電池之創新科技及燃料電池之應用、產氫技術等。部份足以為我國所參考之依據，另相關論述主題亦十分具參考價值。

　　本人計有口頭報告及壁報展示各乙篇，透過各國學者不同領域的經驗，於問答間各取所需，達到智識精進功效，並積極與各國學者交換演講意見達到學術交流目的。經過此次研討會歷練，使本人對未來之研究更具信心，將持續於此領域探討研析，並且對於後續之研究將會秉持精益求精的精神戮力完成。本次會議提供個相當好的知識交流平台，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，真是獲益匪淺。

肆、 建議事項

　　本研討會歷年與會人員及論文發表數目眾多，探討範圍亦相當廣泛，值得相關研究人員與學者參與。建議未來可增加國內專家學者參與機會，藉以吸收國際新知並分享研究成果。很可惜，我的博士後研究這次未獲得國科會的輔助，希望未來能在補助的員額及經費予以提高，鼓勵博士後研究或研究生積極參與國際會議，相信對國內各方面研究及學術工作的提昇，必定有所助益。願以此次的與會心得與大家分享共勉之，本次研討會攜回會議論文集資料。

作者發表之論文

Removal of Coke during Steam Reforming of Ethanol over

La-CoO$_x$ Catalyst

REMOVAL OF COKE DURING STEAM REFORMING OF ETHANOL OVER La-CoO$_x$ CATALYST

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ABSTRACT

A La-CoO$_x$ 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 ^{o}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 ^{o}C for 3 h. The SRE tests indicated that the 10La-Co and C300 samples possessed better activity. The tested lifetime of the 10La-Co catalyst was at least 60 h, no coke accumulated on the surface of the catalyst. According to the distribution of CO$_2$ and CO in the SRE reaction and the XRD characterization of used catalyst, the formation of La$_2$O$_2$CO$_3$ came from the interaction of La$_2$O$_3$ with CO$_2$. Under reforming reaction conditions, La$_2$O$_2$CO$_3$ species can react with 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: Steam reforming of ethanol, Lanthanum oxycarbonate, Removal of coke

INTRODUCTION

Hydrogen is a fuel often used to generate electricity through 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 cylinders or gas tanks, transportation costs are relatively high. These costs 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 could make the use of hydrogen viable while at the same time removing problems related to storage and distribution (Haryanto et al., 2005; Vaidya et al., 2006; Cheekatamarla et al., 2006; Eberle et al., 2009).

The steam reforming of ethanol (SRE) is a catalytic process for generating hydrogen from an ethanol solution at high temperature. Direct production of hydrogen from SRE over oxide catalysts such as MgO, Al_2O_3, SiO_2, TiO_2, ZnO, V_2O_5, La_2O_3, CeO_2 and Sm_2O_3 has been reported (Llorca et al., 2001), in which the MgO, La_2O_3, CeO_2 and Sm_2O_3 showed poor ethanol conversion (< 38 %) even with the reaction temperature up to 450 ^{o}C. Otherwise, the SRE reaction over supported catalysts can improve their catalytic ability; the metal cobalt was especially effective in exhibiting catalytic ability. Llorca et al. (Llorca et al., 2002; Llorca et al., 2003) reported that Co/ZnO was the preferential catalyst for producing CO-free hydrogen through SRE. Also, Haga et al. (Haga et al., 1997) reported that Co/Al_2O_3 catalyst showed high selectivity for the SRE reaction by suppressing the methanation of CO and the decomposition of ethanol. The oxide-supported cobalt catalysts showed good activity and fewer by-products; however, coke produced and accumulated 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 SRE reaction may be satisfactory, the cost of the raw material [i.e. cobalt carbonyl [$Co_2(CO)_8$] as precursor] is too expensive to render such a method practical in terms of commercial value. An improved method using cobalt nitrate [$Co(NO_3)_2$] as the starting material for the preparation of a cobalt oxide catalyst is therefore suggested as a practical hydrogen producing process (Llorca et al., 2004; Wang et al., 2009) as well as for oxidation reaction (Kirchnerova et al., 2002; Lin et al., 2003; Lin et al., 2003). Furthermore, cobalt oxide materials can be prepared by the citrate method (Llorca et al., 2004; Kirchnerova et al., 2002) and the precipitation-oxidation method (Wang et al., 2009; Lin et al., 2003; Lin et al., 2003; Wang et al, 2004). Among cobalt oxides, we recognize that CoO and Co_3O_4 are more stable and active, whereas Co_3O_4 would be reduced to CoO and further metallic cobalt under high temperature SRE conditions.

Although La_2O_3 is not suitable for an 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_2O_3 catalyst and both showed good activity and stability (Zhang et al., 1996; Fatsikostas et al., 2001; Fatsikostas et al., 2002; Sánchez-Sánchez et al., 2007). In addition, lanthanum oxide may react with carbon dioxide to form another stable compound, lanthanum oxycarbonate ($La_2O_2CO_3$) (Fatsikostas et al., 2002). Under reforming reaction conditions, $La_2O_2CO_3$ 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 (Wang et al., 2009), the as-prepared cobalt oxide showed high

activity under low temperature, where Y_{H2} reached 5.72 and minor of CO and CH_4 were detected. These results also showed that the deactivation of reforming catalysts was caused by carbon formation and cobalt oxides phase transformation. 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_x catalyst with or without calcined treatment.

EXPERIMENTAL

Catalysts preparation

A high valence cobalt oxide support, CoO_x, was synthesized by the precipitation-oxidation method described earlier in detail (Lin et al., 2003). 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 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 oven at 110 ^{o}C for 24 h to remove moisture, and the obtained as-prepared product of lanthanum-modified cobalt oxide was labeled as 10La-Co. The as-prepared sample was further calcined for 3 h under 300, 500 and 700^{oC} (labeled as C300, C500 and C700), respectively.

Catalysts characterization

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu $K_{\alpha 1}$ radiation (λ = 1.5405 Å) at 40 kV and 30 mA. The diffraction patterns were recorded with a step size of 0.01° and 1 s per step. The crystallite sizes of the 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 the cobalt oxides was studied by temperature- programmed reduction (TPR). About 50 mg sample was heated in a flowing 10% H_2/N_2 gas (10 ml·min^{-1}) with a heating rate 7 °C·min^{-1}. Hydrogen consumption was detected by a thermal conductivity detector (TCD).

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_2O and Ar (purity 99.9995%, supplied by a mass flow controller). The composition of the reactant mixture (H_2O/EtOH/Ar = 37/3/60 vol.%) was controlled by a flow of Ar streamed through a saturator (maintained at 130 ^{o}C) containing EtOH and H_2O. The gas hourly space velocity

(GHSV) was maintained at 23,000 h^{-1} and the H$_2$O/EtOH molar ratio was 13 (H$_2$O:EtOH = 80:20 by volume). Prior to the reaction, the sample was activated by reduction with hydrogen at 200 ^{o}C for 3 h. The SRE activity was tested in increments, while increasing the temperature from 350 to 475 ^{o}C. A 5 h reaction time was maintained for each measured temperature. The analysis of the reactants 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$_{EtOH}$), the distribution of products (mol%) and the yield of hydrogen (Y$_{H2}$).

RESULTS AND DISCUSSION

Characterization of 10La-Co series catalysts

The structural distinction can be judged from the XRD and Raman spectrum. Figure 1 shows the XRD profiles of 10La-Co series catalysts, which indicate 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$_3$O$_4$ for C300 and C500 samples with particle size 7 and 14 nm, respectively. As the calcined temperature is raised to 700^{oC} [Fig. 1(d)], in addition to the Co$_3$O$_4$ phase (the particle size is 17 nm), a new component, LaCoO$_3$, 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.
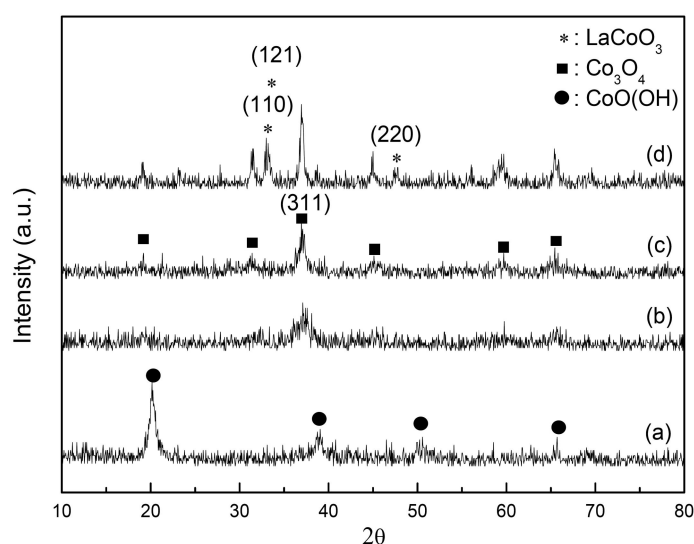

Fig. 1 XRD patterns of 10La-Co catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700.

Figure 2 shows the TPR profiles of a series of 10La-Co catalysts. The as-prepared 10La-Co sample [Fig. 2(a)] presents a continuous reduction which occurs at 228 (T$_{r1}$), 250

(T_{r2}), and 359 °C (T_{r3}), respectively. According to our previous results (Wang et al., 2009; Lin et al., 2003; Wang et al., 2004), the reduction of CoO(OH) is a three-step process: it is initially reduced to Co_3O_4, 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_3O_4 to CoO; furthermore, CoO is reduced to Co. Each step in the reduction temperature shifting to higher temperature may be due to the stronger interaction of lanthanum with cobalt-oxides. These results also show the same phenomena in the 10La-Co sample [Fig. 2(a)]. As the calcined temperature rises to 700 °C, the addition of lanthanum can enhance the interaction with CoO_x to form a new component of $LaCoO_3$. In addition to the reduction of Co_3O_4 (356 and 396 °C), in particular a new signal was observed at 546 °C [Fig. 2(d)], and confirmed with XRD analysis.
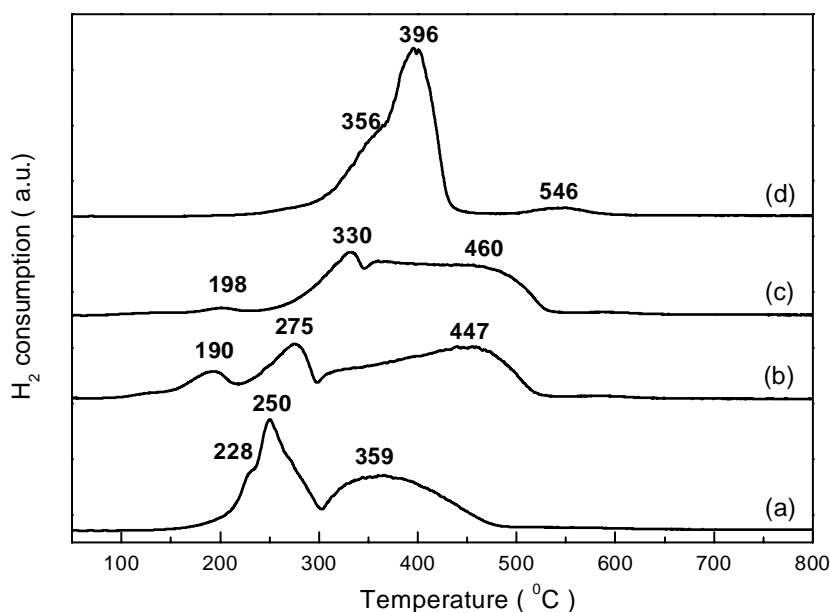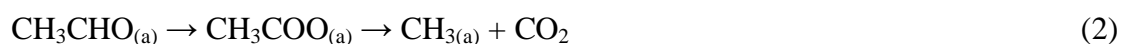

Fig. 2 TPR profiles of 10La-Co catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700.

Catalytic performance on the SRE reaction

The SRE reaction was studied between 350 and 475 °C at atmospheric pressure. The catalytic performance of La-CoO_x catalysts at different temperatures (T_R) is summarized in Figs. 3-6. 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 Figs. 3 and 4. In looking at the distribution of products (only H_2, CO_2, CH_3CHO, CH_3COCH_3, CO and CH_4) at different temperatures, some side-reactions

have been excluded in SRE over La-CoO$_x$ catalysts: ethanol dehydration to ethylene and ethanol decomposition to CO, CH$_4$ and H$_2$ (since only minor CO and CH$_4$ is detected at all temperature ranges). The conversion of ethanol increased with T$_R$ and completed at 425 ^{o}C for the 10La-Co sample and 450 ^{o}C for the C500 sample. Large amounts of CH$_3$CHO were obtained in the lower T$_R$ (< 400 ^{o}C) and were further decreased by increasing T$_R$ accompanied with H$_2$ production. The formation of acetaldehyde suggests that the dehydrogenation of ethanol occurs first at 350 ^{o}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 to the methyl group and CO$_2$:

$$CH_3CHO \rightarrow CO + CH_4 \qquad\qquad\qquad (1)$$

$$CH_3CHO_{(a)} \rightarrow CH_3COO_{(a)} \rightarrow CH_{3(a)} + CO_2 \qquad\qquad\qquad (2)$$

From the minor distribution of CO and CH$_4$ at all temperature ranges for La-CoO$_x$ catalysts, pathways of (3) and (4) are plausible (Domok et al., 2007). Also, accompanying the water gas shift (WGS) reaction with CO oxidation on cobalt oxides generates a minor CO distribution.

$$CH_{3(a)} + OH_{(a)} \rightarrow CO + 2\ H_2 \qquad\qquad\qquad (3)$$

$$2\ CH_{3(a)} + 2\ H_2O \rightarrow 2\ CO + 5\ H_2 \qquad\qquad\qquad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad\qquad\qquad (5)$$

By increasing temperature, the formation of acetone was detected and the overall reaction could be described by the following reaction (Nishiguchi et al., 2005):

$$2\ C_2H_5OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4\ H_2 \qquad\qquad\qquad (6)$$
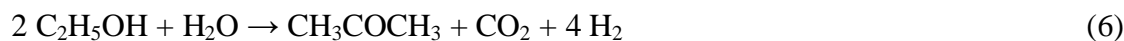
Moreover, the selectivity of H$_2$ and CO$_2$ were up to 80 and 13%, respectively, and the CH$_3$CHO was neglected at 425 ^{o}C for the 10La-Co sample. The lower CO$_2$ value came from the La$_2$O$_3$ reacting with CO$_2$ to form La$_2$O$_2$CO$_3$ species (Fatsikostas et al., 2002). Incidentally, for the C500 sample, the H$_2$ selectively raised to 74% and negligible CH$_3$CHO were obtained at 450 ^{o}C.
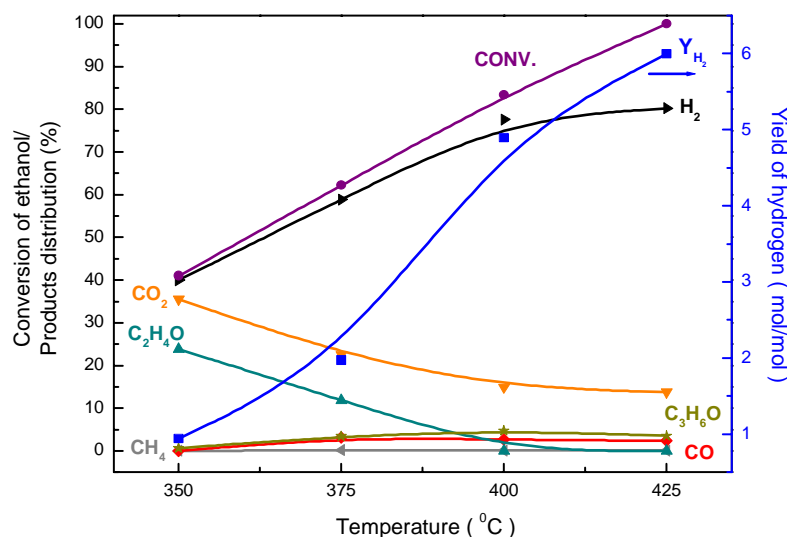
Fig. 3 Catalytic performance of 10La-Co catalyst on the SRE reaction.
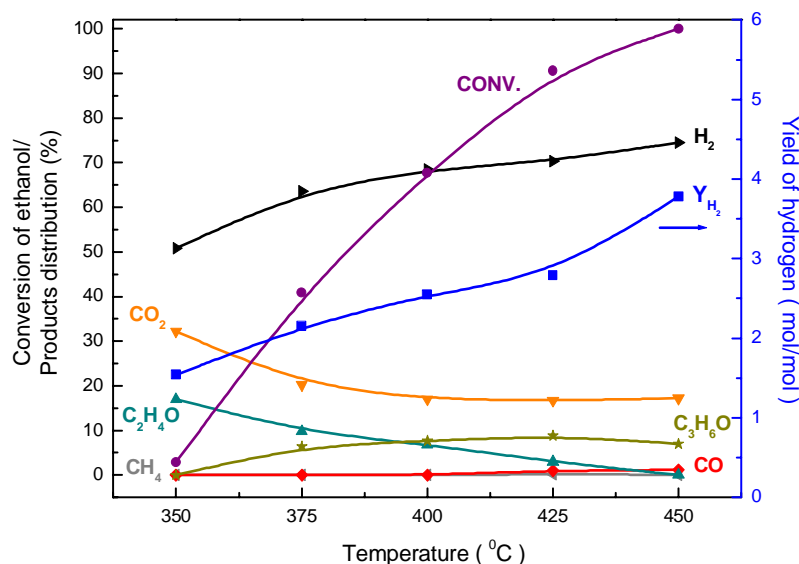

Fig. 4 Catalytic performance of C500 catalyst on the SRE reaction.

Figures 5 and 6 summarize the effects of temperature on X_{EtOH} and Y_{H2} 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_R and a higher Y_{H2}, which can be expressed as a relationship between catalytic activity and crystallite size. Under H_2O/EtOH molar ratio of 13 and 23,000 h^{-1} GHSV for the as-prepared 10La-Co catalyst, the Y_{H2} reaches 5.9 under 425 ^{o}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.
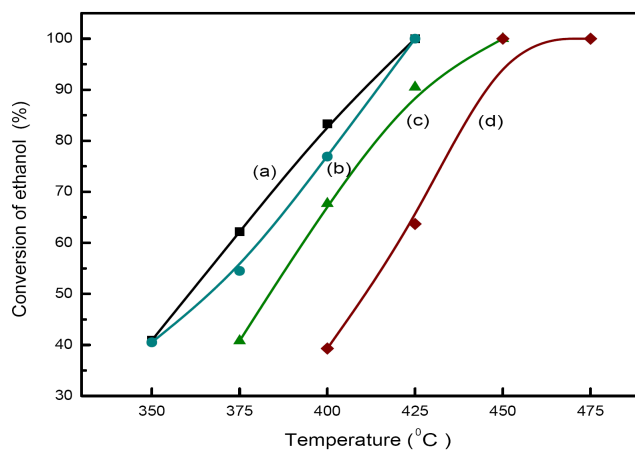
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Fig. 5 Effects of reaction temperature for the ethanol conversion toward SRE reaction over 10La-Co catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700.
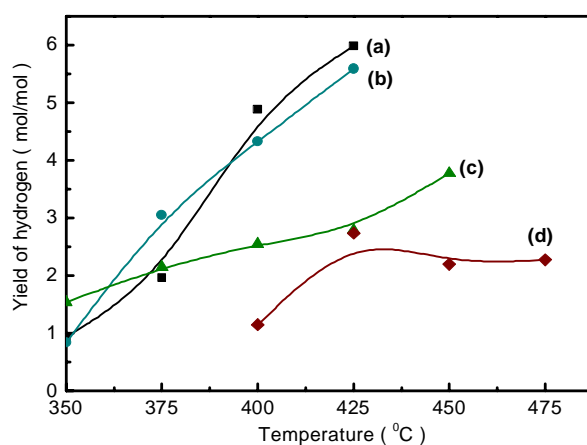

Fig. 6 Effects of reaction temperature for the yield of hydrogen toward SRE reaction over 10La-Co catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700.

Characterization of used catalysts

Figure 7 showed the TEM micrographs of fresh and used (the durability had been tested above 60 h) 10La-Co samples. These results indicate that the addition of lanthanum could inhibit the sinter of cobalt oxide, and differ from those of our previous study of cobalt oxide without the modification of lanthanum. A comparison between the fresh and used sample indicated no deposition of coke on the used 10La-Co sample after the SRE reaction.
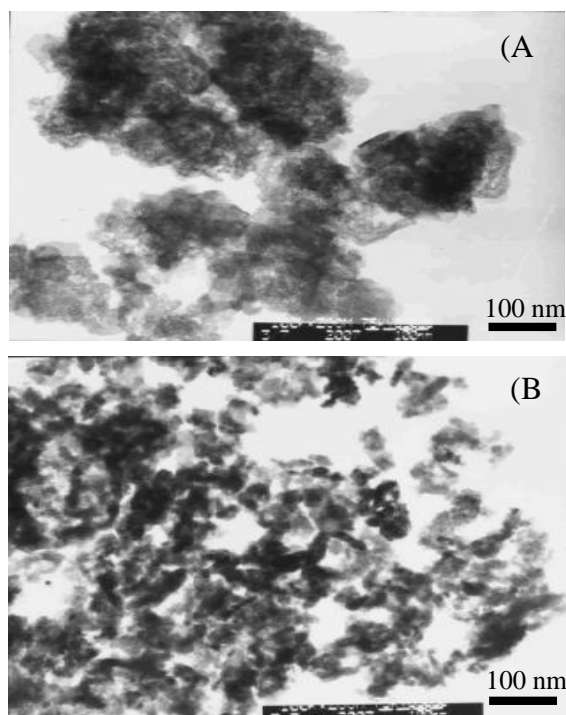
Fig. 7 TEM micrographs of 10La-Co catalyst: (A) fresh (B) spent.

The XRD patterns of used catalysts of the 10La-Co series are shown in Fig. 8, and TPR profiles are shown in Fig. 9. The Co_3O_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 La_2O_3 and $LaCoO_3$ phases. The used 10La-Co sample had two reduction temperatures at 298 and 354 ^oC related to the reduction of Co_3O_4 species and can be confirmed by the XRD pattern.
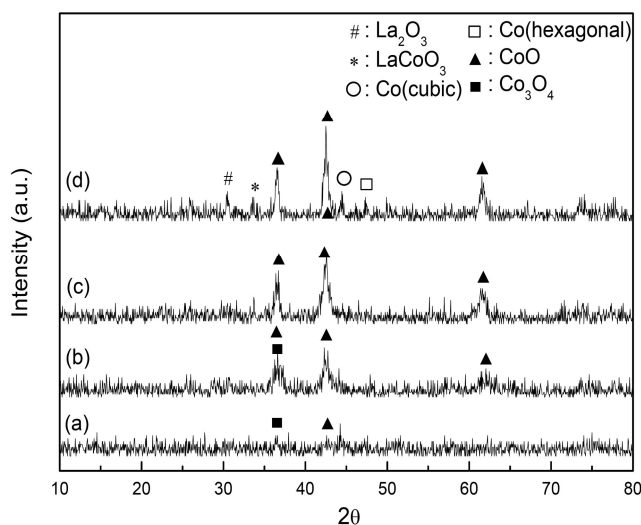

Fig. 8 XRD patterns of spent catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700
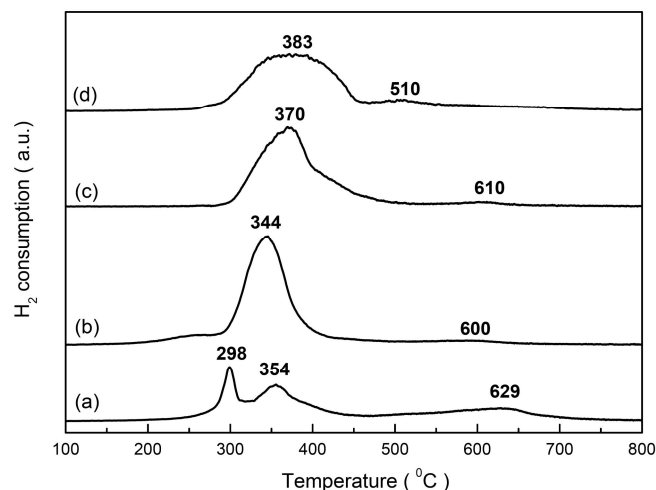
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Fig. 9 TPR profiles of spent catalysts: (a) 10La-Co (b) C300 (c) C500 (d) C700

According to the XRD and TPR characterization of used catalyst and product (CO_2 and CO) distribution from the SRE reaction, we suggest that the formation of $La_2O_2CO_3$ came from the reaction of La_2O_3 with CO_2 (Fatsikostas et al., 2002). The sensitive TPR profiles showed the new reduction signal at around 600 ^{o}C for 10La-Co, C300 and C500 samples, which were the reduction of $La_2O_2CO_3$ species.

$$La_2O_2CO_3 + H_2 \rightarrow La_2O_3 + CO + H_2O \qquad (7)$$

Furthermore, the deposited carbon on the catalyst could also be removed by the $La_2O_2CO_3$ species via reaction (Eq. 10) to prolong the lifetime of catalyst. Figure 10 displays a schematic diagram to describe the decarbonation that deposits on the peripheral of cobalt oxide. Within it, recycle reactions 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.
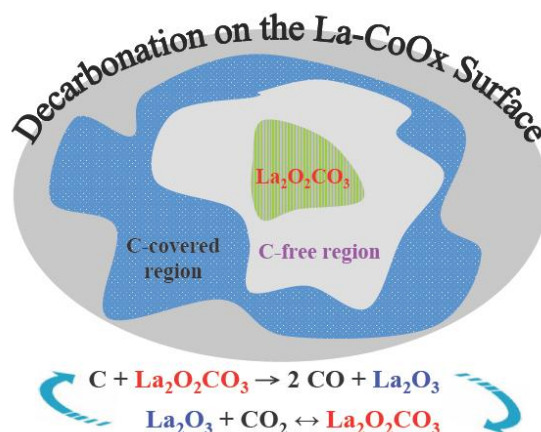
$$La_2O_2CO_3 + C \rightarrow La_2O_3 + 2\ CO \qquad (8)$$

Fig. 10 Model proposed for the decarbonation on the peripheral of 10La-Co catalyst

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CONCLUSIONS

The preferential cobalt-based catalyst has been designed with modification of lanthanum. Effect of calcination temperature on the 10La-Co sample, the C500 and C700 would form the unactivated $LaCoO_3$ species. Furthermore, the formation of special species "$La_2O_2CO_3$" on the 10La-Co and C300 were able to remove the peripheral deposited coke to prolong the lifetime of catalysts. Over 10La-Co in a SRE at 425 ^{o}C, up to 5.9 mol of H_2 per mole of ethanol, fewer byproducts and a longer catalyst lifetime of up to 60 h were obtained.

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