HYDROGEN PRODUCTION FROM ETHANOL DRY REFORMING OVER LANTHANIA-PROMOTED Co/Al_2O_3 CATALYST

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ABSTRACT: La-promoted and unpromoted 10%Co/Al_2O_3 catalysts were synthesized using wet a impregnation method and evaluated in a quartz fixed-bed reactor at different CO_2:C_2H_5OH ratios of 2.5:1-1:2.5 and a reaction temperature of 973 K under atmospheric pressure. X-ray diffraction measurements detected the presence of Co_3O_4 and $CoAl_2O_4$ phases on the surface of both promoted and unpromoted catalysts. BET surface area of promoted and unpromoted 10%Co/Al_2O_3 catalysts was about 143.09 and 136.04 $m^2.g^{-1}$, respectively. The La promoter facilitated Co_3O_4 reduction, improved the degree of reduction from 86 to 98% and increased metal dispersion from 9.11% to 16.64%. The La-promoted catalyst appeared to be a better catalyst in terms of catalytic activity and product yield regardless of reactant partial pressure. Both C_2H_5OH and CO_2 conversions improved significantly with an increase in CO_2 partial pressure from 20 to 50 kPa for both catalysts whilst a decline in catalytic performance was observed with rising C_2H_5OH partial pressure. La addition improved C_2H_5OH and CO_2 conversions up to about 74.22% and 33.80%, respectively.

ABSTRAK: Penggalak-La dan bukan penggalak-La mangkin 10%Co/Al_2O_3 dihasilkan menggunakan kaedah impregnasi basah dan dinilai dalam reaktor alas-tetap quarza pada pelbagai nisbah CO_2:C_2H_5OH sebanyak 2.5:1-1:2.5 dan suhu tindak balas sebanyak 973 K di bawah tekanan atmosfera. Hasil daripada ukuran pembelauan X-ray, didapati terdapat kehadiran fasa Co_3O_4 dan $CoAl_2O_4$ pada permukaan kedua-dua mangkin penggalak dan bukan penggalak. Permukaan kawasan BET pada penggalak dan bukan penggalak mangkin 10%Co/Al_2O_3 adalah masing-masing sebanyak 143.09 dan 136.04 $m^2.g^{-1}$. Penggalak-La membantu dalam pengurangan Co_3O_4, membaiki peratus penurunan daripada 86 kepada 98% dan menambah penyebaran logam daripada 9.11% kepada 16.64%. Mangkin penggalak-La dilihat sebagai mangkin terbaik dari segi aktiviti pemangkinan dan hasil pengeluaran, biarpun pada tekanan separa reaktan. Kedua-dua penukaran C_2H_5OH dan CO_2 meningkat dengan ketara dengan kenaikan separa tekanan CO_2 daripada 20 kepada 50 kPa bagi kedua-dua pemangkin, sementara penurunan dalam aktiviti pemangkinan dilihat dengan kenaikan tekanan separa C_2H_5OH. Penambahan La meningkatkan penukaran C_2H_5OH dan CO_2, masing-masing sebanyak 74.22% dan 33.80%.

KEYWORDS: *Co-based catalyst; ethanol dry reforming; hydrogen; syngas*

1. INTRODUCTION

Global warming issues, increasing greenhouse gas emissions, and the diminishing availability of fossil fuels have resulted in growing interest in exploring an ecofriendly and alternative energy for substituting petroleum-based energy. Hydrogen, a green energy carrier, has received significant attention from both academia and industry due to its outstanding energy capacity of 120.7 $kJ.g^{-1}$, zero emission during combustion, and employment as a main feedstock for Fischer-Tropsch synthesis (FTS) to produce synfuel [1, 2]. However, currently, industrial hydrogen production uses unsustainable fossil fuels, namely; natural gas and oil-derived naphtha leading to considerable emissions of undesirable CO_2 greenhouse gas [3]. Hence, ethanol dry reforming (EDR) has been regarded as an attractive route for H_2 synthesis since ethanol is a renewable and CO_2-neutral feedstock that can be easily derived from lignocellulosic biomass via hydrolysis-fermentation [4]. Additionally, EDR not only consumes unwanted CO_2 gas but also converts it to a value-added syngas, a mixture of H_2 and CO for the downstream FTS.

In reforming processes, γ-Al_2O_3 is normally used as support material owing to its mechanical stability, high melting temperature, and low cost [5-7]. In addition, Ni-based catalysts are conventionally employed for ethanol reforming reactions because of their low cost and high capability of cleaving C-C and C-O bonds [8-11]. However, carbon deposition via Boudouard, methane cracking, and ethylene polymerization reactions, as well as catalyst sintering, are the major issues resulting in the deactivation of Ni-based catalysts during the EDR reaction [12, 13]. In order to improve the stability of the catalyst and suppress the formation of deposited carbon, Ni-based catalysts are normally modified with promoters. La_2O_3 has been employed as a dopant for reforming catalysts due to its basic properties enhancing CO_2 adsorption [14] and outstanding oxygen storage capacity hindering carbon formation on the catalyst surface [15]. However, to the best of our knowledge, there is no previous study about promoted Co-based catalysts for EDR reaction. Thus, the objective of this study was to investigate the promotional effect of La dopant on the physicochemical properties and catalytic performance of Co/Al_2O_3 catalyst for hydrogen production from EDR reaction.

2. EXPERIMENTAL

2.1 Catalyst Preparation

Both 3%La-10%Co/Al_2O_3 and 10%Co/Al_2O_3 catalysts were synthesized using a wet impregnation method. Alumina support purchased from Sasol (Puralox SCCa-150/200) was calcined in air at 1023 K for 5 h with a heating rate of 5 K min^{-1} to ensure thermal stability. A measured amount of $La(NO_3)_3$ and $Co(NO_3)_2$ aqueous solutions (Sigma-Aldrich) were mixed and stirred with pretreated Al_2O_3 support for 3 h followed by drying overnight at 383 K and subsequent air-calcination for 5 h at 823 K with a heating rate of 5 K min^{-1}. The resulting solid catalyst was further crushed and sieved to the desired particle size of 125-160 μm before being employed for EDR evaluation.

2.2 Catalyst Characterization

The catalysts were characterized using Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction (XRD), and H_2 temperature-programmed reduction (H_2-TPR) measurements. The multipoint BET surface area was conducted in a Micromeritics ASAP-2010 apparatus using N_2 adsorption-desorption isotherms at 77 K. Before BET measurement, the sample was degassed in N_2 flow at 573 K for 1 h for moisture removal. XRD measurement for identifying crystal structure was studied in a Rigaku Miniflex II system using a Cu target as a radiation source with a wavelength of $\lambda = 1.5418$ Å at 30 kV and 15 mA. All specimens were recorded within 2θ range of 3° to 80° with low scan speed of 1° min^{-1} and step size of 0.02°. H_2-TPR experiments were carried out on a Micromeritics AutoChem II-2920 apparatus for both support and as a catalyst. Roughly 0.1 g of sample sandwiched by quartz wool in a quartz U-tube was initially pre-heated at 373 K for 30 min under 50 $ml.min^{-1}$ of He flow for removal of volatile compounds. The specimen was subsequently heated to 1173 K at 10 K min^{-1} with flowing 10% H_2/Ar mixture (50 $ml.min^{-1}$) and kept isothermally at this temperature for 30 min.

2.3 Ethanol Dry Reforming Experiment

About 0.1 g of catalyst was mounted by quartz wool in the middle of quartz fixed-bed reactor (L = 17 in. and O.D. = 3/8 in.) placed vertically in a split tubular furnace. Ethanol dry reforming reaction was conducted at different CO_2 to C_2H_5OH ratios of 1:2.5 to 2.5:1 and reaction temperature of 973 K and atmospheric pressure. High gas hourly space velocity, GHSV of 42 L $g_{cat}^{-1}.h^{-1}$ was used for all runs to ensure the negligible internal and external transport resistances. A KellyMed KL-602 syringe pump was employed for feeding ethanol to the top of the reactor whilst CO_2 reactant and N_2 diluent gas were accurately regulated by Alicat mass flow controllers. The composition of gaseous products from the bottom of the reactor was analyzed on an Agilent GC 6890 series gas chromatograph equipped with a thermal conductivity detector (TCD).

3. RESULTS AND DISCUSSION

3.1 BET Surface Area Measurements

The multipoint BET surface area, pore volume, and pore diameter of the γ-Al_2O_3 support promoted and unpromoted catalysts are shown in Table 1. Gamma-Al_2O_3 support possesses a BET surface area of 175.29 $m^2.g^{-1}$. The loading of Co active metal and La dopant on the support surface resulted in a drop in surface area, pore volume, and pore diameter from 175.29 to 136.04 $m^2.g^{-1}$, 0.46 to 0.34 $cm^3.g^{-1}$, and 10.65 to 10.41 nm, in that order. The reduction in textural properties for unpromoted and promoted catalysts was reasonably due to pore blockage indicating the successful diffusion of both Co and La metal oxides on the support surface during the impregnation and calcination processes.

3.2. X-ray Diffraction Analysis

The X-ray diffraction patterns of calcined γ-Al_2O_3 support, La-promoted and unpromoted 10%Co/Al_2O_3 catalysts, displayed in Fig. 1, are analyzed using the Joint Committee on Powder Diffraction Standards (JCPDS) database [16]. The γ-Al_2O_3 phase on catalysts and support was detected with typical peaks at 2θ = 18.92°, 32.88°, 36.84°, 45.71° and 67.17°. In addition, the characteristic diffraction peaks of Co_3O_4 phase were observed at 2θ value of 31.45° and 36.84°, 55.61° and 56.12° whilst the spinel $CoAl_2O_4$ phase was identified at about 59.51° and 65.38° for both promoted and unpromoted catalysts. Additionally, as seen in Fig. 1(c), La_2O_3 phase was not observable in XRD pattern of La-promoted catalyst was reasonably due to the high metal dispersion with small La_2O_3 crystallite size lower than the detection limit

Table 1: Textural properties of γ-Al_2O_3 support, La-promoted and unpromoted 10%Co/Al_2O_3 catalysts

Sample	BET surface area [$m^2\ g^{-1}$]	Pore volume [$cm^3\ g^{-1}$]	Pore diameter [nm]
γ-Al_2O_3	175.29	0.46	10.65
10%Co/Al_2O_3	143.09	0.36	10.63
3%La-10%Co/Al_2O_3	136.04	0.34	10.41

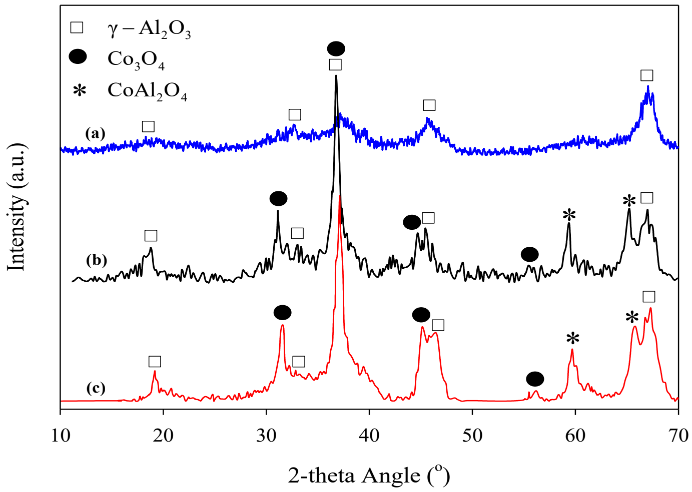

Fig. 1: XRD patterns of (a) γ-Al_2O_3 support, (b) 10%Co/Al_2O_3 and (c) 3%La-10%Co/Al_2O_3 catalysts.

As seen in Table 2, the average crystallite size of catalyst was computed using Debye-Scherrer equation (see Eq. (1)) [17].

$$d\,(nm) = \frac{0.94\lambda}{B\cos\theta} \tag{1}$$

where d is the crystallite size, B is the line broadening at half of the maximum intensity (FWHM) and λ is the X-ray wavelength while θ is the Bragg angle. Based on the relative molar volumes of Co_3O_4 and metallic Co^0 phases, cobalt metal particle size, $d(Co^0)$ may be estimated via Eq. (2) [18].

$$d(Co^0) = 0.75 \times d(Co_3O_4) \tag{2}$$

Hence, the dispersion, D (%) of metallic cobalt can be computed from the average cobalt metal particle size (see Eq. (3)) assuming spherical and uniform Co^0 particles with Co^0 density of 14.6 atoms nm^{-2} [18, 19].

$$D = \frac{96}{d(Co^0)} \tag{3}$$

As seen in Table 2, La addition significantly reduced the average Co_3O_4 crystallite size from 14.05 to 7.70 nm. Thus, active metal dispersion was improved from 9.11% to 16.64%. The La_2O_3 promoter could act as a diluent preventing the agglomeration of Co_3O_4 particles on catalyst surface and hence increasing metal dispersion.

Table 2**:** Physical properties of La-promoted and unpromoted 10% Co/Al_2O_3 catalysts

Catalyst	Co_3O_4 crystallite size, $d(Co_3O_4)$ [nm]	Co^0 crystallite size, $d(Co^0)$ [nm]	Metal dispersion, D [%]
10%Co/Al_2O_3	14.05	10.53	9.11
3%La-10%Co/Al_2O_3	7.70	5.77	16.64

3.3 H_2 Temperature-Programmed Reduction

The H_2-TPR profiles of the catalysts and Al_2O_3 support are shown in Fig. 2. There was no peak detected for the Al_2O_3 support during H_2-TPR measurement. Hence, three discrete peaks (P1, P2, and P3) were observed for 10%Co/Al_2O_3 and 3%La-10%Co/Al_2O_3 catalysts belonged to the reduction of active metal oxides. The first (P1) and second (P2) peaks were attributed to the reduction of Co_3O_4 to CoO phase and the subsequent conversion of the CoO intermediate phase to the final metallic Co^0 form, respectively [20]. The high temperature peak (P3) at about 950 K was also ascribed to the reduction of $CoAl_2O_4$ phase possessing strong metal-support interaction to metallic Co^0 phase [21]. Noticeably, the reduction temperature of peak P1 was shifted towards lower temperature of about 51 K with La-promotion indicating that the transformation of Co_3O_4 to CoO phase was more facile with La-addition.

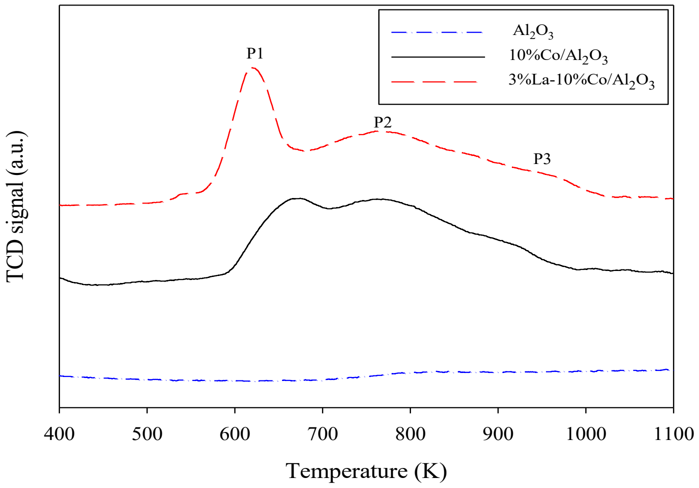

Fig. 2: Temperature-programmed reduction (H_2-TPR) profiles of Al_2O_3 support, La-promoted and unpromoted 10%Co/Al_2O_3 catalysts.

As seen in Table 3, both H_2 uptake during H_2-TPR and degree of reduction increased from 1453 μmol g_{cat}^{-1} and 85.92% to 1660 μmol g_{cat}^{-1} and 98.27%, respectively with promoter addition. This observation further confirms that H_2 reduction of Co_3O_4 was facilitated with La_2O_3 modification. The improvement in the degree of reduction with La dopant was rationally due to the increasing electron density on catalyst surface donated by

La_2O_3 promoter. The excessive electron population could alleviate the reduction of Co_3O_4 species [22, 23].

Table 3: Summary of H_2 uptake and degree of reduction for promoted and unpromoted 10%Co/Al_2O_3 catalysts

Catalyst	H_2 uptake [μmol g_{cat}^{-1}]	Degree of reduction [%]
10%Co/Al_2O_3	1453.18	85.92
3%La-10%Co/Al_2O_3	1660.94	98.27

4. ETHANOL DRY REFORMING EVALUATION

4.1 Effect of CO_2 Partial Pressure

The effect of CO_2 partial pressure, P_{CO2}, on EDR performance was evaluated at a temperature of 973 K with a constant P_{C2H5OH} of 20 kPa and varying CO_2 partial pressure from 20-50 kPa. As seen in Fig. 3, an increase in CO_2 and C_2H_5OH conversions with rising P_{CO2} from 20 to 50 kPa was observed for both catalysts reasonably due to the enhancement of CO_2 gasification of deposited carbon on catalyst surface in CO_2-rich environment. In addition, Jankhah et al. studied the thermodynamics of EDR and reported that catalytic performance was favored at high ratio of CO_2 to C_2H_5OH [24]. This observation was in agreement with other studies about EDR using Ni-based catalysts [25]. Interestingly, regardless of CO_2 partial pressure, the La-promoted catalyst exhibited higher C_2H_5OH and CO_2 conversions up to about 74.22% and 33.80%, respectively than those of unpromoted catalyst rationally due to the high oxygen storage capacity of La_2O_3 promoter oxidizing deposited carbon [3, 26] and the enhancement of metal dispersion with La-promotion (Table 2).

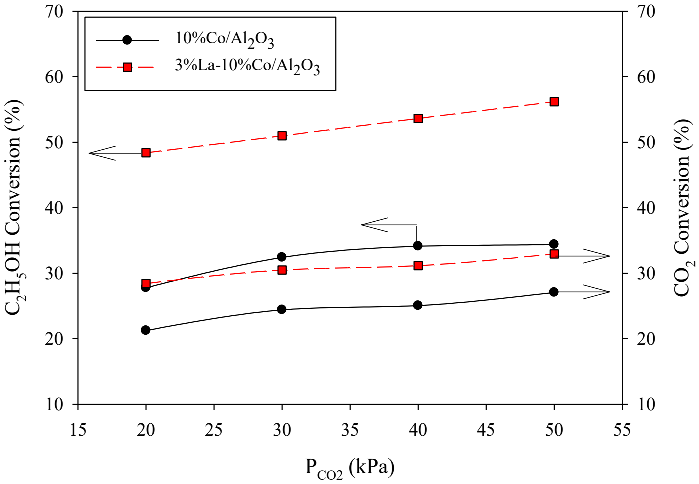

Fig. 3: Influence of CO_2 partial pressure on C_2H_5OH and CO_2 conversions at P_{C2H5OH} = 20 kPa and T = 973 K.

The effect of P_{CO2} on H_2 and CO yields at P_{C2H5OH} = 20 kPa and T = 973 K are shown in Fig. 4. H_2 and CO yields improved with growing CO_2 partial pressure from 20 to 50 kPa for both catalysts owing to the enhancement of CO_2 reforming of CH_4 intermediate product formed from ethanol decomposition [24]. Interestingly, H_2 and CO yields for La-promoted catalyst were always superior to those of unpromoted 10%Co/Al_2O_3 catalyst for all CO_2

partial pressure. The enhancement of product yield with the La addition could be due to the improved metal dispersion (see Table 2) and the basic property of the La_2O_3 promoter [14] increasing the adsorptive capacity of CO_2 reactant and hence resulting high catalytic performance.

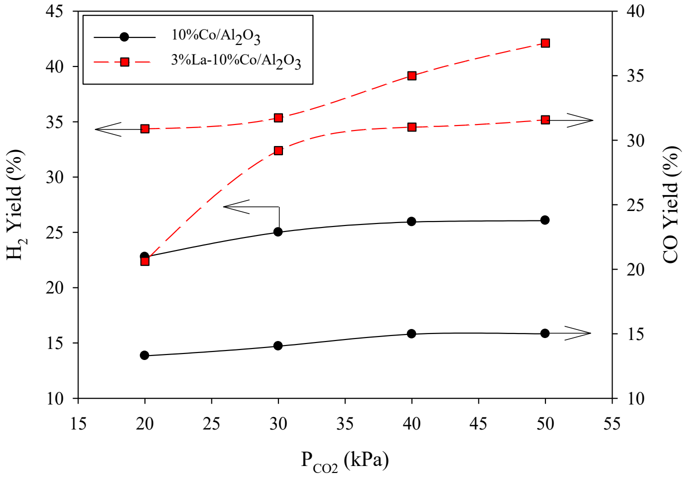

Fig. 4: Influence of P_{CO2} on H_2 and CO yields at P_{C2H5OH} = 20 kPa and T = 973 K.

4.2 Influence of C_2H_5OH Partial Pressure

The effect of ethanol partial pressure on EDR performance was also studied by varying P_{C2H5OH} from 20 to 50 kPa at P_{CO2} = 20 kPa and T = 973 K. As seen in Fig. 5 and Fig. 6, both catalysts experienced a considerable drop in reactant conversions and gaseous product yield with increasing C_2H_5OH partial pressure from 20 to 50 kPa. The reduction in catalytic performance with rising P_{C2H5OH}, exceeding the stoichiometric feed composition was rationally due to the excess presence of ethanol hindering CO_2 adsorption on catalyst surface and hence lessening the EDR reaction. However, irrespective of C_2H_5OH partial pressure, the catalytic performance of the La-doped catalyst was always greater than that of unpromoted catalyst in terms of reactant conversion and product yield (see Fig. 5 and Fig. 6).

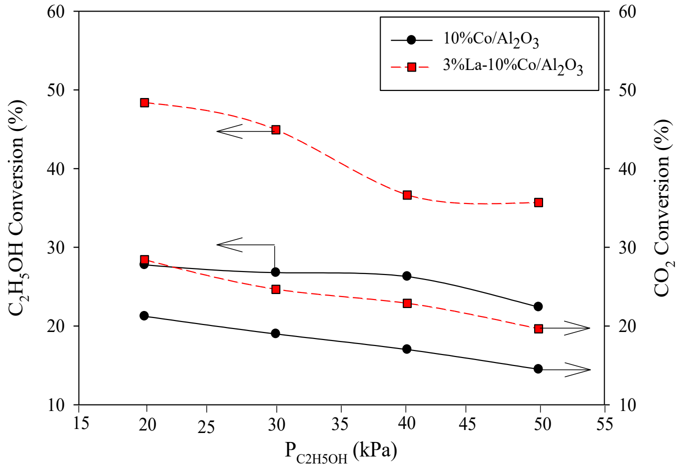

Fig. 5: Influence of P_{C2H5OH} on C_2H_5OH and CO_2 conversions at P_{CO2} = 20 kPa and T = 973 K.

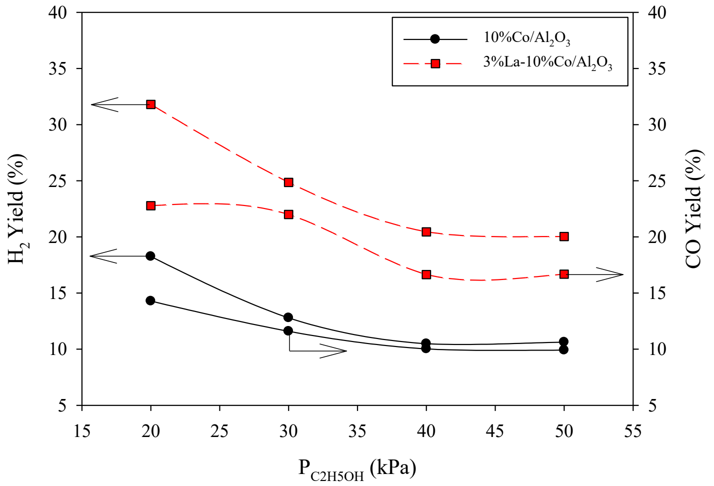

Fig. 6: Influence of P_{C2H5OH} on H_2 and CO yields at P_{CO2} = 20 kPa and T = 973 K.

5. CONCLUSIONS

EDR reaction runs over both La-promoted and unpromoted 10%Co/Al_2O_3 catalysts were evaluated in a quartz fixed-bed reactor at different CO_2:C_2H_5OH ratios of 2.5:1 to 1:2.5 with a reaction temperature of 973 K and atmospheric pressure. The Co_3O_4 and $CoAl_2O_4$ phases were formed on both promoted and unpromoted catalysts. However, the La_2O_3 phase was not detectable, indicating high metal dispersion. The La-addition improved metal dispersion from 9.11 to 16.64% and the degree of reduction from 86% to 98%. The BET surface area, pore volume, and pore diameter were reduced with the introduction of Co and La metal oxides indicating the successful penetration of these metal oxides into the porous Al_2O_3 support. Additionally, the catalyst was reduced completely at a temperature beyond 1000 K, based on H_2-TPR measurements. Regardless of CO_2 and C_2H_5OH partial pressure, the La-promoted catalyst performed superior catalytic activity and product yield to those of the unpromoted catalyst due to the oxygen storage capacity of the La_2O_3 promoter resistant to carbon deposition and the improvement of active metal dispersion as well as the basic attribute of La_2O_3 dopant. Regardless of catalysts, reactant conversions improved significantly with increasing CO_2 partial pressure. However, a considerable decline was observed for both CO_2 and C_2H_5OH conversions with rising C_2H_5OH feed composition.

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