

Research Article

Co₃O₄ Catalysts on CeO₂-ZrO₂ Supports and Co₃O₄-CeO₂ Catalysts on Al₂O₃/SiO₂ Supports for the Oxidation of Propylene

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Different compositions of Co₃O₄ catalysts on CeO₂-ZrO₂ solid solution (Ce_{0.9}Zr_{0.1}O₂ and Ce_{0.8}Zr_{0.2}O₂) have been studied for the oxidation of propylene. The optimal amount of Co₃O₄ active phase on CeO₂-ZrO₂ support of 30 wt% was found. The mixed Co₃O₄-CeO₂-ZrO₂ with the same composition of the optimal supported ones showed approximately the same activity, which was not higher than the activity of the mixed Co₃O₄-CeO₂ catalyst. Catalytic activities of mixed Co₃O₄-CeO₂ with different loading contents supported on high surface area supports (Al₂O₃, SiO₂) were then measured. The optimal composition of active phase was still 30 wt% but the minimum temperature of the highest activity increased to above 300°C due to the inert nature influence of the support.

1. Introduction

Cobalt-based oxides are one of the most active catalysts in catalytic oxidation of hydrocarbons. Co₃O₄ is only slightly weaker than the noble metal catalysts for low temperature catalytic combustion [1, 2]. Furthermore, cobalt spinel in both pure and bimetallic forms seems promising for its low cost and good activity in volatility organic compound combustion [3–5], diesel soot oxidation [6], and particularly total oxidation of light hydrocarbons [7, 8]. The high catalytic activity in oxygen involving reactions of the Co₃O₄-based catalysts is most likely related to the high bulk oxygen mobility [9] and facile formation of highly active electrophilic oxygen (O⁻ or O⁻²) species for hydrocarbon oxidation [10].

Ceria has been the most frequently used catalyst due to its beneficial properties like the ability to enhance the water-gas shift reaction, to improve catalytic activity at the interfacial metal-support sites, to thermally stabilize the alumina support, to promote noble metal dispersion, and to exhibit its own catalytic activity especially when it is used in

nanoparticles [11–15]. However ceria's most prominent effect is its ability to undergo rapid redox cycles, 2CeO₂ → Ce₂O₃ + (1/2)O₂, thus acting as an oxygen buffer by storing/releasing O₂ due to the Ce⁴⁺/Ce³⁺ redox couple. Addition of zirconium is considered the most effective way for ceria stabilization against its sintering at high temperature reactions. Ceria-zirconia solid solution also yields an improvement in ceria's oxygen storage capacity (OSC), redox properties, thermal resistance, and catalytic activity at low temperatures [16–18]. Therefore, system based on CeO₂ is widely used as support or active phase for oxidation reaction of hydrocarbon.

Although both cobalt oxide and ceria/ceria-zirconia catalysts have been widely applied for the oxidation of hydrocarbons, their mixtures are still rare investigated. A series of Co₃O₄ on mesoporous Ce_xZr_{1-x}O₂ (x = 0.75, 0.85, 0.95, 1) catalysts synthesized by surfactant-assisted coprecipitation with subsequent incipient wetness impregnation method were studied. Results showed that the appropriate Ce/(Ce + Zr) ratio in ceria-zirconia support and cobalt oxide loading is required, and the 20 wt.% Co₃O₄/meso-Ce_{0.85}Zr_{0.15}O₂

catalyst exhibits outstanding catalytic performance [19]. Another investigation by Xu et al. has shown that CeO_x - Co_3O_4 catalysts exhibit a better catalytic activity when compared with pure Co_3O_4 . The catalyst with the Ce/Co atomic ratio 1:16 exhibits the best activity [20]. Nanometric CeO_2 -supported cobalt oxide catalysts (molar ratio of 100 Co/Ce = 0.1, 1, 4, 10, 20, 50, 100) were prepared by the method of ultrasonic-assisted incipient wetness impregnation. The best catalytic activity was obtained over the catalyst containing 100 Co/Ce molar ratio of 20 [21]. Studies by Iwaneka et al. have shown that CoO_x - CeO_2 catalysts are in general more active than the undoped cobalt catalyst. It has been found that catalysts with a Co/(Co + Ce) ratio not higher than 0.64 sinter less than those with a higher cobalt content. The catalyst containing 86% cobalt exhibits the highest activity among the studied systems [22].

For the treatment of unburned hydrocarbons, which are toxic components in automobile exhaust gases, mixtures of Co_3O_4 (30 wt %) with CeO_2 and CeO_2 - ZrO_2 (Ce/Zr = 6/4) prepared by precipitation method have also been tested for the combustion of CH_4 under exceeds oxygen conditions. The results showed that the methane oxidation activity of Co_3O_4 (30 wt.%) - CeO_2 / (CeO_2 - ZrO_2) oxides is comparable with pure Co_3O_4 for fresh samples, while the composite systems exhibit higher activity and thermal stability than single Co_3O_4 after ageing at 750°C. The catalysts were able to convert 100% CH_4 at rather high temperature (500°C). The role of ceria and ceria-zirconia is assumed to maintain a good combustion activity of the cobalt composite oxides by dispersing the active phase Co_3O_4 [23].

Meanwhile, the study on the mixtures of Co_3O_4 with CeO_2 or CeO_2 - ZrO_2 for the oxidation of hydrocarbons is still limited with only one ratio of Ce/Zr (Ce/Zr = 6/4) while we found from our previous study that the optimal Ce/Zr ratios for the highest conversion of hydrocarbons are 8/2 and 9/1 [24]. Moreover, the catalytic ability of the reported mixed Co_3O_4 with CeO_2 or CeO_2 - ZrO_2 catalysts was only high at high temperatures (500°C) [24]. Therefore, it is still worth studying more logically the different mixtures of Co_3O_4 with CeO_2 or CeO_2 - ZrO_2 or Co_3O_4 catalysts supported on CeO_2 or CeO_2 - ZrO_2 under different operation oxidation conditions of hydrocarbons (rich and stoichiometric conditions). It may also be interesting to compare the use of active CeO_2 - ZrO_2 support with other popular nonactive but high surface area and cheap supports as Al_2O_3 , SiO_2 . That will be the focus of this present paper.

2. Experimental

2.1. Catalyst Synthesis. The work uses several commercial supports such as Al_2O_3 (purity 100%, Merck) and SiO_2 (purity 100%, Merck). To prepare active phase and mixtures of different components, a sol-gel method was used as described in more detail. It was previously shown that sol-gel method leads to the formation of very pure and homogeneous catalyst powders exhibiting high surface area [25].

13.5697 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (98.5%, Merck) was dissolved in 250 mL distilled water under stirring condition (solution A).

10.0703 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99.0%, Merck) was dissolved in 250 mL distilled water under stirring condition (solution B).

27.7778 g citric acid monohydrate, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (99.5%, Merck), was dissolved in 250 mL distilled water under stirring condition (solution C).

9.0937 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%, Merck) was dissolved in 250 mL distilled water under stirring condition (solution D).

To prepare mixed oxide CeO_2 - ZrO_2 supports ($\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ and $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$), solution B was dropped into a suitable volume of solution A corresponding to different CeO_2 / ZrO_2 molar percentages. If precipitation occurred, a suitable amount of concentrated HNO_3 solution was added. A suitable amount of solution C was dropped into the obtained solution in order to obtain molar ratio of citric acid to metals of 2.6.

Co_3O_4 supported on $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ or $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and CeO_2 - Co_3O_4 supported on Al_2O_3 , SiO_2 were synthesized by impregnation method by mixing solution D and solution C, or solution A, solution D, and solution C, with different ratios and suitable amount of active phases. Concentrated HNO_3 was then added to obtain solution in order to control pH of solution below 1. The obtained solutions were stabilized for 30 minutes. Then, a suitable amount of $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ (or $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, Al_2O_3 , SiO_2) support was added to solution to obtain suspensions. After stirring vigorously for 1 hour, the suspension was vaporized at 60–80°C until the slurry was dried. The obtained solid was dried at 120°C for 2 hours. Then, these samples were calcined at 550°C for 3 hours.

Co_3O_4 supported on CeO_2 - ZrO_2 was labeled as A Co/ $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ or $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, in which A is the weight percentage of the active phase.

CeO_2 - Co_3O_4 supported on Al_2O_3 (SiO_2) was identified as E CeCo P-Q/Al (Si), in which E is the weight percentage of the active phase, P-Q is the ratio of CeO_2 / Co_3O_4 , Ce is the symbol of CeO_2 , Co is the symbol of Co_3O_4 , Al is the symbol of Al_2O_3 , and Si is the symbol of SiO_2 .

2.2. Characterization. The catalysts were characterized by using X-ray, SEM, and BET techniques. The X-ray powder diffraction (XRD) patterns were recorded with a D8 Bruker Advanced diffractometer (Germany).

The specific surface areas of the samples were measured at 77 K by the BET method using N_2 adsorption on an ASAP 2010 and a Gemini VII Micromeritics apparatus.

The morphology of these catalysts was examined on a Hitachi X4800 (Japan) scanning electron microscope.

2.3. Measurement of Catalytic Activities. Catalytic activities (the propylene conversion, which was determined as the ratio of consumed propylene to the amount of propylene introduced into the reactor, and the CO_2 selectivity, which was determined as the amount of the obtained CO_2 per the total amount of all products) were measured in a micro (or differential) reactor set up with an internal diameter of 0.4 cm and length of 60 cm. 0.1 g of catalyst (particle sizes are within the range 250–300 μm , which were prepared by pressing catalyst powders in a hydraulic presser, grinding the obtained

pellets, and sieving into desired particle sizes) was used with a total gas flow of 80 mL/min at a pressure of 1 atm. The catalyst bed length is 5 mm; thus the gas hourly space velocities (GHSV), which were determined from the standard flow rate of the gas divided by the catalyst bed volume, were $76,000 \text{ h}^{-1}$ in the catalyst reactor. The volume composition of gas flow was $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2 = 2.5/2.5/95$ (%) and the reaction temperatures range from 200°C to 500°C . Under the stoichiometric condition (oxygen sufficient), the composition of the gas flow was $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2 = 2.5/11.25/86.25$ (%). The reaction temperature was measured using a thermocouple attached at the position of the catalyst bed inside an electric furnace. The temperature of the catalytic bed was directly controlled by the proportional integral derivative (PID) controller of the furnace. Analysis of propylene, oxygen, CO_2 , CO , and oxygenated products was performed using an online Focus-Thermo scientific gas chromatograph with a thermal conductivity detector (TCD). C_3H_6 and oxygenated products were detected with a column of 80/100 Chromosorb and a column of Carbowax 20 M in series while CO_2 , CO , and O_2 were detected with a column of 60/80 Carboxen and a column of 80/100 Porapak in series.

3. Results

3.1. Characterization and Catalytic Activity of Co_3O_4 Catalysts on CeO_2 - ZrO_2 Supports. From our previous experiment, it was found that mixtures of Co_3O_4 and CeO_2 exhibited high activity for the oxidation of propylene but were unstable at high temperatures. The situation may be improved if Co_3O_4 is impregnated on a stable phase containing CeO_2 . CeO_2 - ZrO_2 mixtures have been determined to be active for the oxidation of propylene as in our previous publication [24]. Amongst CeO_2 - ZrO_2 mixtures, ones with Ce/Zr ratios = 8/2 and 9/1 showed highest activity and possessed high ability of CO_2 formation. Therefore, CeO_2 - ZrO_2 mixtures with Ce/Zr ratios = 8/2 and 9/1 were chosen as supports for Co_3O_4 catalysts. The Co_3O_4 supported on CeO_2 - ZrO_2 samples was characterized and tested for the oxidation of propylene under rich condition.

BET surface area of Co_3O_4 impregnated on different CeO_2 - ZrO_2 supports ($\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ and $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$) is shown in Table I. The results shows that $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ support possesses a little higher surface area than $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ support. When Co_3O_4 was impregnated on the supports, surface area tends to decrease maybe due to lower surface area of Co_3O_4 catalyst ($11.44 \text{ m}^2/\text{g}$) and the influence of the calcination after the impregnation. However, samples with 5% of Co_3O_4 on CeO_2 - ZrO_2 supports showed increased surface area, which is not clearly understood since both SEM and XRD of these samples showed no evidence of strange phases, particle sizes, or morphology.

All samples show structures similar to those of CeO_2 and CeO_2 - ZrO_2 mixed oxides as seen from XRD patterns (Figure 1). The evidence of Co_3O_4 was only seen clearly when the content of Co_3O_4 is over 30%. For the samples with lower Co_3O_4 contents, the presence of Co_3O_4 only made the base line rougher, which indicates the more amorphous nature of Co_3O_4 (which was seen from XRD pattern of its pure sample).

TABLE I: Specific surface area (m^2/g) of Co_3O_4 catalyst on CeO_2 - ZrO_2 supports.

Support	Content of Co_3O_4 on supports (%)			
	0	5	30	50
$\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$	38.75	67.42	23.02	29.17
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	46.97	44.44	23.49	29.87

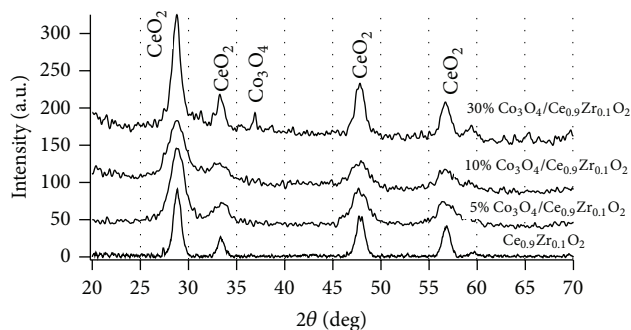


FIGURE 1: XRD patterns of $\text{Co}_3\text{O}_4/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ samples.

SEM images of Co_3O_4 catalyst on $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ support in Figure 2 show a fine dispersion of Co_3O_4 on the honeycomb-like structure of the support. The particle size of Co_3O_4 is only few nm (circle marked in Figures 4(b) and 4(c)) and became larger when Co_3O_4 content increased (sample 30% Co_3O_4). On the sample 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, there are aggregations of Co_3O_4 particles at some places (Figure 4(d)) but the support surface was not impregnated completely yet at some other places (Figure 4(c)).

The comparison of the activity of catalysts with different Co_3O_4 loading contents (5–50%) on CeO_2 - ZrO_2 supports is shown in Figures 3–4. The catalysts were tested in rich condition (oxygen deficient) since it has been found that this condition is close to the real high speed operating conditions of motorcycles, the field of application of these catalysts [24]. It was also expected that if a catalyst exhibits good activity for complete oxidation under rich condition, it might exhibit even better activity under stoichiometric or lean conditions.

It can be seen that CeO_2 - ZrO_2 supports could only reach to high propylene conversions (refer propylene conversions higher than 22.22%, the maximum conversion of propylene for the complete oxidation at the $\text{C}_3\text{H}_6/\text{O}_2$ ratio of 1) at high temperatures (above 300°C). Meanwhile, pure Co_3O_4 and Co_3O_4 catalysts on CeO_2 - ZrO_2 supports exhibited high conversion from 250°C . After reaching to those high conversions at this temperature, the propylene conversion was rather stable. The sample 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ exhibited a sudden increased conversion at 500°C but together with decreased CO_2 selectivity, which is the same as pure Co_3O_4 catalyst. However, pure Co_3O_4 even exhibited much lower CO_2 selectivity at high temperatures. Thus, the deposition of Co_3O_4 catalyst on CeO_2 - ZrO_2 supports decreased the temperature to obtain high activity of the catalysts compared with that of the support (250°C for catalysts on support instead of 350°C for the support) even at low Co_3O_4 loading

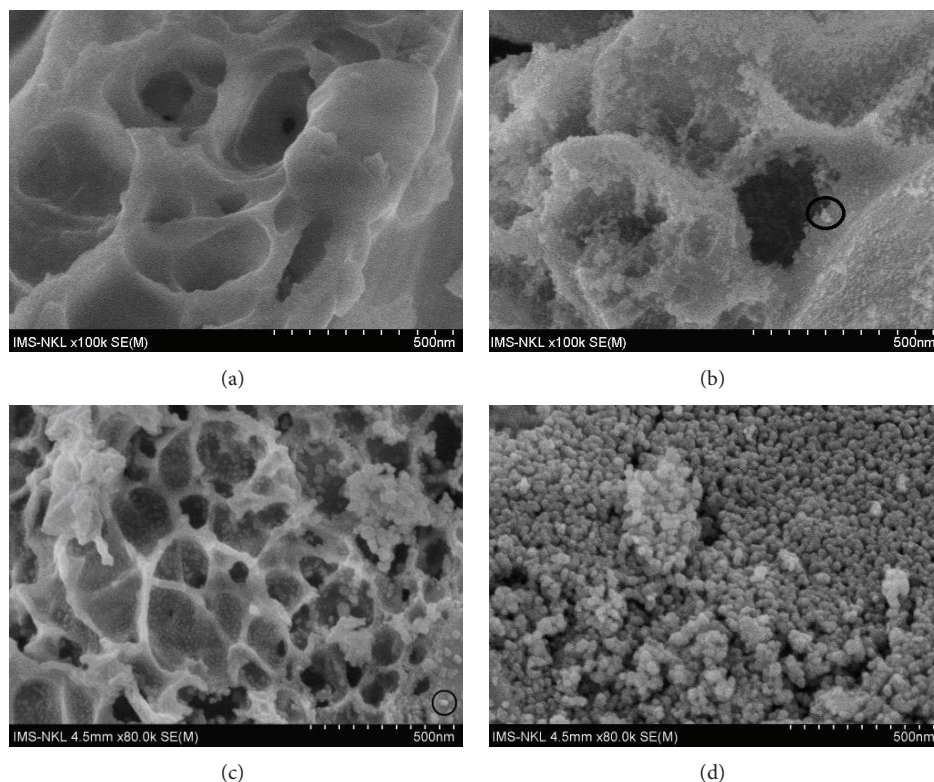


FIGURE 2: SEM images of pure $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (a), 5% $\text{Co}_3\text{O}_4/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (b), and 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (c and d).

contents (3–5%). The deposition of Co_3O_4 catalyst on CeO_2 - ZrO_2 supports also simultaneously increased CO_2 selectivity compared with that of the pure Co_3O_4 catalyst at high temperatures (400–500°C).

To investigate the role of active site and support, samples prepared by chemical mixing using sol-gel synthesis with the same compositions as 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ and 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ samples were also tested. The samples prepared by chemical mixing showed similar activities as supported sample prepared by impregnation method. These samples also possess high surface area as those of CeO_2 - ZrO_2 support. This observation shows that CeO_2 - ZrO_2 components in 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ and 30% $\text{Co}_3\text{O}_4/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ catalysts play roles as active sites too. Therefore, it is possible to simply prepare Co_3O_4 - CeO_2 - ZrO_2 mixed catalyst by sol-gel method instead of more complex impregnation method while still maintaining surface area and catalytic activity of the catalysts.

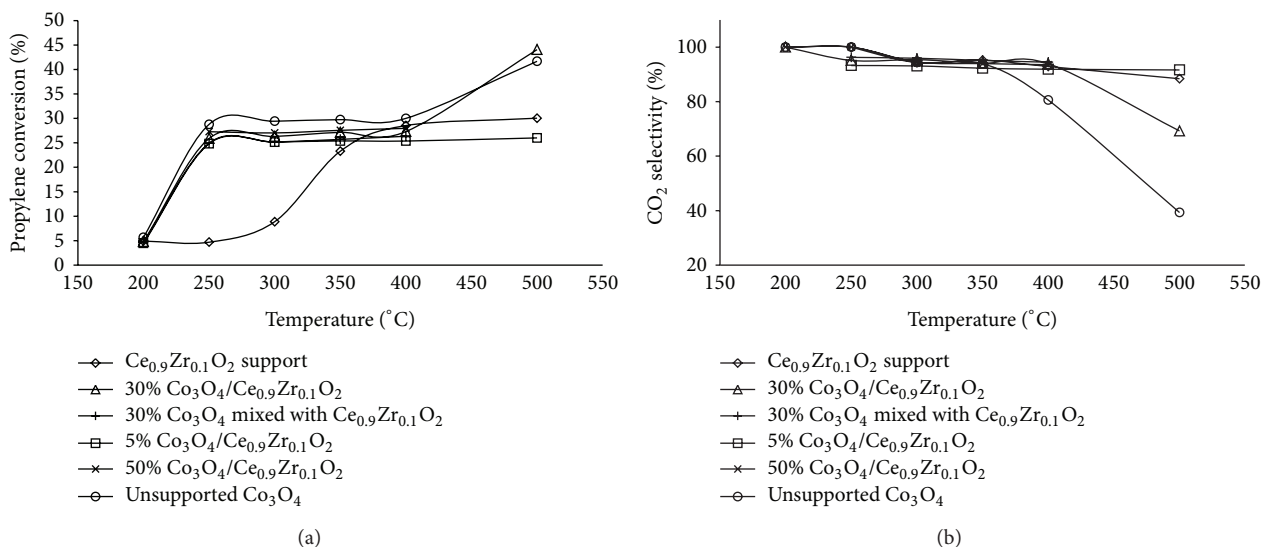
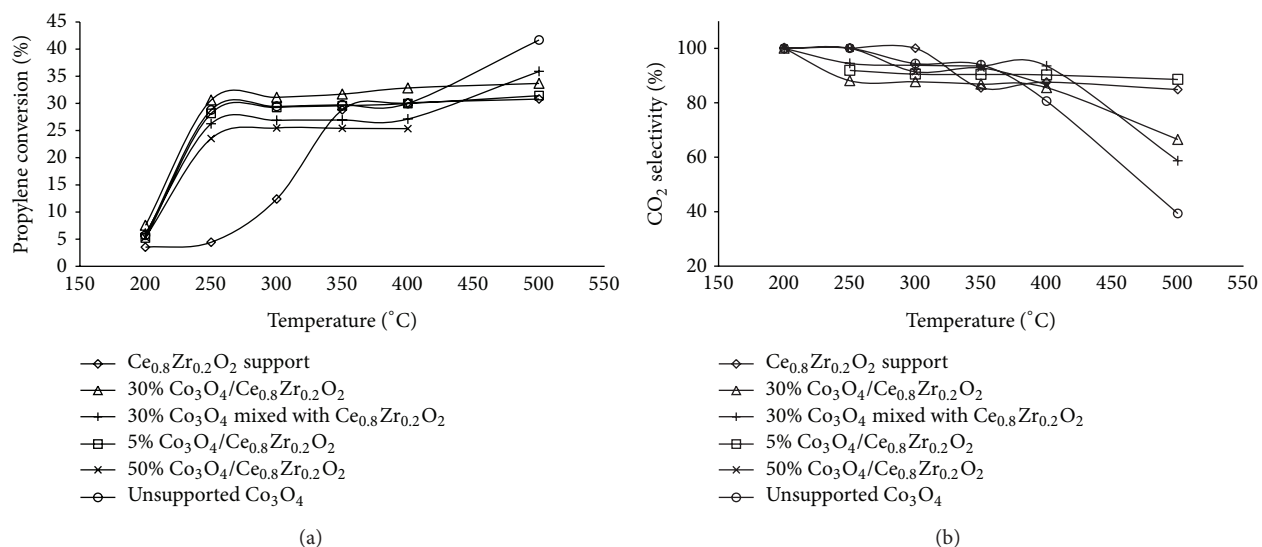
3.2. Characterization and Catalytic Activity of Co_3O_4 - CeO_2 Supported on Al_2O_3 and SiO_2 . In our previous study, it was found that the sample containing 50 and 20 mol% of CeO_2 (CeCo 50-50 and CeCo 20-80, resp.) exhibited excellent catalytic activities, which were even higher than those of Co_3O_4 catalysts on CeO_2 - ZrO_2 supports described in Section 3.1. Co_3O_4 - CeO_2 catalysts were able to convert a large amount of propylene from 200°C already [24]. The catalysts also possessed the same high surface area as those of CeO_2 - ZrO_2 supports (around 45 m^2/g). However, these

catalysts (the same as 30–50% $\text{Co}_3\text{O}_4/\text{CeO}_2$ - ZrO_2 catalysts) were unstable at high temperatures; the catalyst particles were observed broken at high temperatures (400–500°C), resulting in blocking of the reactor. Therefore, it may be helpful to impregnate Co_3O_4 - CeO_2 catalysts on other high surface area and thermal stable supports (γ - Al_2O_3 and SiO_2) to increase surface area of the catalysts as well as make them more stable at high temperatures. Thus, we decided to study Co_3O_4 - CeO_2 catalysts on support. CeO_2 - ZrO_2 would not be chosen as a support for Co_3O_4 - CeO_2 catalysts since the composition of the catalyst already contains CeO_2 ; moreover, CeO_2 - ZrO_2 supports possess much less surface areas. Although high surface area is not the most important factor in the reaction where a Mars Van Krevelen mechanism is usually invoked as in hydrocarbons oxidation [26], high surface area still helps in the adsorption of reactants.

The use of high surface area Al_2O_3 and SiO_2 supports resulted in much high surface area catalysts than in the case of using CeO_2 - ZrO_2 supports. The surface area of the CeO_2 - Co_3O_4 catalysts on Al_2O_3 and SiO_2 supports was only slightly lower than that of pure supports even if the catalyst loading contents were high (30–50 w%) (Table 2). Morphology of CeO_2 - Co_3O_4 catalysts on Al_2O_3 and SiO_2 supports is a little different. Figure 5 shows SEM images of CeO_2 - Co_3O_4 catalyst with Ce/Co molar ratio of 5/5 on Al_2O_3 and SiO_2 supports. The deposition of CeO_2 - Co_3O_4 catalysts on Al_2O_3 resulted in more amorphous morphology and less particle sizes. The images also show that the catalyst loading content of 30 w% made the surface of the supports covered almost completely

TABLE 2: Specific surface area (m^2/g) of $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalyst on Al_2O_3 and SiO_2 supports.

Support	Content of $\text{CeO}_2\text{-Co}_3\text{O}_4$ on supports (%)								
	0	5		10		30		50	
		Ce/Co = 2/8	Ce/Co = 5/5	Ce/Co = 2/8	Ce/Co = 5/5	Ce/Co = 2/8	Ce/Co = 5/5	Ce/Co = 2/8	Ce/Co = 5/5
Al_2O_3	118	115.26	116.75	117.31	120.33	115.63	106.20	109.16	104.15
SiO_2	228					222.66	245	203.13	210.55

FIGURE 3: Propylene conversions (a) and CO_2 selectivity (b) under rich condition of Co_3O_4 catalyst with different loading contents on $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ support.FIGURE 4: Propylene conversions (a) and CO_2 selectivity (b) under rich condition of Co_3O_4 catalyst with different loading contents on $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ support.

by $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalyst particles. This may be the reason for the fact that the samples with catalyst loading contents above 30 w% were the samples which exhibited highest propylene conversion (Figure 6).

Propylene conversions and CO_2 selectivity (under rich condition) of $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalyst on Al_2O_3 and SiO_2

supports were presented in Figures 6-7. The catalytic loading content was investigated in a wide range (5–50 w%) with the aim of optimizing it and finding out a catalyst with as low catalytic loading content as possible but as high activity as possible. It can be seen that the pure $\text{CeO}_2\text{-Co}_3\text{O}_4$ active phases were able to reach to the maximum activity at lower

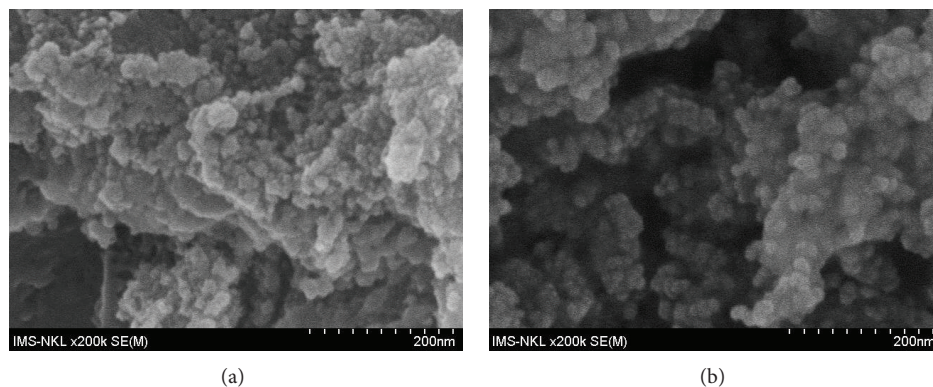


FIGURE 5: SEM images of $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalyst with Ce/Co molar ratio of 5/5 on Al_2O_3 (a) and SiO_2 supports (b).

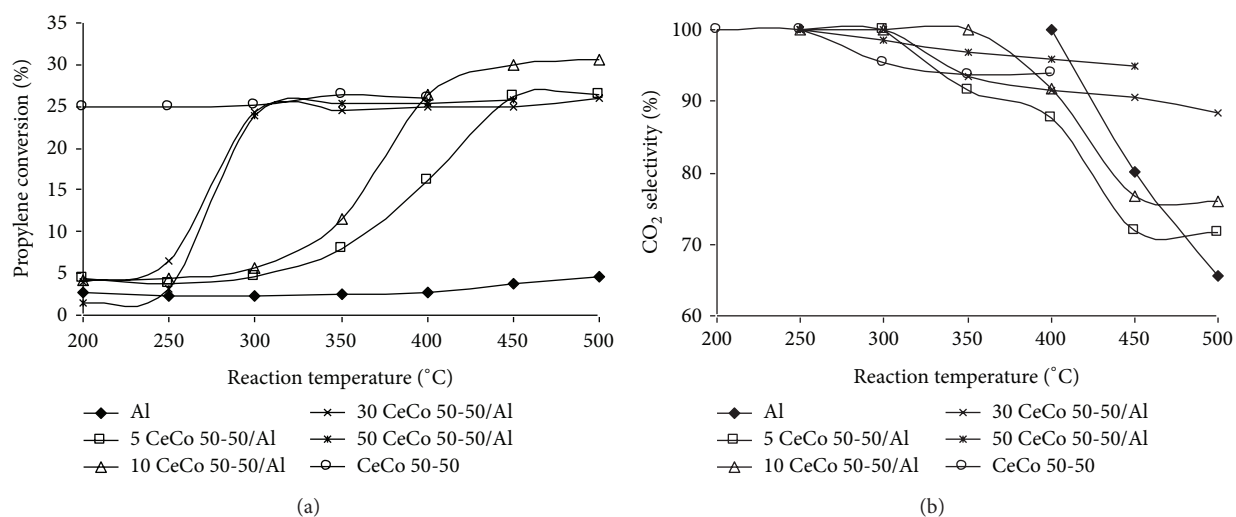


FIGURE 6: Propylene conversion (a) and CO_2 selectivity (b) of $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalyst with Ce/Co molar ratio of 5/5 on Al_2O_3 support at different reaction temperatures.

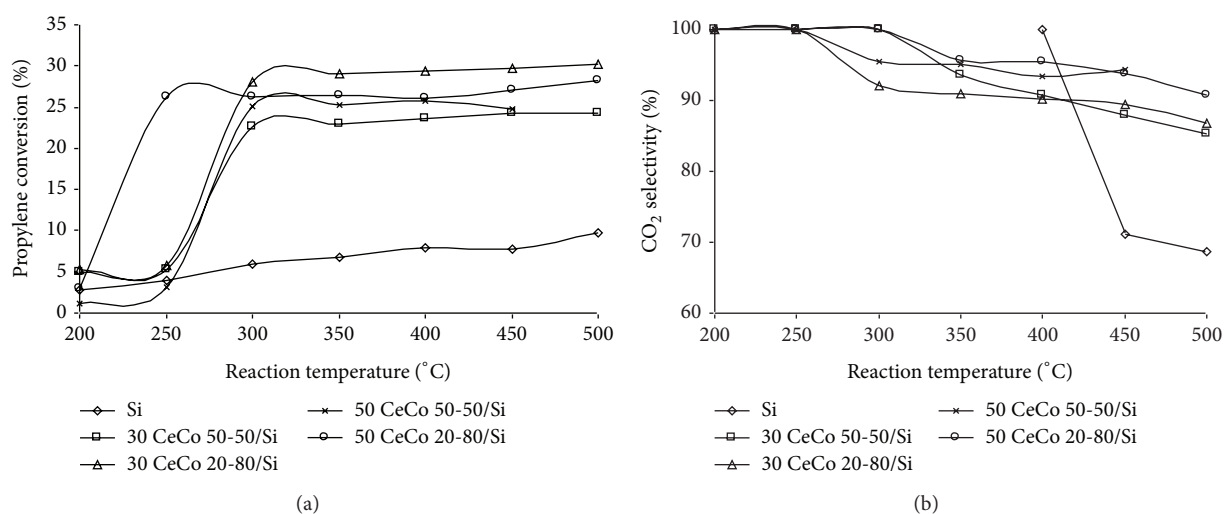


FIGURE 7: Propylene conversion (a) and CO_2 selectivity (b) of $\text{CeO}_2\text{-Co}_3\text{O}_4$ catalysts with Ce/Co molar ratios of 5/5 and 2/8 on Al_2O_3 support at different reaction temperatures.

TABLE 3: Propylene conversion (C, %) and CO₂ selectivity (S, %) of catalysts with Co₃O₄/CeO₂-Co₃O₄ catalysts on different supports at different reaction temperatures under stoichiometric condition.

Catalysts	200°C		250°C		300°C		350°C		400°C		500°C		
	C	S	C	S	C	S	C	S	C	S	C	S	
30% Co ₃ O ₄ /Ce _{0.9} Zr _{0.1} O ₂	6.1	100	99.7	100	100	100	100	100	100	100	100	100	100
30 CeCo 50-50/Si	6.1	100	12.9	100	84.8	100	98.2	100	100	100	100	100	100
30 CeCo 50-50/Al	6.1	100	8.5	100	16.7	100	68.0	100	100	100	100	100	100

temperatures than when they were deposited on the supports. The samples with high CeO₂-Co₃O₄ loading contents (30–50 w%) on Al₂O₃ support could convert a maximum amount of propylene at 300°C while the samples with lower CeO₂-Co₃O₄ loading contents (5–10 w%) could only obtain the maximum conversion at 400–450°C (Figure 6). Thus, when the catalyst was impregnated on the support, high loading contents of the active phase (above 30%) are required to lower the minimum temperature of the maximum conversion. High CeO₂-Co₃O₄ loading contents also help to maintain CO₂ selectivity at high temperature close to that of the pure active phase. The sample with low CeO₂-Co₃O₄ loading contents (5–10 w%) showed decreased CO selectivity at high temperatures, which is similar to that of the pure support. The results also show that catalytic activities of the samples with Ce/Co molar ratios of 5/5 and 2/8 are quite similar. The sample containing 50 w% CeO₂-Co₃O₄ (Ce/Co = 2/8) on SiO₂ support exhibited a little better activity than those of other samples since it could convert a maximum amount of propylene sooner (from 250°C). CO₂ selectivity on catalysts using SiO₂ support is also a little higher than those of the catalysts using Al₂O₃ support. This is probably due to the higher acidity of Al₂O₃ support, which made some exposed places of the support become sites for coke formation. The catalysts on Al₂O₃ support after the reaction are usually observed becoming black. Catalytic activity of the best CeO₂-Co₃O₄ catalyst on Al₂O₃ and SiO₂ supports was not higher than those of the best of Co₃O₄ catalyst on CeO₂-ZrO₂ supports although the activity of the unsupported CeO₂-Co₃O₄ catalyst was higher than that of the unsupported Co₃O₄ catalyst, showing that active CeO₂-ZrO₂ supports made certain meanings compared with inert Al₂O₃ and SiO₂ supports.

3.3. Activity of CeO₂-Co₃O₄ Catalysts for the Treatment of Propylene under Stoichiometric Condition. To understand details about the ability of the catalysts in different reaction conditions, CeO₂-Co₃O₄ catalysts on supports were also tested for the oxidation of propylene under stoichiometric condition (enough oxygen), in which the ratio of O₂ to propylene was maintained at 4.5 according to the stoichiometric ratio of the complete oxidation reaction. The best Co₃O₄ catalyst on Ce_{0.9}Zr_{0.1}O₂ support (30% Co₃O₄/Ce_{0.9}Zr_{0.1}O₂) was also tested under stoichiometric condition for comparison. The results show that all catalysts were able to convert 100% propylene into CO₂ (Table 3). However, only 30% Co₃O₄/Ce_{0.9}Zr_{0.1}O₂ catalyst was able to convert almost 100% propylene from low temperature (250°C); the catalysts on

Al₂O₃ and SiO₂ supports were only able to convert propylene completely at high temperatures (from 400°C). Although Al₂O₃ and SiO₂ supports possess much higher surface area than that of Ce_{0.9}Zr_{0.1}O₂ support, they are almost inert for the oxidation of propylene while Ce_{0.9}Zr_{0.1}O₂ support, itself, is a good catalyst for the oxidation of propylene as seen in Section 3.1; therefore, the catalyst on Ce_{0.9}Zr_{0.1}O₂ support exhibited an excellent activity. Between Al₂O₃ and SiO₂ supports, catalyst on Al₂O₃ showed worse activity than that of SiO₂, which may be due to higher acidity of Al₂O₃, making exposed Al₂O₃ particles become sites for coke formation even under stoichiometric condition.

Different from the rich condition, under stoichiometric condition, the only product is CO₂ at all temperatures. Thus, the catalysts catalyze well the complete oxidation of propylene but under rich condition, CO and oxygenated products were still formed since there was not enough oxygen for the reaction of propylene.

When the complete oxidation was performed under lean condition (excess oxygen), the catalytic activities of these catalysts were even better, resulting in the decrease of the minimum temperature to convert 100% propylene of all catalysts.

4. Conclusions

Two series of catalysts with suitable loading contents (above 30 w%) investigated in this work, Co₃O₄ on CeO₂-ZrO₂ supports and CeO₂-Co₃O₄ catalysts on Al₂O₃ and SiO₂ supports, exhibited good activities for the treatment of propylene under all rich, stoichiometric, and lean conditions. Under stoichiometric condition, 30% Co₃O₄/Ce_{0.9}Zr_{0.1}O₂ catalyst was able to oxidize 100% propylene to pure CO₂ from 250°C; 30% CeO₂-Co₃O₄ catalysts on Al₂O₃ and SiO₂ supports were able to do the same at higher temperatures (400°C). Thus, Ce_{0.9}Zr_{0.1}O₂ was proved to be the more active support than inert Al₂O₃ and SiO₂ supports for the catalysts for the complete oxidation of propylene since Ce_{0.9}Zr_{0.1}O₂, itself, was also a good active phase for the reaction. However, catalysts on Ce_{0.9}Zr_{0.1}O₂ exhibited much lower surface areas and much less thermal stability. Further work will be performed to explore more details on the characteristics of the catalysts and the supports.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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