Research Article

Co$_3$O$_4$ Catalysts on CeO$_2$-ZrO$_2$ Supports and Co$_3$O$_4$-CeO$_2$ Catalysts on Al$_2$O$_3$/SiO$_2$ Supports for the Oxidation of Propylene

Tien The Nguyen,$^1$ Phuong Thi Mai Pham,$^1$ Thang Minh Le,$^2$ and Isabel Van Driessche$^3$

$^1$Laboratory of Environmental Friendly Materials and Technology, Advanced Institute of Science and Technology, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi 10000, Vietnam
$^2$Department of Organic and Petrochemical, School of Chemical Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi 10000, Vietnam
$^3$Department of Inorganic and Physical Chemistry, SCriPTS, Ghent University, Krijgslaan 281-S3, 9000 Gent, Belgium

Correspondence should be addressed to Thang Minh Le; thang.leminh@hust.edu.vn

Received 10 November 2014; Revised 27 February 2015; Accepted 1 March 2015

Academic Editor: Albert Demonceau

Copyright © 2015 Tien The Nguyen et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Different compositions of Co$_3$O$_4$ catalysts on CeO$_2$-ZrO$_2$ solid solution (Ce$_{0.9}$Zr$_{0.1}$O$_2$ and Ce$_{0.8}$Zr$_{0.2}$O$_2$) have been studied for the oxidation of propylene. The optional amount of Co$_3$O$_4$ active phase on CeO$_2$-ZrO$_2$ support of 30wt% was found. The mixed Co$_3$O$_4$-CeO$_2$-ZrO$_2$ with the same composition of the optimal supported ones showed approximately the same activity, which was not higher than the activity of the mixed Co$_3$O$_4$-CeO$_2$ catalyst. Catalytic activities of mixed Co$_3$O$_4$-CeO$_2$ with different loading contents supported on high surface area supports (Al$_2$O$_3$, SiO$_2$) 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. Co$_3$O$_4$ 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 Co$_3$O$_4$-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, 2CeO$_2$ → Ce$_2$O$_3$ + (1/2)O$_2$, thus acting as an oxygen buffer by storing/releasing O$_2$ due to the Ce$^{4+}/$Ce$^{3+}$ 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 CeO$_2$ 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 Co$_3$O$_4$ on mesoporous Ce$_x$Zr$_{1-x}$O$_2$ (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.% Co$_3$O$_4$/meso-Ce$_{0.85}$Zr$_{0.15}$O$_2$
catalyst exhibits outstanding catalytic performance [19]. Another investigation by Xu et al. has shown that CeO$_2$-Co$_2$O$_4$ catalysts exhibit a better catalytic activity when compared with pure Co$_3$O$_4$. The catalyst with the Ce/Co atomic ratio 1:6 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 CeO$_2$-CeO$_4$ 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$_3$O$_4$ (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 excess oxygen conditions. The results showed that the methane oxidation activity of Co$_3$O$_4$ (30 wt.%) - CeO$_2$/(CeO$_2$ - ZrO$_2$) oxides is comparable with pure Co$_3$O$_4$ for fresh samples, while the composite systems exhibit higher activity and thermal stability than single Co$_3$O$_4$ 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$_3$O$_4$ [23].

Meanwhile, the study on the mixtures of Co$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ with CeO$_2$ or CeO$_2$ - ZrO$_2$ or Co$_3$O$_4$ 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$_2$O$_3$, 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$_2$O$_3$ (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 Ce(NO$_3$)$_3$·6H$_2$O (98.5%, Merck) was dissolved in 250 mL distilled water under stirring condition (solution A).

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

27.7778 g citric acid monohydrate, C$_6$H$_{12}$O$_7$·H$_2$O (99.5%, Merck), was dissolved in 250 mL distilled water under stirring condition (solution C).

9.0937 g Co(NO$_3$)$_2$·6H$_2$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 (Ce$_{0.9}$Zr$_{0.1}$O$_2$ and Ce$_{0.8}$Zr$_{0.2}$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$_3$O$_4$ supported on Ce$_{0.9}$Zr$_{0.1}$O$_2$ or Ce$_{0.8}$Zr$_{0.2}$O$_2$ and Ce$_2$O$_2$-Co$_3$O$_4$ supported on Al$_2$O$_3$, 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 Ce$_{0.9}$Zr$_{0.1}$O$_2$ (or Ce$_{0.8}$Zr$_{0.2}$O$_2$, Al$_2$O$_3$, 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$_3$O$_4$ supported on Ce$_{0.9}$Zr$_{0.1}$O$_2$ was labeled as A Co/Ce$_{0.9}$Zr$_{0.1}$O$_2$ or Ce$_{0.8}$Zr$_{0.2}$O$_2$, in which A is the weight percentage of the active phase.

CeO$_2$ - Co$_3$O$_4$ supported on Al$_2$O$_3$ (SiO$_2$) was identified as E CeCo P-O-Al (Si), in which E is the weight percentage of the active phase, P-O is the ratio of CeO$_2$/Co$_3$O$_4$, Ce is the symbol of CeO$_2$, Co is the symbol of Co$_3$O$_4$, Al is the symbol of Al$_2$O$_3$, 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 h⁻¹ in the catalyst reactor. The volume compression of gas flow was C₆H₅/O₂/N₂ = 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 C₆H₅/O₂/N₂ = 2.5/1.25/86.25 (%). 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, CO₂, CO, and oxygenated products was performed using an online Focus-Thermo scientific gas chromatograph with a thermal conductivity detector (TCD). C₆H₅ and oxygenated products were detected with a column of 80/100 Chromosorb and a column of Carbowax 20 M in series while CO₂, CO, and O₂ 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 Co₃O₄ Catalysts on CeO₂-ZrO₂ Supports

From our previous experiment, it was found that mixtures of Co₃O₄ and CeO₂ exhibited high activity for the oxidation of propylene but were unstable at high temperatures. The situation may be improved if Co₃O₄ is impregnated on a stable phase containing CeO₂. CeO₂-ZrO₂ mixtures have been determined to be active for the oxidation of propylene as in our previous publication [24]. Amongst CeO₂-ZrO₂ mixtures, ones with Ce/Zr ratios = 8/2 and 9/1 showed highest activity and possessed high ability of CO₂ formation. Therefore, CeO₂-ZrO₂ mixtures with Ce/Zr ratios = 8/2 and 9/1 were chosen as supports for Co₃O₄ catalysts. The Co₃O₄ supported on CeO₂-ZrO₂ samples was characterized and tested for the oxidation of propylene under rich condition.

BET surface area of Co₃O₄ impregnated on different CeO₂-ZrO₂ supports (Ce₀₀.₉Zr₀₀.₁O₂ and Ce₀₀.₈Zr₀₀.₂O₂) is shown in Table I. The results show that Ce₀₀.₅Zr₀₀.₅O₂ support possesses a little higher surface area than Ce₀₀.₉Zr₀₀.₁O₂ support. When Co₃O₄ was impregnated on the supports, surface area tends to decrease mainly due to lower surface area of Co₃O₄ catalyst (11.44 m²/g) and the influence of the calcination after the impregnation. However, samples with 5% of Co₃O₄ on CeO₂-ZrO₂ 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 CeO₂ and CeO₂-ZrO₂ mixed oxides as seen from XRD patterns (Figure I). The evidence of Co₃O₄ was only seen clearly when the content of Co₃O₄ is over 30%. For the samples with lower Co₃O₄ contents, the presence of Co₃O₄ only made the base line rougher, which indicates the more amorphous nature of Co₃O₄ (which was seen from XRD pattern of its pure sample).

<table>
<thead>
<tr>
<th>Support</th>
<th>Content of Co₃O₄ on supports (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀₀.₉Zr₀₀.₁O₂</td>
<td>38.75 67.42 23.02 29.17</td>
</tr>
<tr>
<td>Ce₀₀.₈Zr₀₀.₂O₂</td>
<td>46.97 44.44 23.49 29.87</td>
</tr>
</tbody>
</table>

**Table I: Specific surface area (m²/g) of Co₃O₄ catalyst on CeO₂-ZrO₂ supports.**

**Figure I: XRD patterns of Co₃O₄/Ce₀₀.₉Zr₀₀.₁O₂ samples.**

SEM images of Co₃O₄ catalyst on Ce₀₀.₈Zr₀₀.₂O₂ support in Figure 2 show a fine dispersion of Co₃O₄ on the honeycomb-like structure of the support. The particle size of Co₃O₄ is only few nm (circle marked in Figures 4(b) and 4(c)) and became larger when Co₃O₄ content increased (sample 30% Co₃O₄). On the sample 30% Co₃O₄/Ce₀₀.₈Zr₀₀.₂O₂, there are aggregations of Co₃O₄ 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 Co₃O₄ loading contents (5–50%) on CeO₂-ZrO₂ 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 CeO₂-ZrO₂ 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 C₆H₅/O₂ ratio of 1) at high temperatures (above 300°C). Meanwhile, pure Co₃O₄ and Co₃O₄ catalysts on CeO₂-ZrO₂ 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% Co₃O₄/Ce₀₀.₈Zr₀₀.₁O₂ exhibited a sudden increased conversion at 500°C but together with decreased CO₂ selectivity, which is the same as pure Co₃O₄ catalyst. However, pure Co₃O₄ even exhibited much lower CO₂ selectivity at high temperatures. Thus, the deposition of Co₃O₄ catalyst on CeO₂-ZrO₂ 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 Co₃O₄ loading conditions.
contents (3–5%). The deposition of CoO catalyst on CeO2-ZrO2 supports also simultaneously increased CO selectivity compared with that of the pure CoO 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% CoO/Ce0.9Zr0.1O2 and 30% Co3O4/Ce0.9Zr0.1O2 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 CeO2-ZrO2 support. This observation shows that CeO2-ZrO2 components in 30% Co3O4/Ce0.9Zr0.1O2 and 30% Co3O4/Ce0.9Zr0.1O2 catalysts play roles as active sites too. Therefore, it is possible to simply prepare CoO4-CeO2-ZrO2 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 Co3O4-CeO2 Supported on Al2O3 and SiO2. In our previous study, it was found that the sample containing 50 and 20 mol% of CeO2 (CeCo 50-50 and CeCo 20-80, resp.) exhibited excellent catalytic activities, which were even higher than those of CoO4 catalysts on CeO2-ZrO2 supports described in Section 3.1. CoO4-CeO2 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 CeO2-ZrO2 supports (around 45 m2/g). However, these catalysts (the same as 30–50% Co3O4/CeO2-ZrO2 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 Co3O4-CeO2 catalysts on other high surface area and thermal stable supports (γ-Al2O3 and SiO2) to increase surface area of the catalysts as well as make them more stable at high temperatures. Thus, we decided to study Co3O4-CeO2 catalysts on support. CeO2-ZrO2 would not be chosen as a support for Co3O4-CeO2 catalysts since the composition of the catalyst already contains CeO2; moreover, CeO2-ZrO2 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 Al2O3 and SiO2 supports resulted in much high surface area catalysts than in the case of using CeO2-ZrO2 supports. The surface area of the CeO2-Co3O4 catalysts on Al2O3 and SiO2 supports was only slightly lower than that of pure supports even if the catalyst loading contents were high (30–50 wt%) (Table 2). Morphology of CeO2-Co3O4 catalysts on Al2O3 and SiO2 supports is a little different. Figure 5 shows SEM images of CeO2-Co3O4 catalyst with Ce/Co molar ratio of 5/5 on Al2O3 and SiO2 supports. The deposition of CeO2-Co3O4 catalysts on Al2O3 resulted in more amorphous morphology and less particle sizes. The images also show that the catalyst loading content of 30 wt% made the surface of the supports covered almost completely
Table 2: Specific surface area (m$^2$/g) of CeO$_2$-Co$_3$O$_4$ catalyst on Al$_2$O$_3$ and SiO$_2$ supports.

<table>
<thead>
<tr>
<th>Support</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>30</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce/Co = 2/8</td>
<td>Ce/Co = 5/5</td>
<td>Ce/Co = 2/8</td>
<td>Ce/Co = 5/5</td>
<td>Ce/Co = 2/8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>118</td>
<td>115.26</td>
<td>116.75</td>
<td>117.31</td>
<td>120.33</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>228</td>
<td>222.66</td>
<td>245</td>
<td>203.13</td>
<td>210.55</td>
</tr>
</tbody>
</table>

Figure 3: Propylene conversions (a) and CO$_2$ selectivity (b) under rich condition of Co$_3$O$_4$ catalyst with different loading contents on Ce$_{0.9}$Zr$_{0.1}$O$_2$ support.

Figure 4: Propylene conversions (a) and CO$_2$ selectivity (b) under rich condition of Co$_3$O$_4$ catalyst with different loading contents on Ce$_{0.8}$Zr$_{0.2}$O$_2$ support.

by CeO$_2$-Co$_3$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 CeO$_2$-Co$_3$O$_4$ catalyst on Al$_2$O$_3$ 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 CeO$_2$-Co$_3$O$_4$ active phases were able to reach to the maximum activity at lower
Figure 5: SEM images of CeO$_2$-Co$_3$O$_4$ catalyst with Ce/Co molar ratio of 5/5 on Al$_2$O$_3$ (a) and SiO$_2$ supports (b).

Figure 6: Propylene conversion (a) and CO$_2$ selectivity (b) of CeO$_2$-Co$_3$O$_4$ catalyst with Ce/Co molar ratio of 5/5 on Al$_2$O$_3$ support at different reaction temperatures.

Figure 7: Propylene conversion (a) and CO$_2$ selectivity (b) of CeO$_2$-Co$_3$O$_4$ catalysts with Ce/Co molar ratios of 5/5 and 2/8 on Al$_2$O$_3$ support at different reaction temperatures.
Table 3: Propylene conversion (C, %) and CO₂ selectivity (S, %) of catalysts with Co₃O₄/Co₃O₄ catalysts on different supports at different reaction temperatures under stoichiometric condition.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>200°C</th>
<th>250°C</th>
<th>300°C</th>
<th>350°C</th>
<th>400°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>S</td>
<td>C</td>
<td>S</td>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>30% Co₃O₄/Co₃O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 CeCo 50-50/Si</td>
<td>6.1</td>
<td>100</td>
<td>12.9</td>
<td>100</td>
<td>84.8</td>
<td>100</td>
</tr>
<tr>
<td>30 CeCo 50-50/Al</td>
<td>6.1</td>
<td>100</td>
<td>8.5</td>
<td>100</td>
<td>16.7</td>
<td>100</td>
</tr>
</tbody>
</table>

temperatures than when they were deposited on the supports. The samples with high CeO₂-CoO₃ loading contents (30–50 w%) on Al₂O₃ support could convert a maximum amount of propylene at 300°C while the samples with lower CeO₂-CoO₃ 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-CoO₃ loading contents also help to maintain CO₂ selectivity at high temperature close to that of the pure active phase. The sample with low CeO₂-CoO₃ 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-CoO₃ (Ce/Co = 2/8) on SiO₂ support exhibited a 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-CoO₃ catalyst on Al₂O₃ and SiO₂ supports was not higher than those of the best of CoO₃ catalyst on CeO₂-ZrO₂ supports although the activity of the unsupported CeO₂-CoO₃ catalyst was higher than that of the unsupported CoO₃ catalyst, showing that active CeO₂-ZrO₂ supports made certain meanings compared with inert Al₂O₃ and SiO₂ supports.

3.3. Activity of CeO₂-CoO₃ Catalysts for the Treatment of Propylene under Stoichiometric Condition. To understand details about the ability of the catalysts in different reaction conditions, CeO₂-CoO₃ 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 CeO₂-Co₃O₄ catalyst on CeO₂-ZrO₂, support (30% Co₃O₄/Co₃O₄ZrO₂) 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/Co₃O₄ZrO₂ 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 CeO₂-ZrO₂ support, they are almost inert for the oxidation of propylene while CeO₂-ZrO₂ support, itself, is a good catalyst for the oxidation of propylene as seen in Section 3.1; therefore, the catalyst on CeO₂-ZrO₂ 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/Co₃O₄ZrO₂ 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, CeO₂-ZrO₂ was proved to be the more active support than inert Al₂O₃ and SiO₂ supports for the catalysts for the complete oxidation of propylene since CeO₂-ZrO₂, itself, was also a good active phase for the reaction. However, catalysts on CeO₂-ZrO₂ 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.
Acknowledgment

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under Grant no. 104.03-2011.I6.

References


Submit your manuscripts at
http://www.hindawi.com