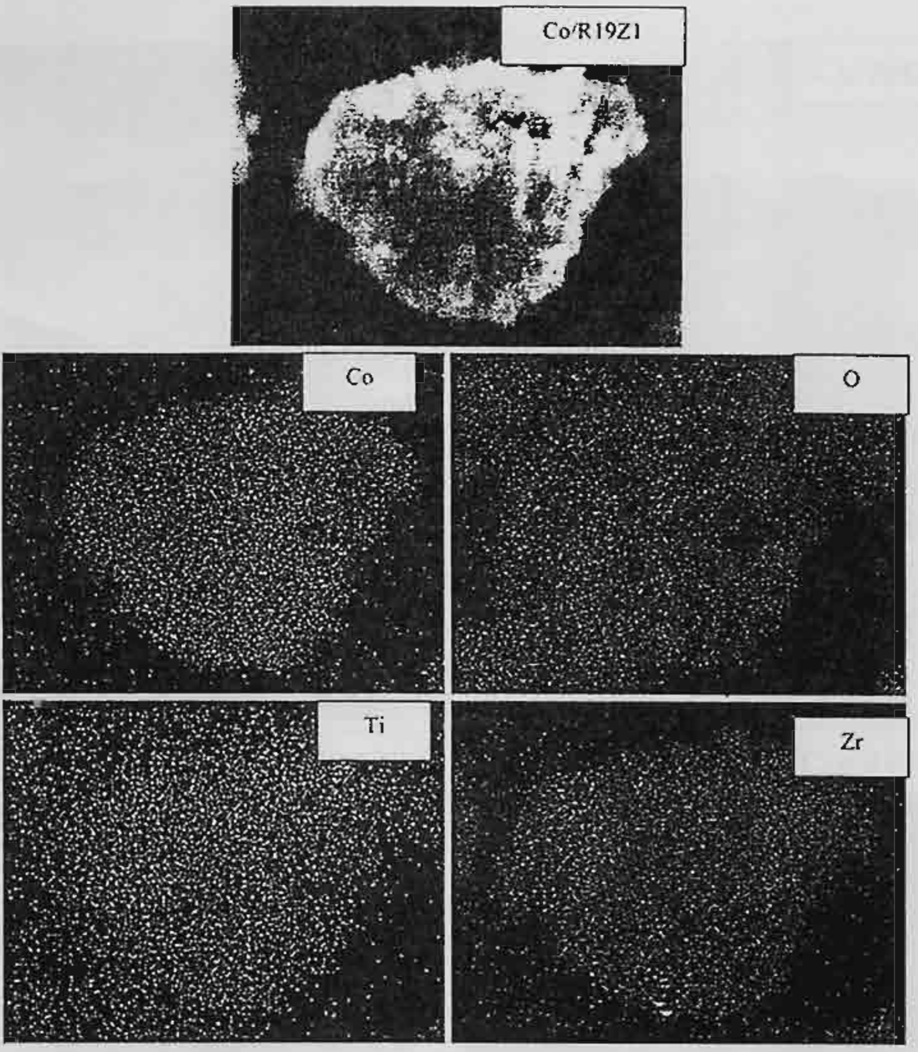

Figure 3. A typical SEM micrograph and EDX mapping for Co/R19Z1 sample.

presence of rutile phase could facilitate the reduction of Co oxide species as also reported in our previous work [14]. In order to determine the number of reduced Co metal surface atoms, which is related to the overall activity of samples during CO hydrogenation, H_2 chemisorption was performed. The results of H_2 chemisorption are shown in table 2. As seen, the amounts of H_2 chemisorption for samples with the modified R0 supports decreased consistently compared to that for samples with the unmodified ones. It should be mentioned that SMSI effect [22] is the characteristics of titania supports. However, due to the low reduction temperature (350 °C), the SMSI should not be present. Based on the results, it indicated that the catalysts (on the R0 ones) exhibited such a low H_2 chemisorption. Considering samples with the modified R19 supports, it appeared that effect of zirconia modification was observed based on the amounts of zirconia loading. On the other hand, with the low (0.5 wt% of Zr) and moderate (1 wt% of Zr) zirconia loading, the amounts of H_2 chemisorption were found to increase dramatically. However, no effect on the H_2 chemisorption was found with high (5 wt% of Zr) zirconia loading. It should be noted that the number of active sites for cobalt on the modified R19 supports increased with zirconia modification upon the low and moderate zirconia loading. The reaction study was further discussed in the next part.

3.2. *Reactivity*

In order to determine the catalytic behaviors of the catalyst samples dispersing on various modified titania supports, CO hydrogenation ($H_2/CO = 10/1$) was performed to determine the overall activity and product selectivity of the samples. Hydrogenation of CO was carried out at 220 °C and 1 atm. A flow rate of $H_2/CO/He = 20/2/8$ cc/min in a fixed-bed flow reactor was used. In fact, a relatively high H_2/CO ratio was used to minimize deactivation due to carbon deposition during reaction. The resulted reaction study is also shown in table 3. As expected, based on the H_2 chemisorption

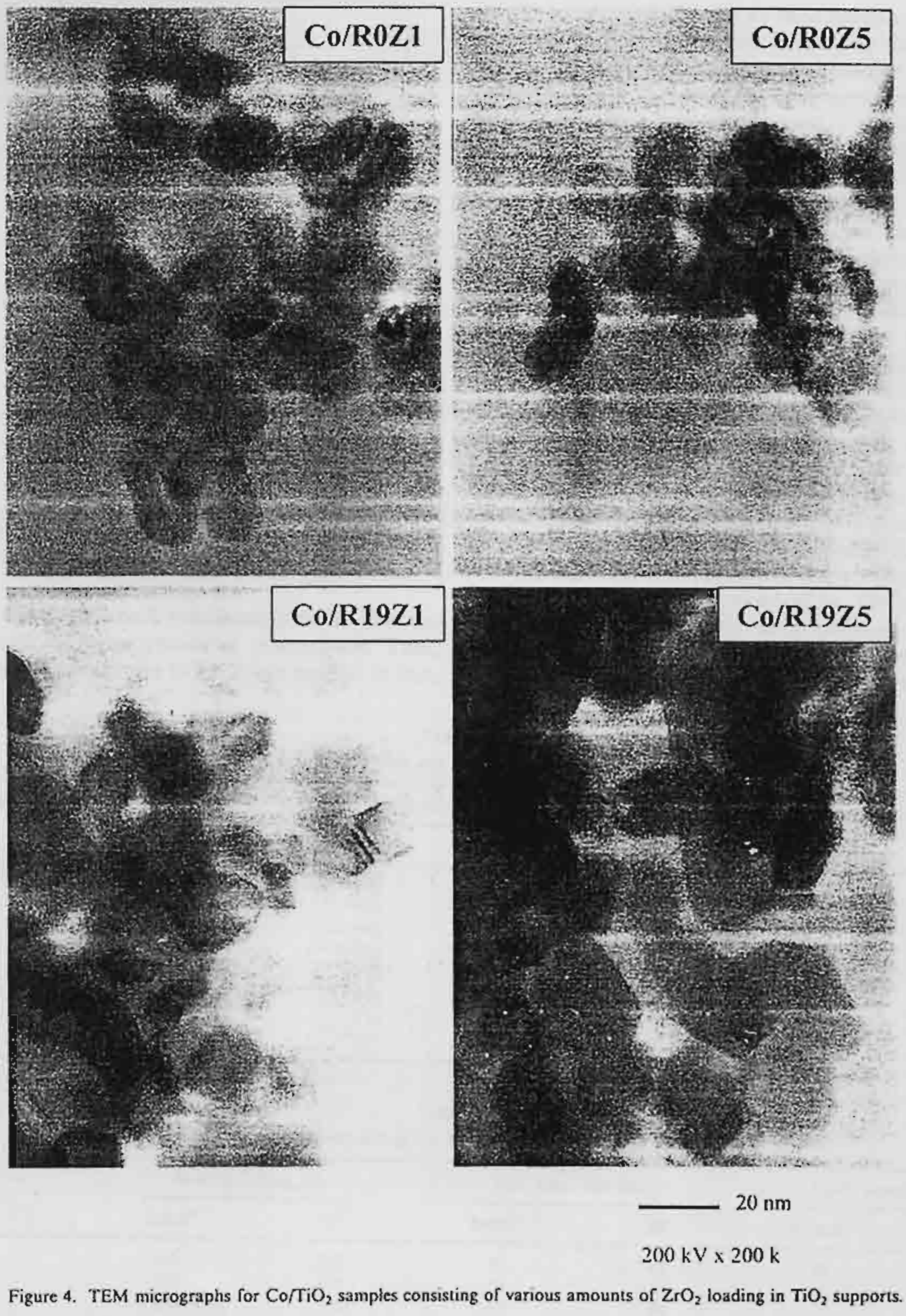

Figure 4. TEM micrographs for Co/TiO$_2$ samples consisting of various amounts of ZrO$_2$ loading in TiO$_2$ supports.

results, the steady-state rate of samples with low and moderate zirconia loading on R19 supports was the highest among any other samples with the R19 supports. For high zirconia loading, the modification would result in a decreased rate for the R19 support. There was no change in product selectivity upon the modification of the R19 supports. In contrary, the rate was found to decrease with zirconia modification for the R0 support with all amounts of zirconia loading used in this study. This was basically due to the less number of reduced cobalt metal surface atoms as seen from the results of H$_2$ chemisorption. Based on TPR results (figure 5), it was

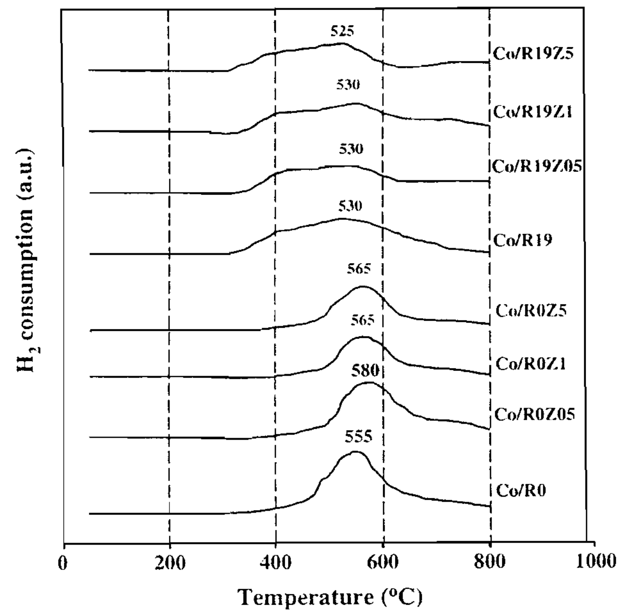

Figure 5. TPR profiles for Co/TiO$_2$ samples consisting of various amounts of ZrO$_2$ loading in TiO$_2$ supports.

suggested that the zirconia modification of the R0 supports resulted in higher reduction temperature. Thus, this inhibited the reduction of Co oxide species. In fact, for Co on alumina [5], the Zr modification resulted in increased activity about two times. For Co on silica [19,20], the activity also increased about two times with Zr modification. However, for both cases, the change in product selectivity was not observed. Compared to our results based on Co on titania (R19), the activity increased by 1.4 times with the Zr modification (low and moderate Zr loading) without changing the selectivity. However, with some consideration on the product selectivity obtained, an interesting discovery can be observed in this present study for the Co on R0 supports. Considering the selectivity of product for the sample with R0 support containing the low loading of zirconia, it showed that the selectivity to methane (C_1) essentially decreased. On the other hand, more amounts of longer chain hydrocarbons (C_2–C_4) can be obtained with the catalyst sample containing the low loading of zirconia on the R0 support. It is known that CO hydrogenation is a kind of polymerization reactions where insertion of the $-CH_2^-$ (methylene group) occurs through the active center. Thus, the product distribution strongly depends on the nature of active centers, rate of propagation, and rate of termination. Obviously, the termination of chain growth occurs and is recognized as the chain growth probability. Based on product selectivity found here, it was suggested that of R0 with a low

Table 2
Reduction temperatures and H$_2$ chemisorption of samples

Catalyst samples	Reduction temperature (°C)			H$_2$ chemisorption (μmol H$_2$/g$_{cat.}$)
	Initial	Final	Maximum	
Co/R0	370	695	550	0.93
Co/R0Z0.5	400	735	580	trace
Co/R0Z1	440	760	565	trace
Co/R0Z5	440	780	565	trace
Co/R19	320	735	530	2.44
Co/R19Z0.5	315	760	530	9.05
Co/R19Z1	315	750	530	8.54
Co/R19Z5	310	625	525	2.37

Table 3
Activity and selectivity during CO hydrogenation for various samples

Catalyst samples	Rate[a] (gCH$_2$/g$_{cat.}$h)		CH$_4$ selectivity (%)		C_2–C_4 selectivity (%)	
	Initial[b]	SS[c]	Initial[b]	SS[c]	Initial[b]	SS[c]
Co/R0	1.4	0.8	71	68	29	32
Co/R0Z0.5	1.2	0.2	32	31	68	69
Co/R0Z1	0.02	0.02	97	96	3	4
Co/R0Z5	0.01	0.01	98	90	2	10
Co/R19	3.3	2.6	98	98	2	2
Co/R19Z0.5	3.7	3.7	98	98	2	2
Co/R19Z1	3.7	3.7	97	96	3	4
Co/R19Z5	2.9	2.7	97	97	3	3

[a] CO hydrogenation was carried out at 220 °C, 1 atm, and H$_2$/CO/He = 20/2/8.
[b] After 5 min of reaction.
[c] After 5 h of reaction.

Table 4

Summarized results on the effect of zirconia modification on titania supports consisting of different phases for cobalt catalysts toward CO hydrogenation ($H_2/CO = 10$)

Samples	Activity (with zirconia modification)			Selectivity to C_2-C_4 (with zirconia modification)		
	Low Zr loading	Moderate Zr loading	High Zr loading	Low Zr loading	Moderate Zr loading	High Zr loading
Co/R0	■	■	■	▨	■	■
Co/R19	▨	▨	☐	☐	☐	☐

No effect. Positive effect. Negative effect.

☐ No effect

▨ Positive effect

■ Negative effect

loading of zirconia for cobalt catalyst apparently enhanced the chain growth probability (C_2–C_4). As a matter of fact, it resulted in the observation of longer chain hydrocarbons even at the specified methanation condition where the high ratio of H_2/CO (10/1) was applied. However, at moderate and high zirconia loading of R0 supports, the selectivity to methane was majority. In order to give a better understanding the effect of zirconia modification of R0 and R19 supports on the activity and selectivity during CO hydrogenation, results are summarized in table 4.

4. Conclusions

In summary, we revealed the effect of zirconia modification in titania supports consisting of different phases on activity and selectivity of cobalt catalysts during CO hydrogenation. It was found that the modification on the R0 (pure anatase phase) supports resulted in decreased activities. However, the chain growth probability (C_2–C_4) was apparently enhanced by the low zirconia loading for the R0 support. In contrary, the increased activities were found for the catalysts consisting of R19 (mixed anatase/rutile phase) with the low and moderate zirconia loading. In addition, the product selectivity of catalysts with modified R19 supports was unchanged upon zirconia modification.

Acknowledgments

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EFFECT OF Si ADDITION ON THE PROPERTIES OF NANOCRYSTALLINE ZrO_2-SUPPORTED COBALT CATALYSTS

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Received August 17, 2005
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Abstract

This study shows that Si addition during the glycothermal synthesis of nanocrystalline zirconia modified the properties of the zirconia, *i.e.* particle morphology and crystallite size, resulting in an improvement in the catalytic performance of Co/ZrO_2 catalysts in CO hydrogenation.

Keywords: Nanocrystalline zirconia, Co/ZrO_2, Fischer-Tropsch synthesis

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INTRODUCTION

Zirconia is an important material in the areas of ceramics and catalysis. Its catalytic properties are especially promising because zirconia has both acidic and basic properties as well as high thermal stability. For a number of reactions, *i.e.*, Fischer-Tropsch synthesis [1-3], zirconia is used as a catalyst support because high activity and selectivity can be obtained. Enache *et al.* reported that compared to conventional alumina supported Co catalysts, the ones supported on zirconia showed better reducibility and capable of hydrogen adsorption via spillover mechanism. As a catalyst support, high surface area is usually preferred in order to provide a high dispersion of metal. It has been reported that Si-modified zirconia can improve the stability of tetragonal phase zirconia upon thermal treatment and enhance their surface areas. In this study, nanocrystalline zirconia was prepared by the glycothermal technique developed by Inoue *et al.* [4-5] with various amounts of Si addition. By thermal decomposition of zirconium alkoxide in organic solvents, large surface area

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zirconia can be obtained directly without bothersome procedures such as purification of the reactants or handling in an inert atmosphere. Effect of Si addition in small quantities on the properties and catalytic activities of zirconia supported Co catalysts in Fischer-Tropsch synthesis were investigated.

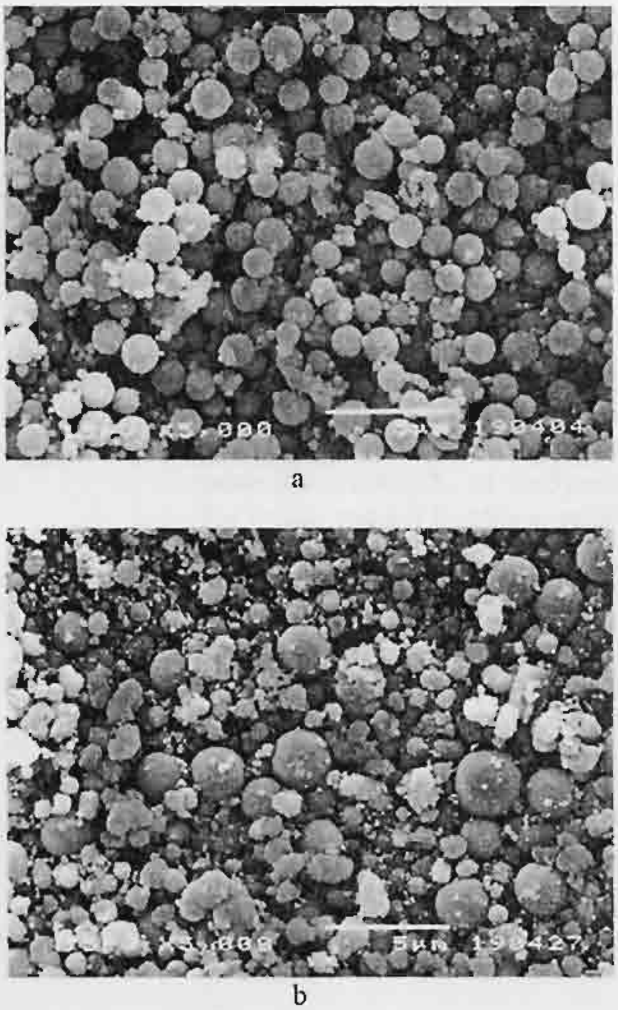
EXPERIMENTAL

Nanocrystalline zirconia was prepared by the glycothermal method according to the procedure described in ref. [6]. Approximately 15 g of zirconium tetra *n*-propoxide (Strem Chemicals) and a desired amount of tetraethyl orthosilicate was added to 100 mL of 1,4-butanediol. This mixture was placed in a 300 mL autoclave and purged with nitrogen. The mixture was heated to 300°C at a heating rate of 2.5°C/min and held for 2 h. After cooling to room temperature, the resulting powders were collected after repeated washing with methanol. The products were then air-dried. The zirconia supported cobalt catalysts were prepared by incipient wetness impregnation method using aqueous solution of cobalt (II) nitrate hexahydrate (Aldrich). The catalysts were dried overnight at 110°C and calcined in air at 300°C for 2 h. The final cobalt loading was determined using atomic absorption spectroscopy (Varian Spectra A800) to be *ca.* 8 wt.%.

The particle morphology was obtained using a JEOL JSM-35CF scanning electron microscope (SEM) operated at 20 kV. The XRD spectra of the sample powders were measured using a SIEMENS D5000 X-ray diffractometer using Cu K_α radiation with a Ni filter in the 20-80°2θ regions. The TPR profiles of supported cobalt catalysts were obtained by temperature programmed reduction using an in-house system and a temperature ramp of 5°C/min from 30 to 800°C in a flow of 5% H_2 in argon. CO hydrogenation was carried out at 220°C and 1 atm total pressure in a fixed-bed stainless steel reactor. A flow rate of H_2/CO/Ar = 20/2/8 cm^3/min was used. Typically, 0.2 g of the catalyst samples was reduced *in situ* in flowing H_2 (50 cm^3/min) at 350°C for 3 h prior to reaction. The product samples were taken at 1-h intervals and analyzed by gas chromatography.

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron micrographs of Co catalysts supported on ZrO_2 and Si-modified ZrO_2. The catalyst particles appeared as spherical particles which are typical for zirconia prepared by the glycothermal method using 1,4-butanediol as the synthesis medium. However, the Co/ZrO_2 catalyst prepared without Si addition had a narrow particle size distribution with average



a

b

Fig. 1. Typical SEM micrographs of the catalyst granules of (a) Co/ZrO_2-0Si and (b) Co/ZrO_2-0.02Si

particle sizes of their primary and secondary particles of 0.4 and 1.2 micron, respectively. The particle size distribution of Co/ZrO_2 catalyst containing silica, on the other hand, was wide suggesting that Si addition altered crystallization of the zirconia. The crystallization mechanism of zirconia during glycothermal synthesis in various glycols can be found in Ref. [7]. It should be noted that the morphologies of the zirconia samples before and after impregnation with 8 wt.% Co were not significantly different due probably to high dispersion of cobalt on the zirconia particles.

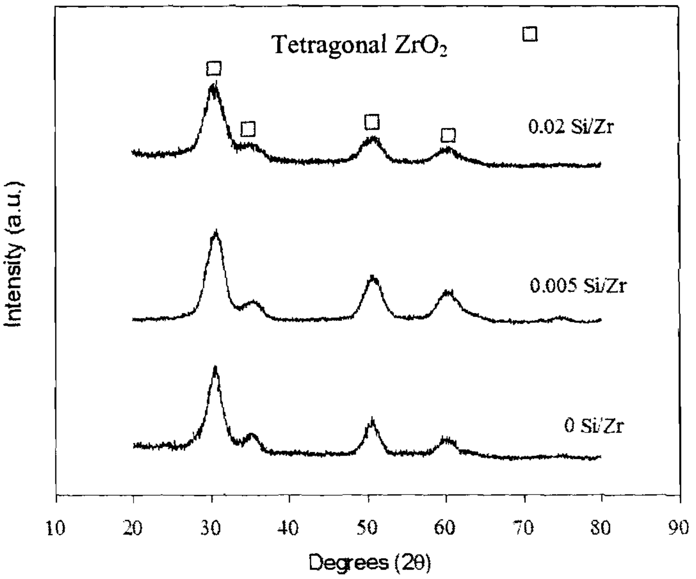


Fig. 2. XRD patterns of Co/ZrO_2 catalysts with various Si/Zr ratios

The XRD patterns of Co/ZrO_2 catalysts with various Si/Zr ratios are shown in Fig. 2. All the samples exhibited tetragonal crystalline zirconia phase. No other crystal structures were observed. The XRD diffraction peaks for cobalt oxide (Co_3O_4, Co_2O_3, or CoO) were not apparent for all the catalyst samples. The results suggest that the crystallite sizes of cobalt oxide on the glycothermal-derived zirconia were probably smaller than the lower limit of XRD detectability (3-5 nm). It is also possible that on glycothermal-derived zirconia, cobalt did not form Co_3O_4 crystallites but may have formed an amorphous cobalt oxide [8]. The average crystallite sizes of tetragonal zirconia were calculated from the X-ray line broadening using Scherrer's equation [9]. It was found that addition of small percentages of Si (0.005 and 0.02 Si/Zr) resulted in a decrease in the crystallite sizes of the tetragonal zirconia from 3.6 nm to 3.1 and 2.8 nm, respectively. It has been reported that the presence of Si-O-Zr bonds in the zirconia powders retarded the crystal growth of zirconia [10]. Modification of surface properties of the zirconia by silica can also be observed by the temperature-program and reduction (TPR) of the Co/ZrO_2 catalysts (Fig. 3). In general, the reduction behavior of supported catalyst is influenced by a wide range of variables such as metal particle size and metal-support interaction. The TPR profiles of the Si-modified ZrO_2 supported Co catalysts were different from that of the ZrO_2 without Si addition supported one in which the reduction peaks tended to shift to lower temperatures. Therefore, cobalt oxides on the Si-modified ZrO_2 supports reduced easier to Co^0 metal which is known to be the active phase for CO hydrogenation reaction. The Co/ZrO_2 catalysts were tested for catalytic activity in CO hydrogenation reaction under methanation conditions (H_2/CO = 10) in order to minimize the catalyst deactivation due to coke formation. It was found that the activities of Co/ZrO_2 catalysts increased with increasing amount of silica addition. The CO hydrogenation rates were 1.6, 2.1, and 3.0 g CH_2 g $cat^{-1}h^{-1}$ for the catalysts with 0, 0.005, and 0.02 Si/Zr, respectively. As expected, the selectivities for longer chain hydrocarbons (C_{4+}) decreased from 59.1 to 37.1% when the activities increased resulting in an increase in methane selectivities (from 29.5 to 59.4%).

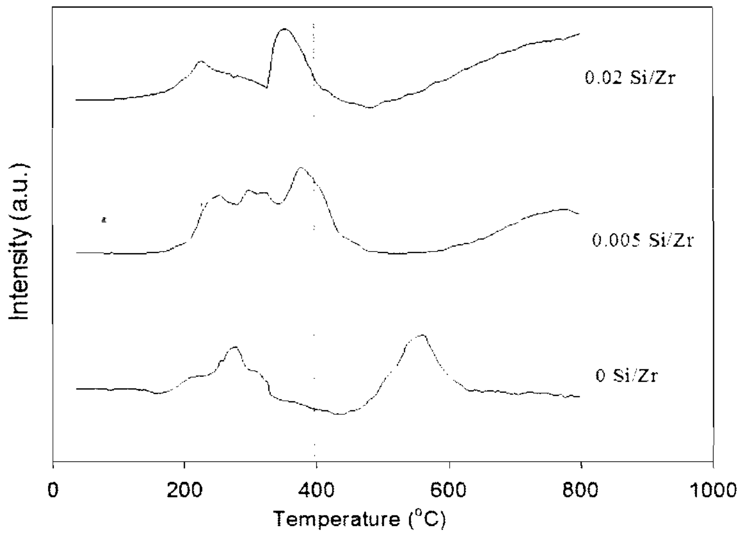


Fig. 3. TPR profiles of Co/ZrO_2 catalysts with various Si/Zr ratios

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A study of alumina–zirconia mixed oxides prepared by the modified Pechini method as Co catalyst supports in CO hydrogenation

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Abstract

In this study, the modified Pechini method has been used to prepare alumina–zirconia mixed oxides with 0.5, 1, 25, 40, and 75 mol% of alumina in zirconia. At low Al contents (<25%), tetragonal phase zirconia was observed, while at higher Al contents, the mixed oxide exhibited only amorphous phase. When they were employed as supports for Co catalyst for CO hydrogenation, it was found that the catalytic activities of low Al-modified zirconia supported Co catalysts increased by ca. 30% compared to the ones supported on pure zirconia or pure alumina, suggesting that the modification of zirconia by alumina has resulted in higher Co dispersion. However, when supports with high alumina contents (40–75 mol% Al) were used, low Co dispersion and poor catalytic performance were obtained despite their higher surface areas. It is likely that cobalt formed metal support compounds with the amorphous phases of these mixed oxides.

Keywords: Nano-crystalline zirconia; Alumina–zirconia mixed oxides; CO hydrogenation; Cobalt catalysts

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1. Introduction

Mixed metal oxides, widely used in ceramic applications, are usually prepared by sol–gel technique, because the method requires lower temperatures compared to conventional ceramic mixing processes and it improves dispersion and homogeneity [1]. Different precursors have been used to prepare sol–gel materials, particularly metal alkoxides [2–4] and citric acid complexes [5,6]. Materials obtained from both precursors are quite similar but gel formation is approached under different conditions. Zirconia prepared by sol–gel method, however, usually possesses low surface area. Recently, it has been reported that solid powders were successfully prepared by the modified Pechini method [7,8], in which citric acid and ethylene glycol are polymerised around metal ions. Because of homogeneous starting solution, this technique leads to closer combination of mixed oxides, which may enhance strong interaction between metal ions. Moreover, high surface area of solid powders is usually obtained by this method, which could bring about high dispersion of metal loading and consequently highly active sites for catalytic reactions [8]. In this study, the modified Pechini method was used to prepare alumina, zirconia, and alumina–zirconia mixed oxides. Zirconia toughened alumina is generally employed in ceramic applications because of its well-known mechanical properties. Moreover, it has recently been introduced in medical application as a biocompatible nano-composite [9]. In catalytic reactions, alumina–zirconia mixed oxide has been used as catalyst and/or support because of its surface property, stability, and mechanical property. Modification of the mixed oxide by sulfate is also well known and has shown very good activity for isomerisation [10].

In this study, alumina–zirconia mixed oxides were prepared by the modified Pechini method with different alumina/zirconia mole ratios and the mixed oxides were employed as Co catalyst supports. The influence of the modification of surface properties of zirconia by alumina on the characteristics of the mixed oxide supported cobalt catalysts were investigated by mean of nitrogen physisorption, X-ray diffraction, H_2 chemisorption, and temperature-programmed reduction. The catalyst performances were tested in CO hydrogenation reaction at 220 °C and 1 atm.

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2. Experimental

2.1. Catalyst preparation

Alumina, zirconia, and alumina–zirconia mixed oxides were prepared using the modified Pechini method in the same manner as that of Refs. [7–11] with different amounts of alumina in zirconia at 0.5, 1, 25, 40, 75, and 100 mol%. Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Aldrich) and zirconyl nitrate ($ZrO(NO_3)_2 \cdot xH_2O$, Aldrich) aqueous solutions were used as starting materials of alumina and zirconia. Both of the solutions were very acidic at a pH ca. 1. Citric acid (UNIVAR) and ethylene glycol (UNILAB) were employed in this method as chelating chemical and polymerizing agent, respectively. In order to obtain the alumina–zirconia mixed oxides, we introduced a desired amount of aluminium nitrate solution was introduced into zirconyl nitrate solution without precipitation. Citric acid [CA] aqueous solution was subsequently added to the solution at a molar ratio of [Al + Zr:CA] = 1:30 to form metal citrate complexes. Prior to addition of the citric acid solution and ethylene glycol [EG], 10 ml of 35% nitric acid solution was provided to adjust the pH conditions to be lowered to ca. 1 before mixing into the metal nitrate solution to avoid precipitation. The ethylene glycol was used at a molar ratio of EG/CA = 7:30. The mixed solution was heated to 70 °C and held at that temperature for 3 days until the volume of the solution was decreased by one-fourth of the starting solution volume. The nitric molecules were decomposed at the boiling conditions as observed from brownish exhausted gases when the solution was heated up to 100 °C. The solution spontaneously became a transparent gel when the temperature approached 120 °C. The gel was calcined at 600 °C for 6 h in dynamic air to remove the organic materials, resulting in a spongy white powder. The obtained powders were employed as supports for cobalt catalysts. $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich) was dissolved in deionized water and impregnated into the support using the incipient wetness impregnation method to give a final catalyst with 8 wt% cobalt. The catalysts were dried at 100 °C for 12 h and calcined in air at 350 °C for 2 h in order to eliminate residual $Co(NO_3)_2$ [12].

2.2. Characterization of the catalysts

The BET surface areas were determined by N_2 physisorption using a Micromeritics ASAP 2020. Each sample was degassed in the system at 300 °C for 3 h prior to N_2 physisorption. A SIEMENS D5000 X-ray diffractometer using Cu Kα radiation with Ni filter in the 10–80° 2θ angular regions was employed to obtain XRD spectra of the sample powders. Referring to the procedures described by Reuel and Bartholomew [13], we carried out H_2 chemisorption by using a Micromeritics Pulse Chemisorb 2750 system. Approximately 0.2 g of each catalyst was reduced at 350 °C after ramping at a rate of 1 °C min^{-1} and the combination was held at that temperature for 3 h. The pulse hydrogen chemisorption was performed at 100 °C. The TPR profiles of supported cobalt catalysts were obtained by temperature programmed reduction using an in-house system and a temperature ramp of 5 °C min^{-1} from 35 to 800 °C in a flow of 3% H_2 in argon. The H_2 consumption was measured by analyzing the effluent gas with a thermal conductivity detector. The reducibility of each catalyst was estimated from the peak areas under the TPR curves, which were calculated using a PeakFit software program version 4.12 with Auto-Fit options.

2.3. Catalytic activity test

CO hydrogenation was carried out in a fixed-bed stainless steel reactor at 220 °C and 1 atm total pressure. A flow rate of CO/H_2/Ar 4/40/16 cm^3 min^{-1} was used. Typically, 0.10 g of the catalyst was reduced in situ in flowing hydrogen (30 cm^3 min^{-1}) at 350 °C for 2 h prior to reaction. The effluent gases were taken at 20 min and 1 h intervals and were analyzed by GC. In all cases, the reaction approached steady state within 6 h.

3. Result and discussions

3.1. Effect of alumina content on the properties of alumina–zirconia mixed oxides

The XRD spectra of the alumina–zirconia mixed oxide powders prepared by the modified Pechini method are shown in Fig. 1. It was found that pure zirconia and Al-modified zirconia samples prepared with 0.5–1 mol% Al content exhibited pure tetragonal phase of zirconia, whereas the ones prepared with higher-in-alumina contents of 25–100 mol% were completely amorphous. Such results suggest that the orientations of alumina and zirconia structures were affected by good dispersion of alumina and zirconia mixed oxides under these preparation conditions. In general, the tetragonal phase zirconia is thermodynamically stable at a temperature above 1170 °C [14]. However, according to the work reported by Garvie [15], the energy from combustion of the polymeric material during calcination at 600 °C was probably sufficient to arrange the crystal structure in tetragonal form with crystal size less than its critical size. The crystallite sizes calculated from Scherrer's equation using 202 diffraction peaks of tetragonal peak and the BET surface areas of the same samples are reported in Table 1.

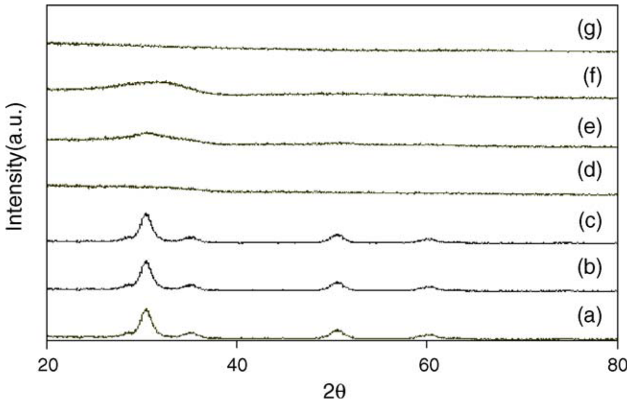

Fig. 1. The XRD patterns of the supports: (a) ZrO_2, (b) Al0.5–ZrO_2, (c) Al1–ZrO_2, (d) Al25–ZrO_2, (e) Al40–ZrO_2, (f) Al75–ZrO_2, and (g) Al_2O_3.

Table 1
Characteristics of alumina–zirconia mixed oxides

Supports	BET surface area of support ($m^2 g^{-1}$)	Crystal size[a] (nm)	Phase Identification of Zirconia (from XRD)
ZrO_2	56	6	Tetragonal
Al0.5–ZrO_2	68	6	Tetragonal
Al1–ZrO_2	65	7	Tetragonal
Al25–ZrO_2	70	–	Amorphous
Al40–ZrO_2	182	–	Amorphous
Al75–ZrO_2	228	–	Amorphous
Al_2O_3	319	–	–

[a] Calculated from XRD broadening peak at 2θ ca. 30.8°.

The average crystallite sizes of the zirconia and the Al-modified zirconia were approximately 6–7 nm. The BET surface areas of support samples were found to be ca. 50–300 $m^2 g^{-1}$. It has been reported that introducing a small amount of alumina (<5%) into zirconia can stabilize the porous structure of the zirconia [16]. A significant increase in BET surface areas was observed for the alumina–zirconia mixed oxides prepared with high alumina contents. Under these preparation conditions (40–75 mol% Al), zirconia may have been introduced into the alumina matrix; thus the powders possessed high surface areas of alumina.

3.2. The physicochemical properties and performances of alumina–zirconia mixed oxide supported cobalt catalysts

The X-ray diffraction patterns of Co/Alx–ZrO_2 (x = mol% of alumina), Co/Al_2O_3, and Co/ZrO_2 catalysts are shown in Fig. 2. The XRD characteristic peak of Co_3O_4 at 2θ of ca. 36.8° was observed for all the catalyst samples except Co/Al40–ZrO_2 and Co/Al75–ZrO_2. The crystallite size of cobalt oxide on those supports was probably below the limit of XRD detectability (3–5 nm) and/or cobalt did not form Co_3O_4 crystallites on Co/Al40–ZrO_2 and Co/Al75–ZrO_2 but existed in the amorphous form [17]. The average crystallite sizes of Co_3O_4 derived from X-ray line broadening using Scherrer's equation were 8–19 nm and the sizes increased with increasing amount of alumina content. The BET surface areas, the reducibility, the amounts of H_2 chemisorption, and %cobalt dispersion are reported in Table 2. Surface areas of the supported cobalt catalysts were found to be slightly less than that of the original supports, thus cobalt appears to have been in some the pores of the support. The impact of high surface area of alumina on the BET surface areas of the mixed oxide supported Co catalysts were observed only for Co/Al40–ZrO_2 and Co/Al75–ZrO_2 thus at low alumina contents (<25 mol%), the modification of zirconia properties was not due to the changes in BET surface areas. It was found that H_2 chemisorption and %Co dispersion of these low alumina content oxide supported Co catalysts were higher than those of Co/ZrO_2 and Co/Al_2O_3. The surface properties of zirconia were probably modified by the alumina, resulting in high amounts of active surface cobalt being measured by H_2 chemisorption. Surprisingly, for the higher alumina contents, Co/Al40–ZrO_2 and Co/Al75–ZrO_2, despite their relatively high surface areas, exhibited low H_2 chemisorption and Co dispersion. The interaction of cobalt oxide species and the supports was further investigated by means of temperature-programmed reduction (TPR).

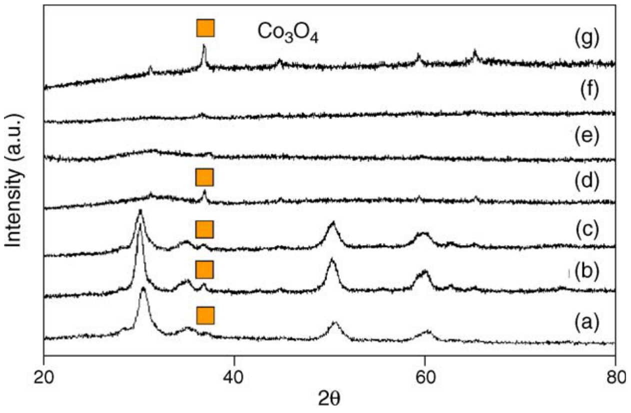

Fig. 2. The XRD patterns the catalysts: (a) 10%Co/ZrO_2, (b) 10%Co/Al0.5–ZrO_2, (c) 10%Co/Al1—ZrO_2, (d) 10%Co/Al25–ZrO_2, (e) 10%Co/Al40–ZrO_2, (f) 10%Co/Al75–ZrO_2, and (g) 10%Co/Al_2O_3.

TPR profiles of all the catalysts are shown in Fig. 3. Reduction of cobalt in the oxide form, Co_3O_4 or CoO, to Co^0 involves a two-step reduction: first reduction of Co_3O_4 to CoO and then the subsequent reduction of CoO to Co^0 [18,19]. A

Table 2
Physicochemical properties of co catalysts supported on alumina–zirconia mixed oxides

Sample	BET surface area of the catalyst ($m^2 g^{-1}$)	Hydrogen chemisorption (molecules g^{-1} cat.$^{-1}$) $\times 10^{18}$	Reducibility[a] (%)	Crystal size of Co_3O_4 (nm)[b]	Co dispersion (%)
Co/ZrO_2	34	8.3	47	8	34
Co/Al0.5–ZrO_2	41	10.3	36	11	56
Co/Al1–ZrO_2	39	10.3	38	10	53
Co/Al25–ZrO_2	42	10.3	37	19	55
Co/Al40–ZrO_2	109	3.2	17	n.d.[c]	37
Co/Al75–ZrO_2	137	1.5	12	n.d.[c]	25
Co/Al_2O_3	191	8.5	48	19	35

[a] Calculated from reducibility $(\%) = \frac{\text{The amount of hydrogen used to reduce 1 g of the catalyst} \times 100}{\text{The theoretical hydrogen amount needed to reduce 1 g of the catalyst}}$.

[b] Calculated from XRD broadening peak at 2θ ca. 36.8°.

[c] n.d., not detected.

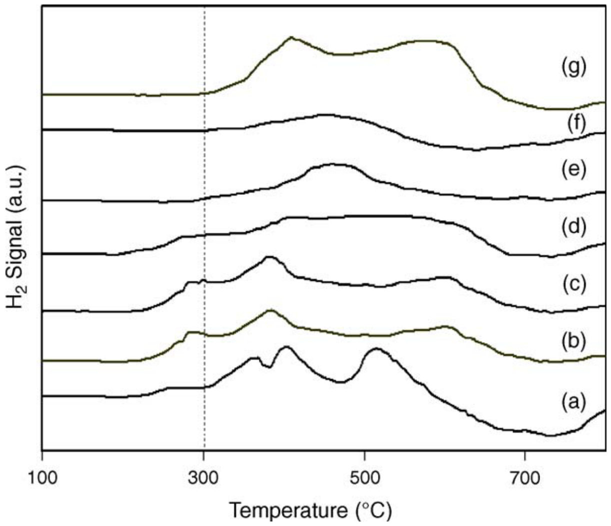

Fig. 3. Influence of alumina–zirconia support on the reduction behavior of the cobalt catalysts: (a) 10%Co/ZrO_2, (b) 10%Co/Al0.5–ZrO_2, (c) 10%Co/Al1–ZrO_2, (d) 10%Co/Al25–ZrO_2, (e) 10%Co/Al40–ZrO_2, (f) 10%Co/Al75–ZrO_2, and (g) 10%Co/Al_2O_3.

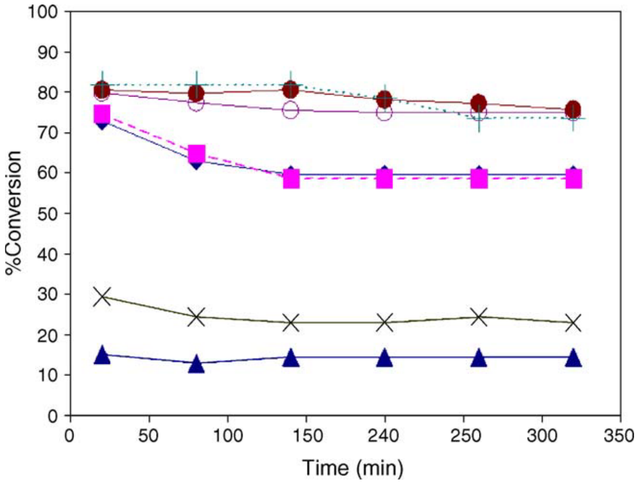

Fig. 4. Typical time-on-stream behavior of the catalyst samples in the CO-hydrogenation: (◆) Co/ZrO_2, (■) Co/Al_2O_3, (●) Co/Al0.5–ZrO_2, (+) Co/Al1–ZrO_2, (○) Co/Al25–ZrO_2, (×) Co/Al40–ZrO_2, and (▲) Co/Al75–ZrO_2.

wide range of variables, such as metal particle size and metal–support interaction, have an influence on the reduction behavior of cobalt catalysts, resulting in the observation of different locations of the TPR peaks [20,21]. It was found that, for the Co catalyst supported on the mixed oxides with low alumina content (<25%), the reduction peaks below 400 °C shifted slightly to low temperatures, whereas the Al40–ZrO_2 and Al75–ZrO_2-supported ones exhibited only a single reduction peak at temperatures higher than 400 °C. The higher reduction peak may be attributed to formation of non-reducible phases, i.e. cobalt–aluminate [20,21] and cobalt–zirconate [22,23].

The reducibilities of all the alumina–zirconia mixed oxide supported catalysts during TPR 30–800 °C were found to be lower than those of Co/ZrO_2 and Co/Al_2O_3. Such results suggest that the surface properties of the mixed oxide-supported catalysts were different from those of the pure oxide. Furthermore, it was found that Co/Al40–ZrO_2 and Co/Al75–ZrO_2 exhibited distinctly low reducibilities (12–17%). In the XRD results, only amorphous phase was observed and no XRD peaks for Co_3O_4 were found on these samples. It is likely that amorphous forms of alumina and zirconia caused formation of cobalt–aluminate and/or cobalt–zirconate by combining unreduced cobalt oxides with amorphous alumina and/or amorphous zirconia [22,23]. It should, however, be noted that the reducibility of pure amorphous alumina supported Co catalyst was similar to that of tetragonal zirconia-supported catalyst. Although cobalt aluminate compounds can be formed on the amorphous alumina surface as suggested for Al40–ZrO_2 and Al75–ZrO_2 supported catalysts, some large cobalt oxide crystallites were found on amorphous alumina so that the higher reducibility was obtained.

Fig. 4 displays the time-on-stream behaviors of the mixed oxides supported Co catalysts during CO hydrogenation. In all cases, the steady state was reached within 2 h of run. The catalytic activity and the product selectivity of all the catalysts in CO hydrogenation are given in Table 3. There was no significant difference in the product selectivities since, under the reduction conditions used, all the catalysts exhibited methane selectivities ca. 95–99%. The CO hydrogenation rates of the mixed oxide-supported cobalt catalysts prepared with low alumina contents (0.5, 1, and 25 mol%) increase by 30% at steady state compared to those of Co/ZrO_2 and Co/Al_2O_3 even though their reducibilities were slightly lower. The 0.5–25 mol% Al-modified zirconia supports may have a positive

Table 3
Results of CO hydrogenation reaction

Sample	Product selectivity (%)			Rate of CO hydrogenation (mmol of –CH_2– g^{-1} s^{-1})[a]		TOF (s^{-1})	
	C_1	C_2–C_3	C_4–C_{4+}	Initial	Final	Initial	SS
Co/ZrO_2	94.4	4.8	0.7	22	18	0.79	0.65
Co/Al0.5–ZrO_2	99.3	0.7	0.0	24	23	0.79	0.71
Co/Al1–ZrO_2	98.8	1.1	0.1	24	22	0.79	0.74
Co/Al25–ZrO_2	98.9	1.1	0.0	24	22	0.70	0.65
Co/Al40–ZrO_2	95.4	4.5	0.1	9	7	0.83	0.64
Co/Al75–ZrO_2	96.7	3.3	0.0	5	4	0.92	0.87
Co/Al_2O_3	99.3	0.7	0.0	22	17	0.79	0.62

[a] Refers to the unit of CO hydrogenation rate per gram catalyst.

influence on a phase dispersion of cobalt oxide and active metallic phases derived from the Co_3O_4 particles. Enache et al. [23] proposed a relation between the degree of crystallization of Co_3O_4 particles and the types of cobalt active phase after hydrogen reduction, i.e. crystalline metallic cobalt derived from the crystalline Co_3O_4 particles and poor crystalline metallic cobalt derived from the amorphous Co_3O_4 particles. The catalyst that consisted of poorly crystalline metallic cobalt appeared to be more catalytic-active than the one with more perfect crystalline metallic cobalt. It is possible that the surface properties of zirconia modified by low amount of alumina resulted in high dispersion of active metallic cobalt phase, so that high CO hydrogenation activities were obtained.

4. Conclusions

Alumina–zirconia mixed oxide supports with various mol% of alumina prepared by the modified Pechini method exhibited interesting properties when employed as Co catalyst supports in CO hydrogenation. For the low alumina contents (i.e. 0.5–25 mol%), alumina modified the surface properties of zirconia leading to high dispersion of cobalt and high performance in CO hydrogenation reaction. However, for higher alumina contents (i.e. 40 and 75 mol%), the catalysts showed much lower Co dispersion and CO hydrogenation activities, due probably to compound formation from cobalt and amorphous alumina/zirconia.

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Effects of Si- and Y-modified nanocrystalline zirconia on the properties of Co/ZrO_2 catalysts

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Abstract

Nanocrystalline zirconia and m-modified zirconia (m = Si and Y) have been prepared by the modified Pechini's method and employed as supports for cobalt catalysts. Addition of a small amount of Si or Y during the preparation of nanocrystalline zirconia did not alter the average crystallite sizes and BET surface areas of the tetragonal zirconia. However, zirconia primary particles appeared to be more agglomerated when Si/Zr and Y/Zr were greater than 0.005 and 0.01, respectively. The Si- and Y-modified zirconia supported cobalt catalysts with higher m/Zr showed higher H_2 chemisorption and CO hydrogenation activities.

Keywords: Nanocrystalline zirconia; Y-modified ZrO_2; Si-modified ZrO_2; CO hydrogenation; Cobalt catalyst

1. Introduction

During recent years zirconia has received much attention from researchers in the field of heterogeneous catalysis as a support material as well as a catalyst because it is more chemically inert than the classical supports (e.g., γ-alumina and silica) and it may possess different chemical properties such as acidity, basicity, reducing, or oxidizing ability [1]. Use of zirconia as a catalyst support has shown promising results in many environmental catalysis reactions such as CO_2 hydrogenation [2], CO oxidation [3], and the Fischer–Tropsch reaction [4–7]. Enache et al. [6] reported that the use of zirconium oxide as support in the Fischer–Tropsch synthesis leads to better reducibility of the active phase, hydrogen spillover, and higher CO conversions compared to those of γ-alumina-supported ones. In a recent work from our group, we reported that cobalt catalysts supported on nanocrystalline tetragonal zirconia prepared by solvothermal method exhibited superior CO hydrogenation activities than those of commercial zirconia supported ones [8].

It has been reported that addition of a small amount of second metals such as silicon [9,10], yttrium [11–13], lanthanum [14] and silicotungstate [15] can improve thermal stability of tetragonal phase zirconia. For examples, silica-modified zirconia obtained by the reaction of mixture of zirconium *n*-propoxide and tetraethyl orthosilicate in 1,4-butanediol at 300 °C had large surface area and high stability of tetragonal phase even after calcination at high temperatures [8]. To our knowledge, the effect of Si- or Y-modified zirconia on the properties of zirconia supported catalysts, i.e., Co/ZrO_2 has never been studied. In this article, we reported the synthesis of nanocrystalline zirconia by modified Pechini's method and their applications as cobalt catalyst supports. The modified Pechini's method is known to be a successful method for production of solid powders by polymerization of citric acid and ethylene glycol around metal ions [16]. Due to high surface areas, the obtained materials could bring about high dispersion of metal loading and consequently high active sites for

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catalytic reactions. The catalysts were characterized by N_2 physisorption, XRD, H_2 chemisorption, TPR, TEM, SEM, and tested for catalytic activity in CO hydrogenation reaction.

2. Experimental

2.1. Preparation of Si- and Y-modified nanocrystalline zirconia

Nanocrystalline zirconia was prepared using the modified Pechini's method described in [16]. The Si- and Y-modified zirconia were prepared by adding a small amount of TEOS (tetraethylorthosilicate, Aldrich) and $Y(NO_3)_3 \cdot xH_2O$ (Aldrich) into the solution of $ZrO(NO_3)_2 \cdot xH_2O$ (Aldrich) 0.06 mole in 150 ml distilled water, respectively. The molar ratios of Si/Zr and Y/Zr calculated were in the range 0.001–0.02. A modified pH citric acid (UNIVAR) solution was prepared by adding 10 ml of 35% by volume nitric acid to 150 ml 2.8 M citric acid. The modified pH citric acid solution was then mixed with the precursor solution. Finally, ethylene glycol adjusted pH by 10 ml of the nitric acid was added. The mixed solution was heated to 70 °C and held at that temperature for 3 days until volume of the solution was decreased by 1/4 of the starting solutions. The solution started boiling when heated up to 100 °C. The nitrate molecules were decomposed at the boiling conditions as observed from brownish exhausted gases. When the temperature was increased to 120 °C, the solution became transparent gel. The gel was calcined at 600 °C for 6 h in dynamic air to remove the organic materials resulting in spongy white powder. The obtained powders were used as supports for cobalt catalysts. $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich) was dissolved in deionized water and impregnated into the support using the incipient wetness to give a final catalyst with 10 wt% cobalt. The catalysts were dried at 100 °C for 12 h and calcined in air at 350 °C for 2 h.

$$\%\text{CO conversion} = \frac{\text{mole of CO in feed} - \text{mole of CO in products}}{\text{mole of CO in feed}} \times 100$$

$$\text{Reaction rate } (\text{gCH}_2\text{g cat.}^{-1}\text{ h}^{-1}) = \frac{\%\text{CO conversion} \times \text{flowrate of CO in feed(cc/ min)} \times 60(\text{min /h}) \times \text{mol. wt. of CH}_2\text{(g/mole)}}{\text{catalyst weight(g)} \times 22,400\text{(cc/mole)}}$$

2.2. Catalyst characterization

Phase identification and crystallite size of pure and modified nanocrystalline zirconia were investigated by X-ray diffraction (Siemens D5000) using Ni filter Cu Kα radiation from 20° to 80° 2θ. Crystallite size was calculated from the Scherrer's equation using 202 diffraction peak of tetragonal zirconia as follows

$$D = 0.9\lambda/\beta\cos\theta$$

where D is the crystallite size in nm, λ is the radiation wavelength, β is corrected half-width of the peak profile, and θ is the diffraction peak angle. Surface areas of the samples were measured by the single point BET method. The sample was pretreated at 200 °C in 21 cc/min Helium for 2 h and saturated with 9 cc/min Nitrogen for 30 min at temperature of liquid Nitrogen. Nitrogen desorption profile was reported by TCD signal and integrated area under the profile was used to calculate approximately surface area. Pulse hydrogen chemisorption was carried out to determine the cobalt active sties using a Micromeritic Chemisorb 2750. Prior to hydrogen chemisorption, the samples were reduced in situ at 350 °C for 3 h. The TPR profiles of supported cobalt catalysts were obtained by temperature programmed reduction using an in-house system and a temperature ramp of 5 °C/min from 35 to 800 °C in a flow of 3% H_2 in argon. Approximately 0.10 g of a calcined catalyst was placed in a quartz tube in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). The H_2 consumption was measured by analyzing the effluent gas with a thermal conductivity detector.

2.3. Reaction study

CO hydrogenation was carried out in a down-flow fixed bed stainless steel reactor at 220 °C and 1 atm total pressure. A WSHV of ca. 4500 h^{-1} and a H_2/CO ratio of 10 were used. Typically, 0.10 g of the catalyst was reduced in situ in flowing hydrogen (30 cc/min) at 350 °C for 2 h prior to reaction. The effluent gases were taken at 20 min and 1 h interval and were analyzed by a GC. In all cases, the reaction approached steady state within 6 h. The percentages of CO conversion, reaction rates, and turnover frequencies were defined as:

Turnover frequencies (TOFs) were determined based on the amount of Co^0 active site measured by H_2 chemisorption.

$$\text{TOF} = \frac{\text{rate}}{\text{site. time}}$$

3. Results and discussion

3.1. Effect of Si and Y additions on the properties of ZrO_2

The X-ray diffraction patterns of the zirconia and modified zirconia powders prepared by the modified Pechini's

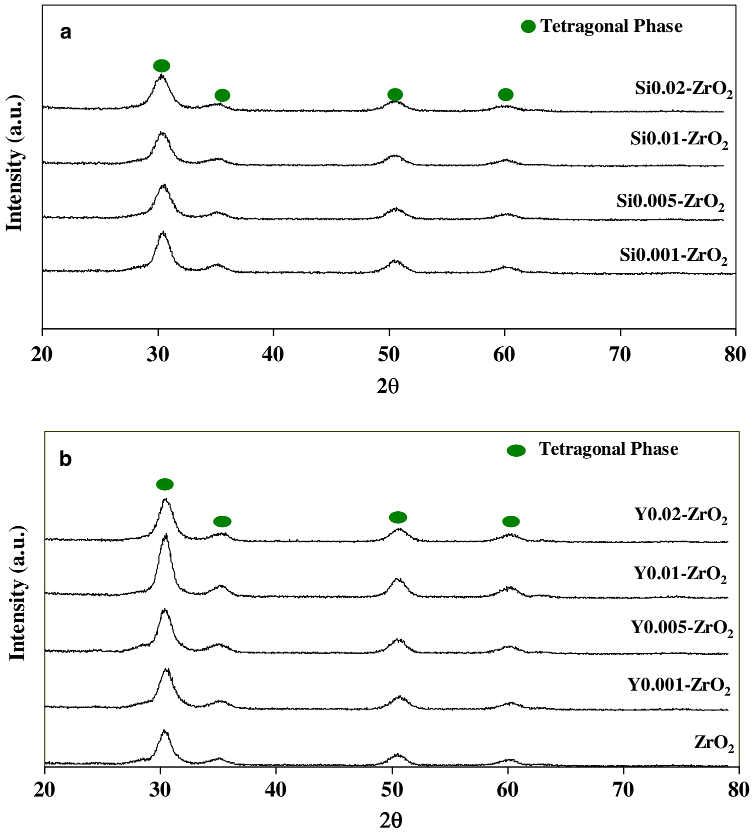

Fig. 1. X-ray diffraction results of (a) Si-doped ZrO_2 and (b) Y-doped ZrO_2.

Table 1
Crystallite sizes and BET surface areas of Si- and Y-doped zirconia

Sample	Avg. crystallite size (nm)[a]	BET surface area[b] (m^2/g)
ZrO_2	6.3	90.4
Si0.001–ZrO_2	6.2	95.2
Si0.005–ZrO_2	5.3	83.1
Si0.01–ZrO_2	5.9	86.4
Si0.02–ZrO_2	5.2	92.1
Y0.001–ZrO_2	5.9	93.1
Y0.005–ZrO_2	6.1	94.5
Y0.01–ZrO_2	6.9	92.2
Y0.02–ZrO_2	5.9	98.4

[a] Calculated from X-ray line broadening.
[b] Error of measurements = ±10%.

method are shown in Fig. 1. All the samples exhibited tetragonal crystalline zirconia phase. No other crystal structures were observed. It has been suggested that the energy from combustion of the polymeric materials during calcination at 600 °C was sufficient to arrange the crystal structure in the tetragonal form with a crystal size less than its critical size [17]. Addition of Si or Y did not have any effect on XRD patterns of the tetragonal zirconia. The crystallite sizes of tetragonal zirconia calculated from the XRD line broadening using the Scherrer's equation and the BET surface areas are reported in Table 1. The average crystallite sizes of the zirconia and the Si- or Y-modified zirconia were approximately 5–7 nm. The BET surface areas of the nanocrystalline zirconia were found to be 85–100 m^2/g. Within experimental error, there was no significant difference in BET surface areas and the crystallite sizes of the zirconia and the modified zirconia. This is in contrast to the work reported by Alvarez and Torralvo [13] that doping of 2–5% by mole of yttria to zirconia prepared by sol–gel method resulted in narrower interparticle pores and formation of denser agglomerates. However, in our study the amounts of Y and Si addition were probably low (ca. 0.10–1.96%) so that no change in BET surface areas was found. Based on SEM results (not shown here), there was also no change in the morphology of the zirconia after Si or Y doping. Both zirconia and modified-zirconia prepared by the modified Pechini's method have irregular long shapes consisting of sandwich parallel pores similar to those of sol–gel derived zirconia that appeared to form from polymeric units of hydrolysed zirconium precursors [18]. These observed pores were in a macro-range.

3.2. Characteristics and catalytic properties of Y- and Si-modified ZrO_2 supported Co catalysts

The X-ray diffraction patterns of the Co/ZrO_2 catalysts are shown in Fig. 2. After impregnation of 10 wt% cobalt, the diffraction peaks of Co_3O_4 were observed at 36.8° 2θ for all the catalyst samples. The average crystallite sizes of Co_3O_4 calculated based on X-ray line broadening using Scherrer's equation for Si-modified ZrO_2 supported cobalt

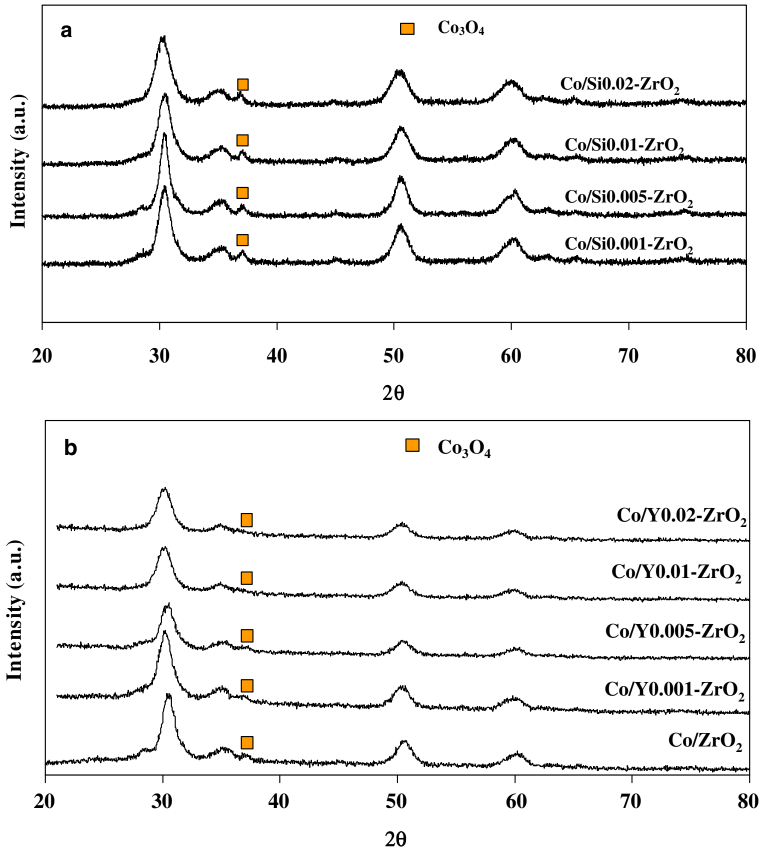

Fig. 2. X-ray diffraction results of Co catalysts supported on (a) Si-doped ZrO_2 and (b) Y-doped ZrO_2.

Table 2
Characteristics of various Co/ZrO_2 catalysts

Sample	BET surface area[a] (m^2/g)	H_2 chemisorption[b] × 10^{18} (molecule H_2/g cat.)	%Co dispersion[c]
Co/ZrO_2	52.1	5.9	14.4
$Co/Si0.001–ZrO_2$	48.7	5.1	12.5
$Co/Si0.005–ZrO_2$	51.5	5.4	13.3
$Co/Si0.01–ZrO_2$	50.8	7.0	17.0
$Co/Si0.02–ZrO_2$	52.4	9.0	21.9
$Co/Y0.001–ZrO_2$	56.2	4.5	11.0
$Co/Y0.005–ZrO_2$	54.3	4.6	11.3
$Co/Y0.01–ZrO_2$	60.1	5.5	13.5
$Co/Y0.02–ZrO_2$	53.8	6.4	15.7

[a] Error of measurements = ±10%.

[b] Error of measurements = ±5%.

[c] %Co dispersion was calculated based on the total amount of cobalt reduced at 350 °C.

catalysts were 20–40 nm. They increased with increasing Si content and were found to be larger than those of Y-modified ZrO_2 supported ones (<5 nm).

The BET surface areas of the various Co/ZrO_2 catalysts and the H_2 chemisorption results are reported in Table 2. The BET surface areas of the zirconia supported cobalt catalysts were slightly less than that of the original zirconia supports suggesting that cobalt was deposited in some of the pores of zirconia. There was no significant difference in BET surface areas of all the Co/ZrO_2 catalysts. However, it was found that at high molar ratios of Si/Zr (0.01–0.02) and Y/Zr (0.02), the amounts of H_2 chemisorption increased by ca. 10–50% with the Si-modified zirconia (Si/Zr = 0.02) exhibited the highest cobalt dispersion. The addition of lower amounts of Si or Y did not seem to have a great impact on the amount of surface cobalt measured by H_2 chemsiorption. The results of this study were found to be in agreement with the well-established trends in the literature on the influence of addition of a second metal on phase stability of zirconia. A considerably high loading of the second metals was used i.e., a commercial available 8% Y stabilized ZrO_2.

TEM micrographs were taken for all the catalysts in order to physically measure the size of cobalt oxide particles and/or cobalt clusters (Fig. 3). Darker spots represent high concentration of cobalt while lighter areas are the zirconia supports. It was found that on the Si-modified zirconia, the areas representing cobalt concentration increased with increasing Si/Zr ratios. On the other hand, on the Y-modified zirconia, small cobalt particles/clusters were observed unless for the high Y/Zr (0.02) that large cobalt clusters was apparent. TEM images were found to be in accordance with the results from XRD that small cobalt oxide particles (<5 nm) were present on Y-modified zirconia supported Co catalysts. Although TEM measurements were only done for a very small portion of each catalyst, the results are able to provide further evidence about Co

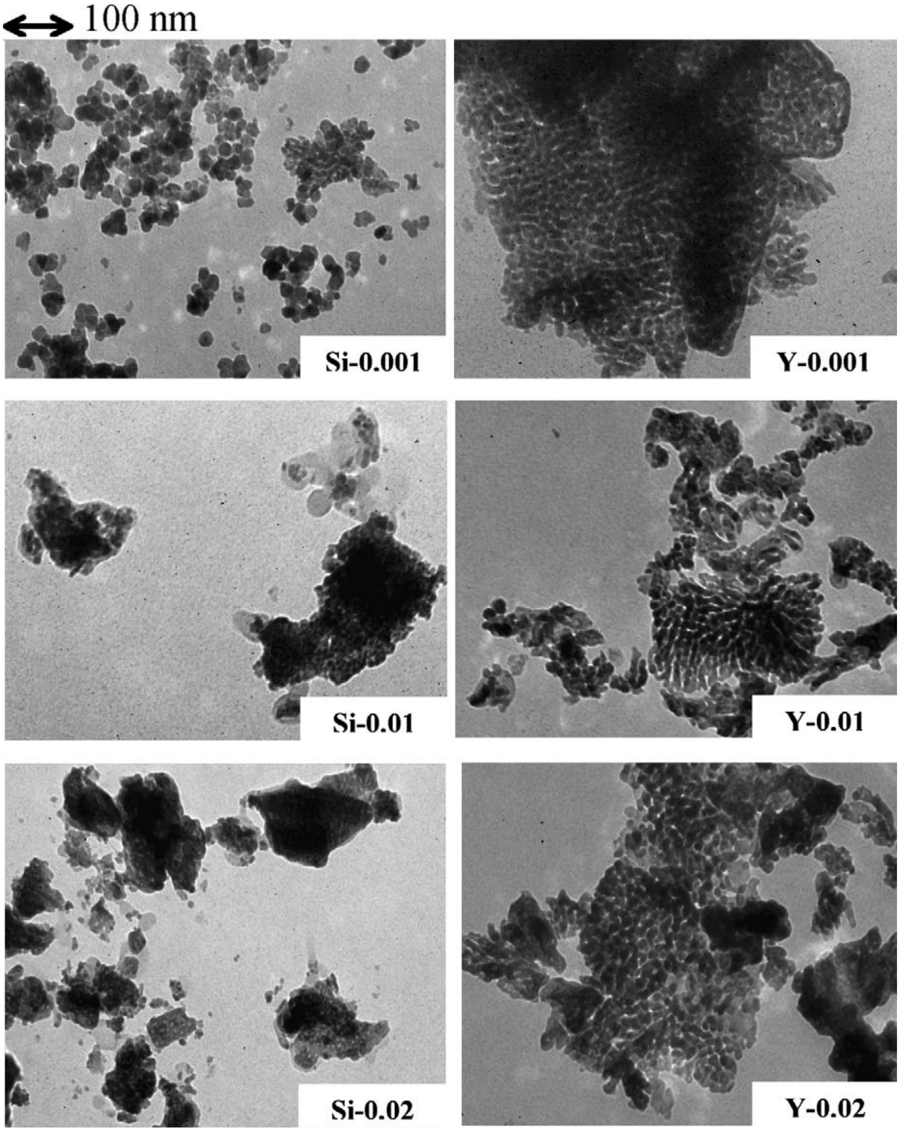

Fig. 3. TEM micrographs of various Si- and Y-modified ZrO_2 loaded with 10 wt% cobalt.

dispersion. Adding a small amount of Si and Y might alter the growth of nucleation of zirconia crystal [19]. In this study, it was found that primary particles of the nanocrystalline zirconia tend to agglomerate upon Si and Y doping. The effect was, however, more pronounced for the modification with silica than yttria as seen by agglomeration of zirconia particles for the lower Si/Zr ratios. The results were in good agreement with Alvarez and Torralvo [13] that increasing %Y addition resulted in larger and packing of primary particles.

Temperature programmed reduction (TPR) profiles of Si- and Y-modified zirconia supported Co catalysts are shown in Figs. 4 and 5, respectively. TPR is a powerful tool to study the reduction behavior of the catalysts. Reduction of cobalt in the oxide form, Co_3O_4 or Co_2O_3, to Co^0 involves a two-step reduction: first reduction of Co_3O_4 to CoO and then the subsequent reduction of CoO to Co^0 [20,21]. A wide range of variables such as, metal particle size and metal-support interaction, have an influence on the reduction behavior of cobalt catalysts resulting in the observation of different locations of the TPR peaks [22]. It was found that for the Si-modified zirconia supported cobalt catalysts reduction peaks below 400 °C tended to shift to lower temperatures, whereas those of Y-modified ones showed similar TPR profiles. The reducibilities of the catalysts calculated by integrating areas under the TPR peaks are given in Table 3. The reducibilities of all the catalysts were only 30–40%. The low reducibility of the catalysts may be due to formation of a solid solution or a zirconate phase between unreduced cobalt oxides and zirconia [6].

The catalytic activities of the Co/ZrO_2 catalysts in CO hydrogenation reaction are also reported in Table 3. As expected, the CO hydrogenation rates increased by 30–40% for the ones supported on Si- and Y-modified zirconia with $Si/Zr > 0.05$ and $Y/Zr > 0.01$ mole ratios. Since the

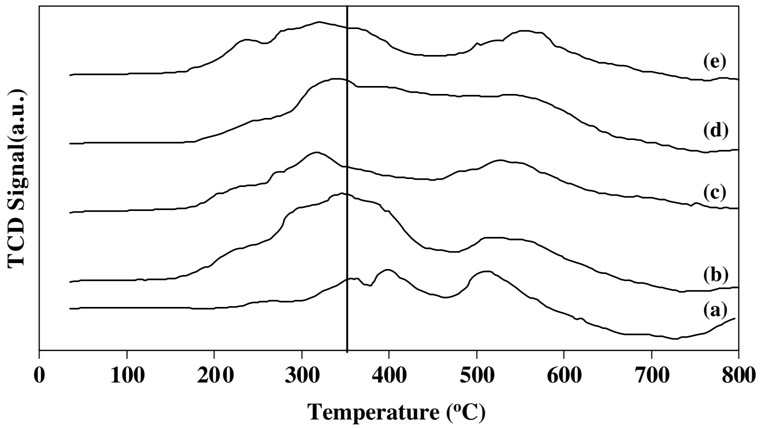

Fig. 4. Temperature-programmed reduction of the catalyst samples (a) 10%Co/ZrO_2; (b) 10%Co/Si0.001–ZrO_2; (c) 10%Co/Si0.005–ZrO_2; (d) 10%Co/Si0.01–ZrO_2 and (e) 10%Co/Si0.02–ZrO_2.

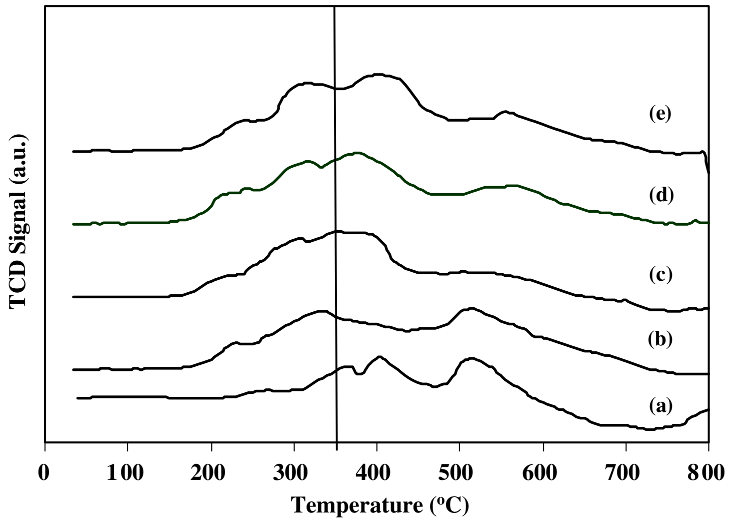

Fig. 5. Temperature-programmed reduction of the catalyst samples (a) 10%Co/ZrO_2; (b) 10%Co/Y0.001–ZrO_2; (c) 10%Co/Y0.005–ZrO_2; (d) 10%Co/Y0.01–ZrO_2 and (e) 10%Co/Y0.02–ZrO_2.

Table 3
Catalytic results in CO hydrogenation (220 °C, 1 atm, and $H_2/CO = 10$)

Catalyst	Reducibility[a] (%)	CO hydrogenation rate[b] (μmol CH_2 g cat.$^{-1}$ s^{-1})	Product selectivity (%)			TOFs[c] (s^{-1})
			C_1	C_2–C_3	C_{4+}	
Co/ZrO_2	32	15.4	88.6	9.1	2.3	0.22
Co/Si0.001–ZrO_2	39	10.7	86.0	10.8	3.2	0.27
Co/Si0.005–ZrO_2	30	10.8	98.0	2.0	0.0	0.72
Co/Si0.01–ZrO_2	34	11.9	98.6	1.4	0.0	0.66
Co/Si0.02–ZrO_2	30	18.8	97.8	2.2	0.1	0.28
Co/Y0.001–ZrO_2	31	10.4	97.6	2.3	0.1	0.28
Co/Y0.005–ZrO_2	29	16.2	89.3	8.7	2.1	0.26
Co/Y0.01–ZrO_2	29	19.6	91.7	7.1	1.3	0.23
Co/Y0.02–ZrO_2	32	24.1	97.7	2.2	0.1	0.30

[a] Based on TPR results from 35–800 °C.

[b] CO hydrogenation rate $= \frac{\%\text{CO conversion} \times \text{flowrate of CO in feed(cc/min)} \times 60(\text{min/h}) \times \text{mol. wt. of } CH_2(\text{g/mole})}{\text{catalyst weight(g)} \times 22400(\text{cc/mole})}$.

[c] Based on H_2 chemisorption results.

TOFs of Co/SiO0.005–ZrO_2 and Co/SiO0.01–ZrO_2 were almost three times higher than that of the non-modified one, there might have been some modification of the ZrO_2 surface by Si atoms resulting in higher active Co^0 surface. However, there was no such evidence for the Y-modified ones; the TOFs for all the Y-modified zirconia

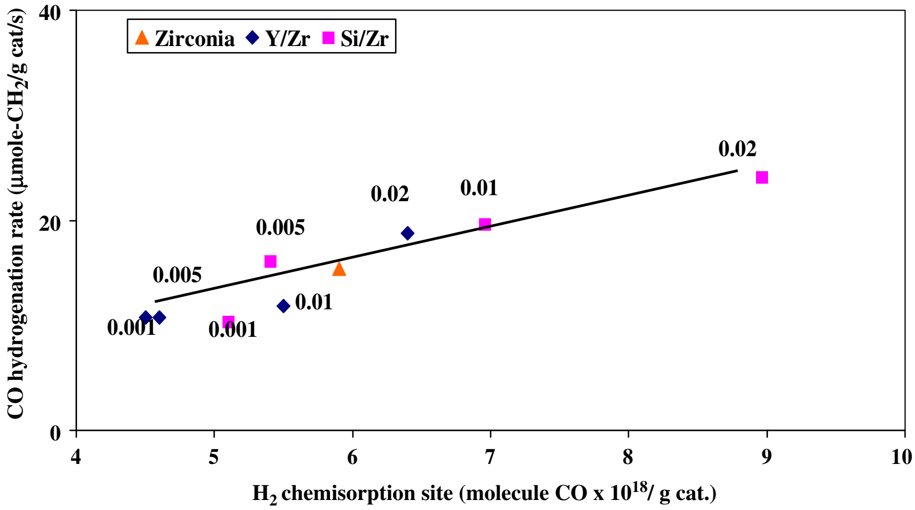

Fig. 6. Correlation of active sites measured by hydrogen chemisorption and CO hydrogenation rates.

supported Co catalysts were similar. A correlation between the amount of active sites and CO hydrogenation activities for various Co/ZrO_2 catalysts is illustrated in Fig. 6 as a straight line. The product selectivities were not significantly different since all the catalysts exhibited methane selectivities ca. 89–99% (expected product under the reaction conditions used).

4. Conclusions

Addition of a small amount of Si or Y during the preparation of nanocrystalline tetragonal zirconia accelerated the agglomeration of zirconia primary particles. However, when used as cobalt catalyst supports the Si- and Y-modified zirconia supported ones with $Si/Zr > 0.005$ and $Y/Zr > 0.01$ exhibited higher H_2 chemisorption and CO hydrogenation activities. The effect was more pronounced for Si-modified ZrO_2 than Y-modified ones as shown by higher TOF values.

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ROLE OF RUTHENIUM IN THE REDUCTION BEHAVIOR OF RUTHENIUM-PROMOTED COBALT/TITANIA FISCHER-TROPSCH CATALYSTS

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Abstract

Role of ruthenium in the reduction behavior of Ru-promoted Co/TiO_2 catalysts was investigated. Ru could facilitate the reduction but had no effect on water production during reduction.

Keywords: Reduction, cobalt catalyst, titania, Fischer-Tropsch

INTRODUCTION

Due to their high activities [1], high selectivity to linear hydrocarbons and low activities for the competitive water-gas shift (WGS) reaction [2,3], supported cobalt (Co) catalyst is considered to be one of the most important catalysts for Fischer-Tropsch synthesis (FTS) as well as carbon monoxide (CO) hydrogenation. During the past decade, titania-supported Co catalysts have been widely investigated by many authors, especially for the application of FTS in a continuously stirred tank reactor (CSTR) [4-6]. In general, to increase the

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catalytic activity of the Co catalysts, many promoters such as ruthenium (Ru), zirconium (Zr), lanthanum (La), rhodium (Rh), boron (B), and platinum (Pt) have been investigated. It has been reported that a variety of these promoters can increase the reducibility of Co, preserve the activity by preventing the formation of coke, exhibit cluster and ligand effects, act as a source of hydrogen spillover and enhance the dispersion. It should be mentioned that the active form of Co catalysts is the reduced Co metal surface atom. Although Ru promotion appears to enhance the rate of FTS, no studies have specifically addressed how Ru promotes the reaction. Understanding how Ru can modify the catalyst properties could lead to the design of more robust and active Co catalysts.

This investigation focused on giving a better understanding of the roles of Ru on reduction behavior of the Ru-promoted Co/TiO_2 catalyst. The impact of Ru promotion on the reducibility of Co in the absence and presence of water vapor was also investigated.

EXPERIMENTAL

Catalyst preparation

The unpromoted-Co/TiO_2 and Ru-promoted (CoRu/TiO_2) catalysts were prepared by the incipient wetness impregnation using cobalt nitrate [$Co(NO_3)\bullet 6H_2O$] and ruthenium(III) nitrosyl nitrate [$Ru(NO)(NO_3)_3$] as precursors. The TiO_2 used contained 81 mol % of anatase phase and 19 mol % of rutile phase (Ishihara Sangyo, Japan). The catalyst samples were dried at 110°C for 12 h and calcined in air at 500°C for 4 h.

Catalyst pretreatments

Standard reduction

Standard reduction of the calcined catalyst was conducted in a fixed-bed flow reactor under differential conditions (no gradient in the catalyst bed) at 1 atm using a temperature ramp from ambient to 350°C at 1°C/min and holding at 350°C for 10 h in a gas flow having a space velocity of 16,000 h^{-1} and consisting of H_2. The high space velocity of the H_2 flow was applied to insure that the partial pressure of water vapor in the catalyst bed produced by cobalt oxide reduction would be essentially zero.

Hydrothermal treatment

In order to evaluate the stability of catalysts and impacts of water vapor during reduction, hydrothermal treatment was also conducted during standard reduction above. In addition, besides using pure H_2, mixtures of H_2 and water vapor (5-10 vol.%) were also applied separately at the same reduction condition as mentioned above.

Catalyst nomenclature

The nomenclature used for the catalyst samples in this study is following:

Co/Ti : Unpromoted cobalt catalyst on the titania support,
CoRu/Ti : Ru-promoted cobalt catalyst on the titania support,
(C) : Calcined catalyst sample,
(RW0), (RW5) and (RW10): Reduced catalyst samples with no water vapor, 5 vol.% of water vapor, and 10 vol.% of water vapor added during standard reduction, respectively.

Catalyst characterization

BET surface area was determined using N_2 adsorption at 77 K in a Micromeritics ASAP 2010.

X-ray diffraction was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α (λ = 1.54439 Å).

The Raman spectra of the samples were collected by projecting a continuous wave laser of argon ion (Ar^+) green (514.532 nm) through the samples exposed to air at room temperature.

Temperature-programmed reduction of calcined samples was carried out using 50 mg of a sample and a temperature ramp from 35 to 800°C at 5°C/min. The carrier gas was 5% H_2 in Ar.

Reaction

CO hydrogenation (H_2/CO = 10/1) was performed to determine the overall activity of the catalyst samples. Hydrogenation of CO was carried out at 220°C and 1 atm. A flow rate of H_2/CO/He = 20/2/8 cc/min in a fixed-bed flow reactor under differential conditions was used.

Table 1

Characteristics and catalytic properties of samples

Samples	BET surface area (m^2/g)[a]	Reducibility (%)[b]	Total H_2 chemisorption (μmol/g cat.)[c]	Reaction rate (x10^2 gCH_2 g cat. h^{-1})[d]		CH_4 Selectivity (%)	
				Initial[e]	Steady state[f]	Initial	Steady state
TiO_2	49	-	-	-	-	-	-
Co/Ti-C	34	78	4.8	25	21	94	96
Co/Ti-RW0	32	74	3.3	23	20	94	94
Co/Ti-RW5	32	72	3.2	23	20	98	98
Co/Ti-RW10	30	68	3.0	23	19	95	96
CoRu/Ti-C	37	87	7.5	37	36	99	98
CoRu/Ti-RW0	37	83	6.7	36	36	98	98
CoRu/Ti-RW5	37	77	5.9	36	35	97	97
CoRu/Ti-RW10	36	75	5.2	36	34	99	99

[a] Measurement error ± 5%

[b] Reducibility was measured during TPR at 30-800°C. The reduced samples were recalcined under the original calcination conditions prior to TPR.

[c] H_2 chemisorption was performed to determine the number of reduced Co surface atoms.

[d] CO hydrogenation was carried out at 220°C, 1 atm and H_2/CO/Ar = 20/2/8 cm^3/min.

[e] After 5 min of reaction

[f] After 5 h of reaction

RESULTS AND DISCUSSION

The present study was conducted in order to investigate the roles of Ru in the reduction behavior of CoRu/TiO_2 catalysts. The characteristics and catalytic properties during CO hydrogenation are summarized in Table 1. It was observed that upon Co loading and Ru promotion, there was no significant change in the BET surface areas, suggesting no pore blocking or phase changes in the TiO_2 support. The XRD peaks (not shown) of all calcined samples at 26, 37,48, 55, 62, 69, 71 and 75° (TiO_2 in anatase form) and 27, 36, 42 and 57° (TiO_2 in rutile form) were observed. As expected, XRD peaks of Co_3O_4 species were also detected at 36, 46 and 65° after calcination of samples. However, after reduction with or without water vapor added, only diffraction peaks at 37 and 63° corresponding to CoO were observed. Thus, XRD revealed that Ru was well dispersed in the catalyst samples. A similar trend was also observed in Raman spectroscopy as seen for XRD results. It was found that the TiO_2 support exhibited the Raman bands at 640, 514 and 397 cm^{-1} (anatase form) and 445 cm^{-1} (rutile form). The calcined samples showed Raman bands of the TiO_2 support along with two shoulders at 690 and 480 cm^{-1}, assigned to Co_3O_4 species. Raman spectra for all reduced samples exhibited the similar Raman bands as seen for the calcined ones indicating Co_3O_4 on the surface. In order to determine the number of reduced Co metal surface atoms, H_2 chemisorption was performed as seen in Table 1. It indicated that water vapor during reduction apparently resulted in both lesser number of reduced Co metal surface atoms and reducibility due to Co-support compound formation (Co-SCF) as reported in our previous works [7, 8]. It should be noted that Ru promotion may result in enhanced activities during CO hydrogenation without changing selectivity of products due to increased number of reduced Co metal surface atoms. Roles of the Ru promotion can be discussed further based on the TPR profiles as shown in Figs 1 (for the unpromoted catalysts) and 2 (for the Ru-promoted catalysts).

It can be observed that Ru can only facilitate the reduction of cobalt oxide species due to the hydrogen spillover effect resulting in lower reduction temperatures. It is known that water vapor as a byproduct of a reduction process can enhance the Co-SCF [7, 8]. Thus, water vapor was also introduced during reduction in order to investigate the roles of Ru promotion as well. As seen from Figs 1 and 2, increased amounts of water vapor during reduction had no effect on the reduction behavior of both unpromoted catalysts and Ru-promoted catalysts, indicating no shift of reduction temperatures. In summary, Ru promotion can only facilitate the reduction of cobalt oxide species but has no effect on water vapor produced during reduction.

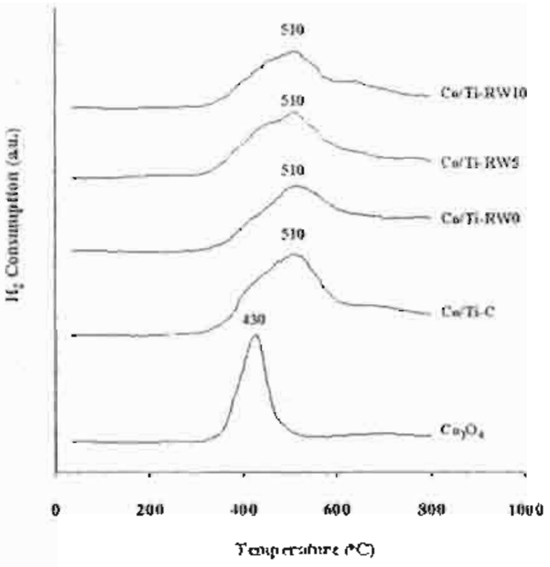

Fig. 1. TPR profiles of the unpromoted cobalt catalysts

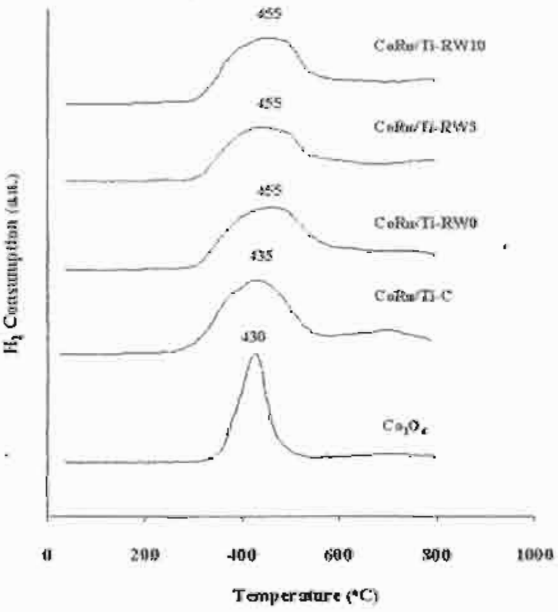

Fig. 2. TPR profiles of the Ru-promoted cobalt catalysts

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Elucidation of reduction behaviors for Co/TiO$_2$ catalysts with various rutile/anatase ratios

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The present study revealed effects of various rutile/anatase ratios in titania on the reduction behaviors of titania-supported cobalt catalysts. It was found that the presence of rutile phase in titania could facilitate the reduction process of the cobalt catalyst. As a matter of fact, the number of reduced cobalt metal surface atoms, which is related to the overall activity during CO hydrogenation increased.

1. INTRODUCTION

Supported cobalt (Co) catalysts are preferred for Fischer-Tropsch synthesis (FTS) based on natural gas [1] due to their high activities for FTS, high selectivity for long chain hydrocarbons and low activities for the competitive water-gas shift (WGS) reaction. Many inorganic supports such as silica, alumina, titania and Zeolites have been extensively studied for supported Co catalysts for years. It is known that in general, the catalytic properties depend on reaction conditions, catalyst compositions, types of inorganic supports and the degrees of metal dispersion as well. It is reported that during the past decades, titania-supported Co catalysts have been investigated widely by many authors, especially for the application of FTS in a continuously stirred tank reactor (CSTR) [2-4]. However, it should be noted that titania itself has different crystalline phases such as anatase, brookite and rutile phase. Thus, the differences in compositions of crystalline phases could result in changes on physical and chemical properties of titania, then consequently for the dispersion of cobalt. In order to give a better understanding of those, the focus of this present study was to investigate the cobalt dispersion on titania consisting various ratios of rutile/anatase. The Co/TiO$_2$ was prepared and then characterized using different characterization techniques.

2. EXPERIMENTAL

2.1 Material preparation

Preparation of titania support

The various ratios of rutile:anatase in titania support were obtained by calcination of pure anatase titania (obtained from Ishihara Sangyo, Japan) in air at temperatures between 800-1000°C for 4 h. The high space velocity of air flow (16,000 h^{-1}) insured the gradual phase transformation to avoid rapid sintering of samples. The ratios of rutile:anatase were determined by XRD according to the method described by Jung et al. [5] as follows: