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Effect of zirconia-modified titania consisting of different phases on characteristics and catalytic properties of Co/TiO_2 catalysts

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The TiO_2 supports consisting of different phases were modified with ZrO_2 for TiO_2-supported Co catalysts. It showed that modification on the pure anatase TiO_2 resulted in decreased activities, but increased chain growth probability. In contrary, the modification on mixed phase TiO_2 resulted in increased activities without effects on selectivity.

KEY WORDS: cobalt catalyst; titania; support; zirconia modification; CO hydrogenation.

1. Introduction

In general, a supported catalyst usually consists of three components; (i) a catalytic phase, (ii) a promoter, and (iii) a support or carrier. As known, the catalytic properties apparently depend upon the components as mentioned above. The catalytic phase can be metals, metal oxides and so on. It can be used under a specified catalytic reaction. It is known that the catalytic performance is usually elevated using a promoter such as a noble metal. Besides the catalytic phase and promoter, it should be mentioned that a support could play a crucial role based on the catalytic performance. Basically, a support material acts as a carrier for the catalytic phase to be well dispersed on it. However, due to the supporting effects along with dispersion of the catalytic phase, the properties of a catalyst could be altered with the various supports used.

It is reported that many inorganic supports such as silica [1–4], alumina [5–9], titania [10–15], zirconia [16], and zeolites [17] have been extensively studied for years. During the past decades, titania-supported cobalt catalysts have been investigated by many authors, especially for the application of Fischer–Tropsch synthesis (FTS) in a continuously stirred tank reactor (CSTR) [10–12]. However, it should be noted that titania itself has different crystalline phases such as anatase, brookite and rutile phases. In our previous work, we reported that different crystalline phase compositions of titania could play important roles on the catalytic performance of titania-supported cobalt catalysts during CO hydrogenation [14,15,18]. In the present work, the modification of the titania support was extensively investigated. Since zirconia promotion appears to increase the rate of FTS on cobalt catalysts with silica support [19,20] and with alumina support [5], thus, it would be interesting to investigate the effect of zirconia modification on titania supports containing different phases.

In this study, a series of titania-supported cobalt catalysts was prepared with a range of zirconia concentrations in the titania supports. The titania supports used were in the pure anatase form and in the mixture of anatase and rutile phases. The catalysts were then characterized and tested for CO hydrogenation activity. The product selectivity was also further investigated.

2. Experimental

2.1. Materials

2.1.1. Zr-modified TiO_2 support

The Zr-modified titania supports were prepared by the impregnation method. There were two kinds of the titania supports used [(i) pure anatase phase and (ii) mixed anatase (81%) and rutile (19%) phases] from Ishihara Sangyo, Japan. First, Zr was impregnated into the support using a solution of zirconium (IV) *n*-propoxide (70 wt% in *n*-propanol, Alfa Aesar) to produce Zr-modified titania supports having 0.5, 1, and 5 wt% of ZrO_2. Second, the Zr-modified supports were calcined at 350 °C for 2 h (ramp rate 5 °C/min) prior to impregnation of cobalt.

2.1.2. Co/Zr-modified TiO_2 catalysts

Cobalt nitrate $[Co(NO_3)_2{\cdot}6H_2O]$ was dissolved in deionized water and impregnated into the support as mentioned above to give a final catalyst with 20 wt% cobalt. The catalyst precursor was dried at 110 °C for 12 h and calcined in air at 500 °C for 4 h.

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2.2. Catalyst nomenclature

The nomenclature used for the supports and catalyst samples in this study is as follows:

R0: TiO_2 support consisting of pure anatase phase
R19: TiO_2 support consisting of 81% anatase and 19% rutile phases
R0Z*i*: Zr-modified R0 with *i* wt% of ZrO_2
R19Z*i*: Zr-modified R19 with *i* wt% of ZrO_2
Co/support: supported cobalt catalyst on various supports as mentioned above

2.3. Characterization

2.3.1. BET surface area

BET surface area of the samples with various rutile: anatase ratios of titania was performed to determine if the total surface area changes. It was determined using N_2 adsorption at 77 K in a Micromeritics ASAP 2010.

2.3.2. X-ray diffraction

XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439$ Å). The spectra were scanned at a rate of 2.4°/min in the range $2\theta = 20$–$80°$.

2.3.3. Temperature-programmed reduction

TPR was used to determine the reduction behaviors of the catalyst samples. It 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. A cold trap was placed before the detector to remove water produced during the reaction.

2.3.4. Scanning electron microscopy and energy dispersive X-ray spectroscopy

SEM and EDX were used to determine the sample morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL model JSM-5800LV was applied. EDX was performed using Link Isis series 300 program.

2.3.5. Transmission electron microscopy (TEM)

The dispersion of cobalt oxide species on the titania supports were determined using a JEOL-TEM 200CX transmission electron spectroscopy operated at 200 kV with 200 k magnification.

2.3.6. Hydrogen chemisorption

Static H_2 chemisorption at 100 °C on the reduced samples was used to determine the number of reduced surface cobalt metal atoms. This is related to the overall activity of the samples during CO hydrogenation. Gas volumetric chemisorption at 100 °C was performed using the method described by Reuel and Bartholomew [21]. The experiment was performed in a Micromeritics ASAP 2010 using ASAP 2010C V3.00 software.

2.4. Reaction

CO hydrogenation (H_2/CO = 10/1) was performed to determine the overall activity and selectivity of the catalyst samples. It 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. A relatively high H_2/CO ratio was used to minimize deactivation due to carbon deposition during reaction. Typically, 20 mg of a catalyst sample was reduced in situ in flowing H_2 (30 cc/min) at 350 °C for 10 h prior to the reaction. Reactor effluent samples were taken at 1 h intervals and analyzed by GC. In all cases, steady-state was reached within 5 h. In fact, the reaction test for each sample was performed at least three times. The average point was reported.

3. Results and discussion

3.1. Characteristics

The BET surface areas of the modified supports and catalysts samples are shown in table 1. For the modified R0 (pure anatase) samples, the surface areas decreased from 70 to 47 m^2/g upon the amounts of zirconia loading. Based on the results of BET surface areas as shown in table 1, it showed that the surface area essentially slightly decreased with 0.5% Zr. The sintering was not the cause since the calcination temperature was only 350 °C. The decrease in surface area should be due to the pore blockage. The modified R19 (mixed phases) also showed decreases in surface areas from 49 to 33 m^2/g with zirconia modification. It can be observed that the surface areas of the catalyst samples on the various unmodified and modified supports slightly decreased with corresponding to the content of supports used. It should be noted that no significant changes in surface areas of samples were observed. After calcination, the various supports were characterized using XRD as shown in figure 1. For the R0 support, XRD peaks of the anatase phase of titania at 25°

Table 1
BET surface areas of various supports and catalyst samples

Supports	BET surface area (m^2/g)[a]	Catalyst samples	BET surface area (m^2/g)[a]
R0	70	Co/R0	52
R0Z0.5	55	Co/R0Z0.5	43
R0Z1	53	Co/R0Z1	42
R0Z5	47	Co/R0Z5	36
R19	49	Co/R19	34
R19Z0.5	38	Co/R19Z0.5	27
R19Z1	34	Co/R19Z1	25
R19Z5	33	Co/R19Z5	25

[a] Measurement error is ±5%.

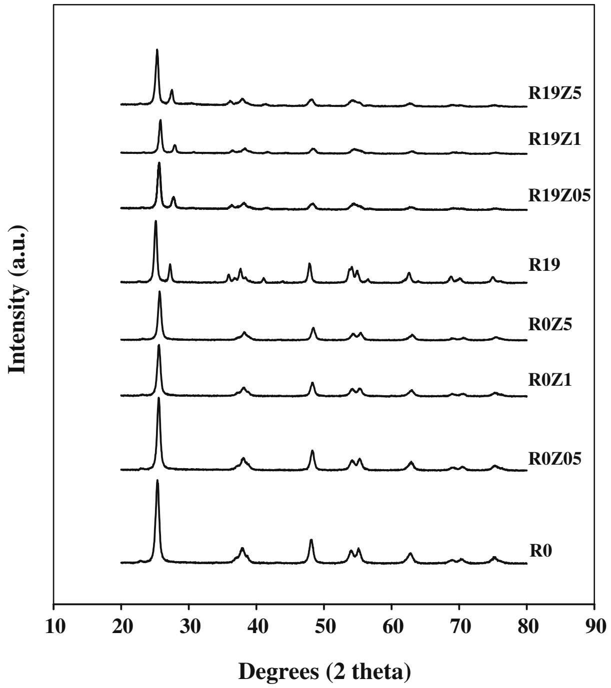


Figure 1. XRD patterns for different TiO$_2$ supports consisting of various amounts of ZrO$_2$ loading.

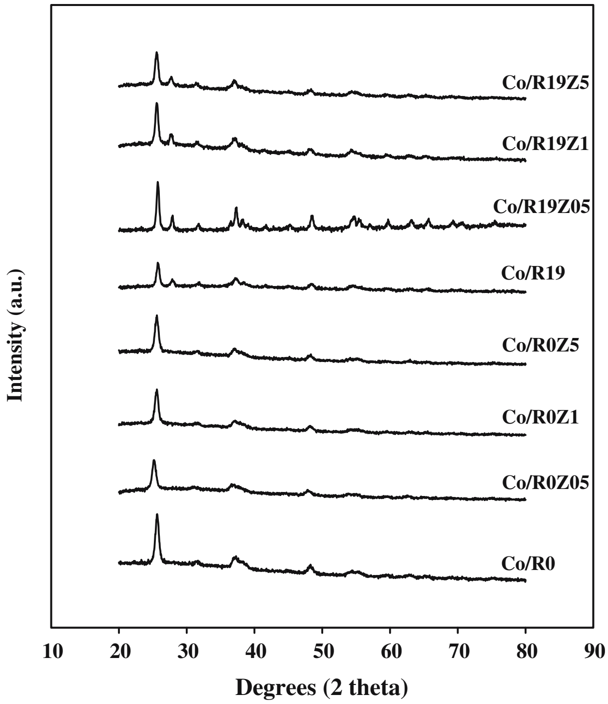


Figure 2. XRD patterns of Co/TiO$_2$ samples consisting of various amounts of ZrO$_2$ loading in TiO$_2$ supports.

(major), 37°, 48°, 55°, 56°, 62°, 71°, and 75° were evident. After the modification of R0 support, it was found that their characteristic peaks were still identical with those for the unmodified R0 support. This suggested that the zirconia was in the highly dispersed form. For the R19 support, it can be observed that besides the XRD peaks of pure anatase titania as mentioned before, the peaks at 28° (major), 36°, 42°, and 57° were detected. These peaks were assigned to the presence of rutile phase in the support along with the anatase phase. None of XRD peaks for zirconia was detected in the modified supports. After impregnation with the cobalt precursor and calcination, all catalyst samples were again identified using XRD. The XRD patterns of all calcined samples are shown in figure 2. It was observed that all calcined samples exhibited XRD peaks, which were identical with those for the corresponding modified supports as shown in figure 1. However, only weak intensity of XRD peak at 31° assigning to the presence of Co$_3$O$_4$ was detected. Therefore, based on the XRD results, it indicated that the presence of zirconia and cobalt oxide species were in the highly dispersed forms.

SEM and EDX were also conducted in order to study the morphologies and elemental distribution of the samples, respectively. In general, there was no significant change in morphologies and elemental distribution of all samples after calcination. The typical SEM micrograph and EDX mapping for Co/R19Z1 sample are illustrated in figure 3. Apparently, the Co oxide species exhibited well distribution on the surface of the support. In order to determine the dispersion of Co oxide species on the various modified supports, a more powerful technique such as TEM was applied to all samples. The TEM micrographs for Co/R0Z1, Co/R0Z5, Co/R19Z1, and Co/R19Z5 samples are shown in figure 4. The dark spots represented cobalt oxide species dispersing on the various modified supports after calcination of samples. The diameter of cobalt oxide particles was ca. 15, 16, 18, and 24 nm for Co/R0Z1, Co/R0Z5, Co/R19Z1, and Co/R19Z5 samples, respectively. Based on the TEM results, it indicated that the sizes of cobalt oxide species were slightly larger for those dispersing on the R19 supports than on the R0 supports as also reported in our previous work [14].

TPR was performed in order to determine the reduction behaviors of samples. The TPR profiles for all catalyst samples are shown in figure 5. The reduction temperatures for initial, final, and maximum temperatures are shown in table 2. It was found that there was only one reduction peak, however, at different reduction temperatures for all calcined samples. The one reduction peak can be assigned to the overlap of two step reduction of Co$_3$O$_4$ to CoO and then to Co metal [9,13]. Upon the TPR conditions, the two-step reduction may or may not be observed. Based on the TPR profiles, it indicated that for the zirconia-modified R0 supports, the reduction temperatures essentially shifted to the higher ones. Thus, zirconia modification of the R0 supports retarded the reduction of cobalt oxide species. Considering the zirconia modification of the R19 supports, it appeared that no effect on reduction behaviors of cobalt oxide species was found. However, it was confirmed that the

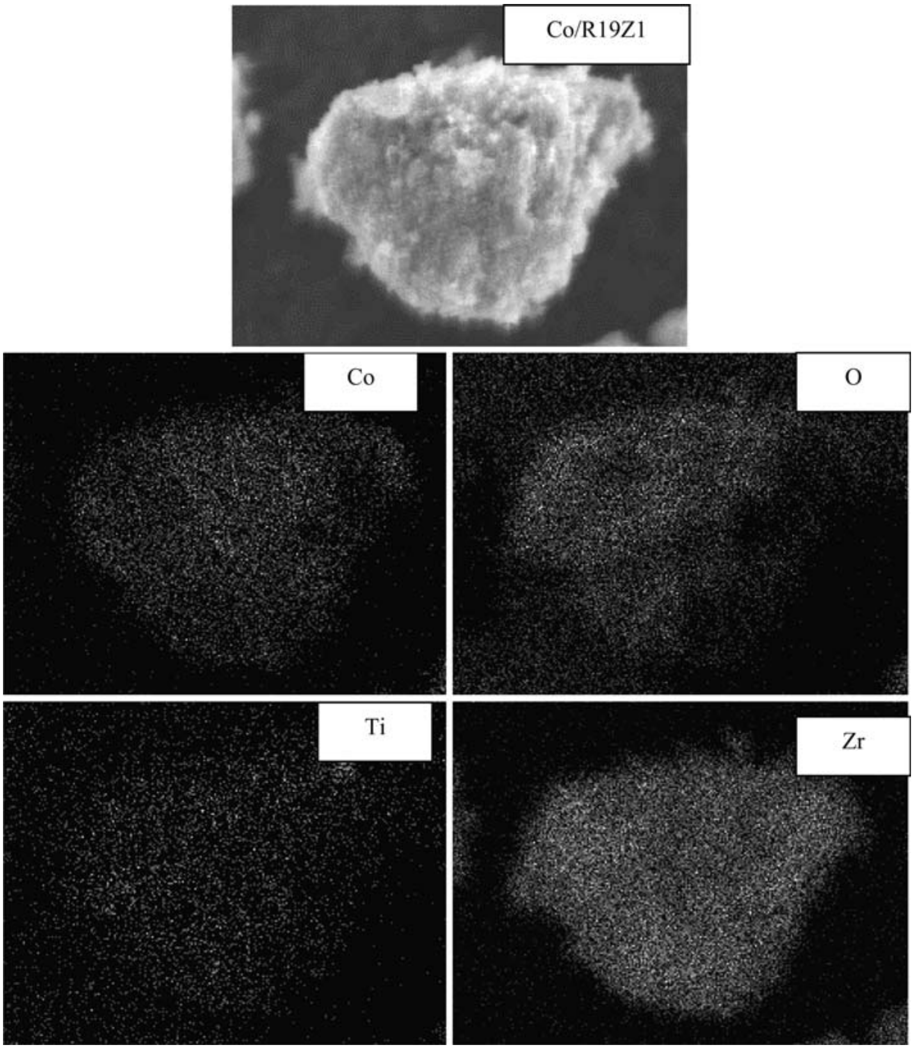


Figure 3. A typical SEM micrograph and EDX mapping for Co/R19Z1 sample.

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

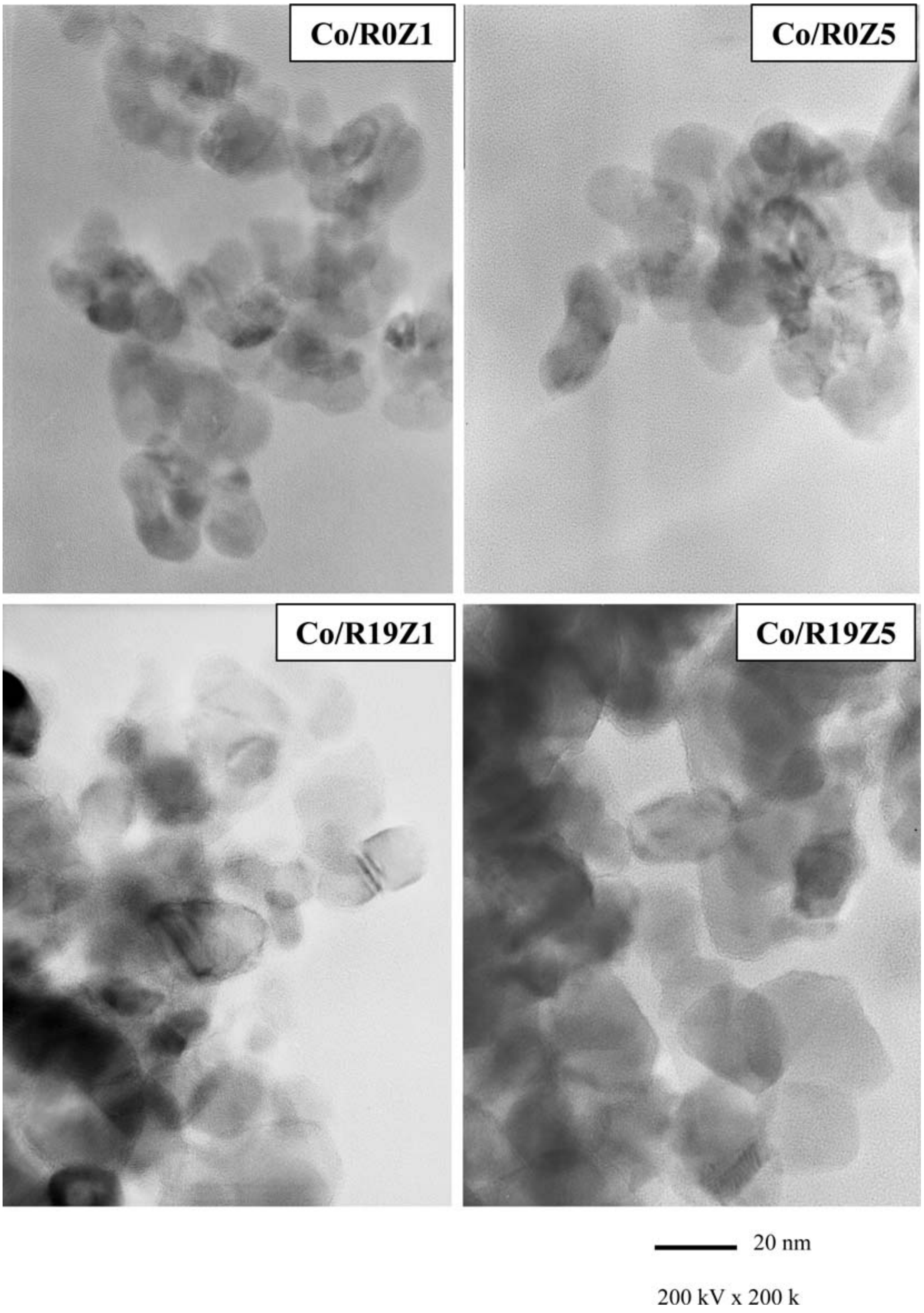


Figure 4. TEM micrographs for Co/TiO$_2$ samples consisting of various amounts of ZrO$_2$ loading in TiO$_2$ supports.

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

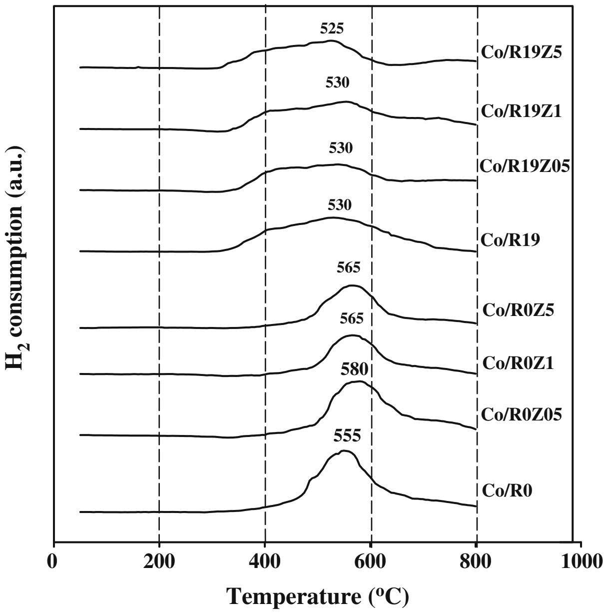


Figure 5. TPR profiles for Co/TiO$_2$ samples consisting of various amounts of ZrO$_2$ loading in TiO$_2$ supports.

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

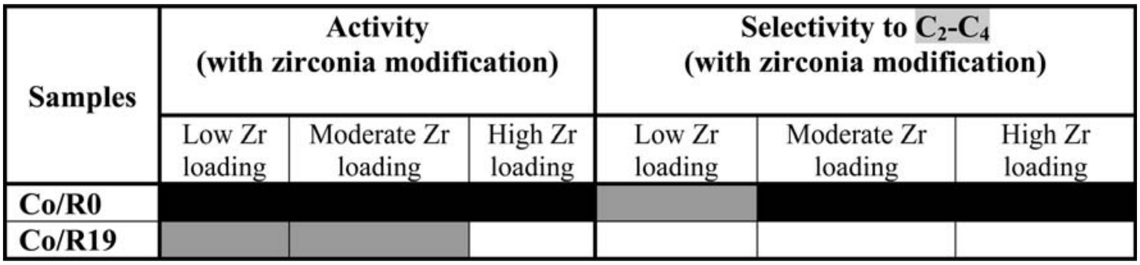
Catalyst samples	Rate[a] (gCH$_2$/g$_{cat.}$h)		CH$_4$ selectivity (%)		C_2–C_4 selectivity (%)	
	Initial[b]	SS[c]	Initial[b]	SS[c]	Initial[b]	SS[c]
Co/R0	1.4	0.8	71	68	29	32
Co/R0Z0.5	1.2	0.2	32	31	68	69
Co/R0Z1	0.02	0.02	97	96	3	4
Co/R0Z5	0.01	0.01	98	90	2	10
Co/R19	3.3	2.6	98	98	2	2
Co/R19Z0.5	3.7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

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