

# CO<sub>2</sub> hydrogenation over micro- and mesoporous oxides supported Ru catalysts

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We prepared relatively uniform supported Ru catalysts by ion-exchange and CVD methods, using an NaY zeolite and a mesoporous FSM-16 as substrates, and carried out CO<sub>2</sub> hydrogenation. They showed high activity for CO<sub>2</sub> hydrogenation. A Ru-ion-exchanged catalyst showed high activity for methanol production. Co addition promoted methanol formation.

**Keywords:** CO<sub>2</sub> hydrogenation, Ru catalyst, porous material, particle size, Co additive, methanol

## 1. Introduction

We have studied CO<sub>2</sub> hydrogenation over supported noble metal catalysts in order to clarify the relationship between CO<sub>2</sub> hydrogenation reactivity and the surface structure of the catalysts [1–3]. From an environmental point of view, it is desirable to produce oxygenates and/or higher hydrocarbons selectively from CO<sub>2</sub> and H<sub>2</sub>. One of our concerns is whether the product distribution (selectivity for oxygenates) is seriously affected by the particle size of the surface metal sites or not. There are many reports which deal with the influence of the particle size (or distribution) on catalytic reactivity. Arakawa et al. examined the catalytic reactivity of SiO<sub>2</sub>-supported Rh catalysts in CO hydrogenation varying the average Rh metal particle size, and claimed that the product distribution drastically changed with the metal particle size (from 1.6 to 3.7 nm) and oxygenates were formed on the particles around 2.5 nm [4]. However, Kellner and Bell claimed that CO hydrogenation proceeded in the same stepwise polymerization mechanism on the Ru particles larger than 1.9 nm [5]. Cho et al. claimed that the size of clusters consisting of 20–60 Ru atoms did not make so much difference in activity of ethane hydrogenolysis [6]. In this work, we used micro- and mesoporous materials with regular pore structures as substrates and tried to make the metal particles grow in the pore so that the size of metal particles was controlled by the pore diameter. Over these catalysts we carried out the reaction.

In our previous report, we prepared Rh-ion-exchanged zeolite catalysts (RhY) and carried out CO<sub>2</sub> hydrogenation. We found that Rh atoms formed relatively uniform particles

as large as 3.3 nm in diameter. RhY showed extraordinarily high CO<sub>2</sub> conversion and it also produced methanol at low temperature [2]. It is well known that Ru catalysts also have high ability toward CO hydrogenation and the reaction mechanism of CO hydrogenation over Ru catalysts has widely been studied [7]. Therefore, in this work, we adopted Ru as active metal species and carried out CO<sub>2</sub> hydrogenation reaction. As explained above, in order to control the metal particle size of Ru, we used an NaY zeolite and an FSM-16 as substrates and introduced Ru species in them by either an ion-exchange method or a CVD method. NaY zeolite has faujasite type structure, which includes a supercage as large as 1.3 nm in diameter. FSM-16 is a mesoporous silicate, which is prepared from a layered silicate (kanemite) [8]. FSM-16 has regular hexagonal straight channels, whose walls consist of amorphous silicate. The diameter of the channel is determined by the kind of surfactant, which is used during synthesis. We carried out CO<sub>2</sub> hydrogenation over these catalysts and elucidated the effect of the particle size as well as that of the preparation method. We also compared the characteristic reactivity of Ru catalysts with that of Rh catalysts.

As will be explained in the later sections, some supported Ru catalysts produce a relatively large amount of methanol but the selectivity was low, because the activity for methane was much higher. In the literature, Co addition to Ru catalysts promoted oxygenates formation from CO + H<sub>2</sub> [9,10], as well as it promoted hydroformylation activity [11], because adsorbed CO species on Ru–Co bimetallic sites were active for oxygenates formation. CO<sub>2</sub> hydrogenation over Ru catalysts was expected to proceed through an adsorbed CO intermediate [12] as in the case of Rh [13,14]. So it is expected that addition of Co to Ru catalysts modifies the reactivity of the adsorbed CO intermediate and promotes oxygenate production from CO<sub>2</sub> + H<sub>2</sub>.

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We prepared Co-doped Ru catalysts and elucidated the influence of Co on CO<sub>2</sub> hydrogenation reactivity.

## 2. Experimental

Three kinds of preparation methods were adopted in this work, that is, ion exchange, CVD, and impregnation. The ion exchange was carried out according to the literature as follows [15]: a Ru precursor (Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>, Strem, 99%) was dissolved into weakly acidic water (pH = 4.5, adjusted by diluted HCl(aq)). An appropriate amount (3 g/1000 cm<sup>3</sup>) of an NaY type zeolite (SK-40, Nishio) was suspended in the Ru solution. This suspension was kept stirred at ambient temperature for 48 h. After the ion-exchange treatment, the catalyst was filtrated, washed and dried at 373 K overnight. The dried catalyst was treated under vacuum at 673 K for 4 h and subsequently reduced in H<sub>2</sub> at 673 K for 1 h. The catalyst was cooled in H<sub>2</sub>, then exposed in the air and kept in a container (RuY, Ru content = 3 wt%). The concentration of Ru supported on the zeolite was estimated from the amount of Ru which remained in the filtrated solution. The concentration of Ru in the residue was measured by the atomic adsorption method (Seiko SAS760).

For the CVD method, porous materials like NaY and FSM-16 were selected as substrates. An FSM-16 substrate was synthesized according to the literature [8]. Ru<sub>3</sub>(CO)<sub>12</sub> was used as a metal precursor. The CVD treatment was carried out according to the literature [16]. Prior to the attachment of the cluster, the substrates were evacuated at 673 K for 2 h in order to eliminate physically adsorbed water. Subsequently, the Ru cluster was mixed with the substrate powder under Ar (99.9995%). The mixture was kept stirred at 403 K for 48 h until the bright orange color of the Ru cluster disappeared. At this point, we regarded all the Ru clusters as attached on the substrate. The catalysts prepared by these methods are represented as Ru<sub>3</sub>/NaY and Ru<sub>3</sub>/FSM (Ru content = 2 wt%).

As a reference, we also used impregnated Ru catalysts and a co-precipitated Cu catalyst (Nissan Girdler Co., MF No. 2). The Cu catalyst is composed of 85% CuO, 5% ZnO, 5% Cr<sub>2</sub>O<sub>3</sub>, and 5% Al<sub>2</sub>O<sub>3</sub> (in weight), and it was the same as the one we reported as an efficient catalyst for methanol production [17]. Impregnated Ru catalysts were prepared in a conventional way. The support (NaY or FSM-16) was evacuated at 473 K for 1 h, then the substrate was immersed in an aqueous solution of Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>. Subsequently, the catalyst was dried under vacuum at 675 K for 4 h, then reduced in a flow of H<sub>2</sub> at 675 K for 1 h. We call the catalysts prepared by impregnation as Imp-Ru/NaY and Imp-Ru/FSM (Ru content = 3 wt%).

Addition of Co to RuY was conducted by ion exchange, as follows: the reduced RuY was suspended in the solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and kept stirred at 343 K for 24 h until the ion-exchange reaction completed, then the catalyst was filtered, washed and dried at 373 K for 12 h. Subsequently,

it was treated under vacuum at 673 K for 4 h (Co–RuY). The loading of Co was determined by atomic adsorption of the filtered solution in the same manner as Ru in RuY. The concentration of Co was Co/Ru = 1, 3, and 5 in atomic ratio, and such catalysts are denoted as Co–RuY(1), Co–RuY(3), and Co–RuY(5), respectively. The amount of dissolved Ru was also monitored by atomic adsorption, and it was found that no back-dissolution of Ru into the Co solution occurred.

The CO<sub>2</sub> hydrogenation reaction was carried out by a fixed-bed high-pressure reactor equipped with on-line gas chromatographs (GC). The calcined catalyst (1 g) was set in the reactor and was pretreated under the flow of hydrogen (100 ml/min) at 723 K for 0.5 h. After the reactor was cooled to 333 K in H<sub>2</sub>, H<sub>2</sub> was replaced by the reactant gas mixture (H<sub>2</sub>/CO<sub>2</sub> = 3, Ar (1%)) was included as an internal standard. Then the total pressure was raised to 3 MPa. The reaction was carried out at 423 K. For analysis of the products, we used an on-line GC with four kinds of columns: 2% squalane/activated carbon (TCD detector) for inorganic components, VZ-10 (FID detector) for hydrocarbons, 10% PEG1500/Silimalite TPA (FID detector) for alcohols, and 10% PEG6000/Silimalite TPA (FID detector) for carboxylic acids.

The XRD measurement (Mac Science MXP18) was carried out to confirm the structure of substrates.

The particle size and shape of the catalyst was also monitored by TEM operated at an accelerating voltage of 400 kV (Jeol JEM-4000FXII). The samples were reduced under a H<sub>2</sub> flow for 0.5 h at 723 K prior to the observation. Subsequently, they were suspended in 2-propanol using an ultrasonic wave. Some of the finest part of the suspension was dropped onto a copper microgrid covered with Collodion film (200 mesh, Nisshin EM Co., Ltd.).

The number of active sites was determined by the volumetric H<sub>2</sub> adsorption. The catalyst was prereduced at 723 K for 0.5 h under the flow of H<sub>2</sub> (100 ml/min). Subsequently, the catalyst was evacuated at 673 K for 1–2 h. After the catalyst was cooled to room temperature, the adsorption of H<sub>2</sub> was carried out.

## 3. Results

### 3.1. Supported Ru catalysts

#### 3.1.1. CO<sub>2</sub> hydrogenation over supported Ru catalysts

We carried out CO<sub>2</sub> hydrogenation over various supported Ru catalysts. Figure 1 and table 1 show the results. We found that on some catalysts, the reactivity varied with reaction time. Therefore, for such catalysts, we show two kinds of data in table 1: one was obtained when the catalyst showed the highest CO<sub>2</sub> conversion, and the other was obtained when the highest selectivity for methanol was observed.

It is well known that the Cu catalysts exhibit high performance for methanol production from CO<sub>2</sub> and H<sub>2</sub>. In

order to compare the activity, we examined a Cu catalyst, which was the most efficient among the catalysts reported in our previous paper [17]. Usually, the reaction proceeds

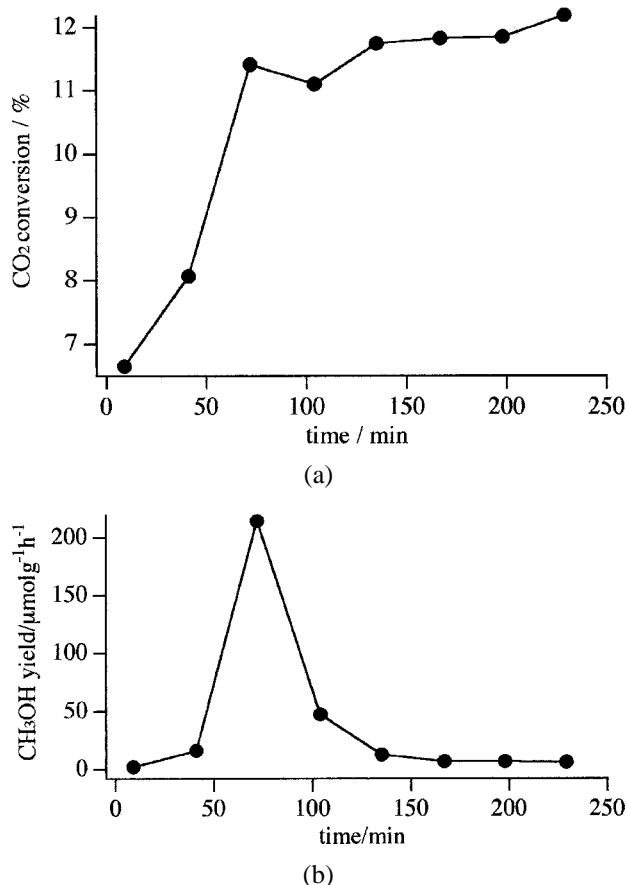


Figure 1. The result of CO<sub>2</sub> hydrogenation over 3 wt% RuY: (a) CO<sub>2</sub> conversion and (b) CH<sub>3</sub>OH yield. The reaction conditions: H<sub>2</sub>/CO<sub>2</sub> = 3, total pressure = 3 MPa, temperature = 423 K, flow rate = 100 ml/min, catalyst = 1 g.

at higher temperature in the Cu system to obtain practical conversion. In the same condition as that in this work, the activity of the Cu catalyst is extremely low, as shown in table 1. In contrast, the RuY catalyst showed high CO<sub>2</sub> conversion (12%). Moreover, a large amount of methanol was formed at 70 min (figure 1).

We also prepared an impregnated Ru/NaY catalyst (Imp-Ru/NaY) and carried out the same reaction. The result is shown in table 1. The total activity is nearly 1/4 of that for RuY. When we compare by TOF (turnover frequencies = specific rate of reaction per unit surface metal site) based in H<sub>2</sub> adsorption (table 2), the total activity is high and is almost in the same level as that for RuY. Meanwhile, the productivity toward methanol was much lower than that of RuY (table 1).

We already reported the study on the CO<sub>2</sub> hydrogenation reactivity of 6 wt% RhY (Rh-ion-exchanged Y-type zeolite catalysts) [2]. There, we reported that RhY catalyst showed high CO<sub>2</sub> conversion (ca. 7%), and we claimed it was 40 times higher than that for a 6 wt% Rh/SiO<sub>2</sub> catalyst (a SiO<sub>2</sub>-supported impregnated Rh catalyst). However, the RuY catalyst showed even higher activity than RhY though the loading of metal was smaller on RuY (3 wt%) than that on RhY (6 wt%), which means that the Ru sites in RuY have essentially higher activity for CO<sub>2</sub> hydrogenation than the Rh ones in RhY. Takeishi et al. found that a Raney ruthenium catalyst showed high CO<sub>2</sub> hydrogenation activity under a similar condition to that of this work and they claimed that their catalysts had enough activity for practical use [12]. Though our reaction conditions were not completely the same as those in [12], we can say that our catalysts (RuY) also had a similarly high activity, compared with the Raney ruthenium catalyst in [12].

We carried out the same reaction over supported Ru catalysts which were prepared by a CVD method (Ru<sub>3</sub>/NaY).

Table 1  
The results of CO<sub>2</sub> hydrogenation over various catalysts.<sup>a</sup>

Sample	Loading		TOF (h <sup>-1</sup> )	Selectivity	CO <sub>2</sub> conv. <sup>b</sup>
	Ru (wt%)	Co/Ru <sup>c</sup>	Total	CH <sub>3</sub> OH (%)	(%)
Cu/Zn/Cr/Al	—	—	—	—	0.025
Imp-Ru/NaY	3	—	67.3	0.3	3.0
RuY	3	—	49.4	2.9	12.4
			52.3	0.1	12.2
Ru <sub>3</sub> /NaY	2	—	63.6	0.1	10.0
			13.4	1.8	2.3
Imp-Ru/FSM	3	—	9.5	0	0.17
Ru <sub>3</sub> /FSM	2	—	21.9	0.5	2.9
			19.4	0.8	2.4
Co-RuY(3)	4	3	20.4	6.9	4.9
			28.9	1.3	7.0
Co-RuY(1)	3	1	56	7.0	3.3

<sup>a</sup> Reaction conditions: CO<sub>2</sub>/H<sub>2</sub> = 1/3, total pressure = 3 MPa, flow rate = 100 ml/min, temperature = 423 K, catalyst = 1 g. TOF was calculated basing on the H<sub>2</sub> adsorption (table 2).

<sup>b</sup> CO<sub>2</sub> conversion.

<sup>c</sup> Atomic ratio.

Table 2  
The results of H<sub>2</sub> adsorption and TEM.

Sample	Loading		H/Ru	Average particle size (nm)	
	Ru (wt%)	Co/Ru <sup>a</sup>		H <sub>2</sub> adsorption	TEM
RuY	3	–	0.51	2.6	2.2
Ru <sub>3</sub> /NaY	2	–	0.62	2.2	2.4
Ru <sub>3</sub> /FSM	2	–	0.40	3.3	3.6
Imp-Ru/NaY	3	–	0.10	13	4.7
Imp-Ru/FSM	3	–	0.16	8	–
Co–RuY(3)	4	3	0.45	–	–
Co–RuY(1)	3	1	0.14	–	–

<sup>a</sup> Atomic ratio.

The results are shown in table 1. The Ru<sub>3</sub>/NaY catalyst showed a relatively high total TOF. Although the TOF of methane on Ru<sub>3</sub>/NaY was even higher than that on RuY, production of methanol was seriously suppressed.

For the Ru<sub>3</sub>/FSM catalyst, the total conversion was lower than that of Ru<sub>3</sub>/NaY. But the total TOF was comparable to those of other supported Ru catalysts. It is found that the formation of methanol was not a favorable process on Ru<sub>3</sub>/FSM either.

We examined the performance of the Imp-Ru/FSM catalyst. The catalyst exhibited much lower activity than Ru<sub>3</sub>/FSM and formed no alcohol.

### 3.1.2. H<sub>2</sub> adsorption and TEM observation of supported Ru catalysts

One of the aims of this work is to study the relationship between particle size and catalytic reactivity. In order to determine the average particle size, we carried out H<sub>2</sub> adsorption and TEM observation. In this work, we used porous materials, and in some cases, the metal particles were formed inside the cages. If a metal particle blocks the entrance of a pore, hydrogen may not reach the metal particles located deeply inside the pores, and the average particle size deduced from dispersion may be overestimated, so we adopted two kinds of methods in order to determine the particle size.

The results of H<sub>2</sub> adsorption are shown in table 2, together with TEM results. Figure 2 shows TEM images. In figure 2 (a) (RuY) and (b) (Ru<sub>3</sub>/NaY), we find very fine particles and the particle sizes found in both images look similar. We measured the size of discernible particles and estimated the average size (table 2). The average particle sizes estimated from TEM agree well with those of H<sub>2</sub> adsorption in RuY and Ru<sub>3</sub>/NaY. Determined particle sizes are nearly the same (around 2.2–2.4 nm) between RuY (figure 2(a)) and Ru<sub>3</sub>/NaY (figure 2(b)).

In Ru<sub>3</sub>/FSM, we find relatively uniform particles, as shown in figure 2(c). The average size from TEM is 3.6 nm, which is smaller than the pore diameter (3.9 nm determined by XRD). So it is suggested that the Ru atoms formed uniform particles inside the pores.

In Imp-Ru/NaY, various sizes of particles from 2.5 to 8.4 nm are found (figure 2(d)). The average particle size observed by TEM is much smaller than that deduced from

H<sub>2</sub> adsorption. One of the possible explanations is that large particles formed on the outer surface blocked the pores and prohibited hydrogen atoms from entering inside the cages. Consequently, the average particle size calculated from adsorbed H<sub>2</sub> was overestimated.

### 3.2. Co-doped supported Ru catalysts

As we see in the previous sections, methane was dominantly formed from CO<sub>2</sub> + H<sub>2</sub> over supported Ru catalysts. In order to modify the reactivity, we tried addition of Co into RuY by an ion-exchange method. The results of CO<sub>2</sub> hydrogenation are shown in table 1 and figure 3. Addition of Co suppressed the total activity. Such a degradation of activity is often observed in doped catalysts [3]. The selectivity for methanol was improved by Co addition. When excess amount of Co (Co–RuY(3), Co/Ru = 3) was doped, the production of methanol exhibited a maximum at the initial stage of the reaction (figure 3) and the absolute amount of methanol yield was higher than that of RuY. For Co–RuY(1) (Co/Ru = 1), the formation of methanol increased as the reaction time and the selectivity for methanol finally reached as high as 7% (figure 3).

### 3.3. CO<sub>2</sub> + CO hydrogenation

We examined the effect of CO addition into the reactant gas. The experiment was conducted in the same way, as explained in section 2, except that the reactant gas contained 1.8% of CO. The results are shown in table 3. The CO<sub>2</sub> conversion was seriously suppressed by CO addition for both RuY and Co–RuY. This fact suggested that affinity between CO and Ru sites was so good that a majority of the surface Ru sites were covered by adsorbed CO species derived from gas-phase CO. In the literature, it is reported that the mechanism of CO<sub>2</sub> hydrogenation is completely different from that of CO hydrogenation, that is, CO<sub>2</sub> hydrogenation begins with monocarbonyl species; on the other hand, CO hydrogenation begins with multicarbonyl species [18]. As a result, activation of H<sub>2</sub> molecules was suppressed in CO-containing reactant gas and total conversion showed a relatively low value. Because of increase of adsorbed CO on the surface, the selectivity for methanol and higher hydrocarbons was promoted. In our previous report, we carried out a similar experiment for RhY and found that when we added 1.8% CO into the reactant gas, hardly no influence on product distribution was observed on RhY and a decrease in CO<sub>2</sub> conversion was relatively small [3]. Therefore, we can conclude that Ru sites had a much higher ability to adsorb CO than Rh sites. In other words, on RuY, the main reaction was switched from CO<sub>2</sub> hydrogenation to CO hydrogenation by the presence of only 1.8% of CO in the reactant gas. In the case of Co-doped supported Ru catalysts, addition of CO in the reactant gas brought about a similar trend, that is, significant decrease in CO<sub>2</sub> conversion and promotion of selectivity for higher hydrocarbons. The difference due to the Co additive was

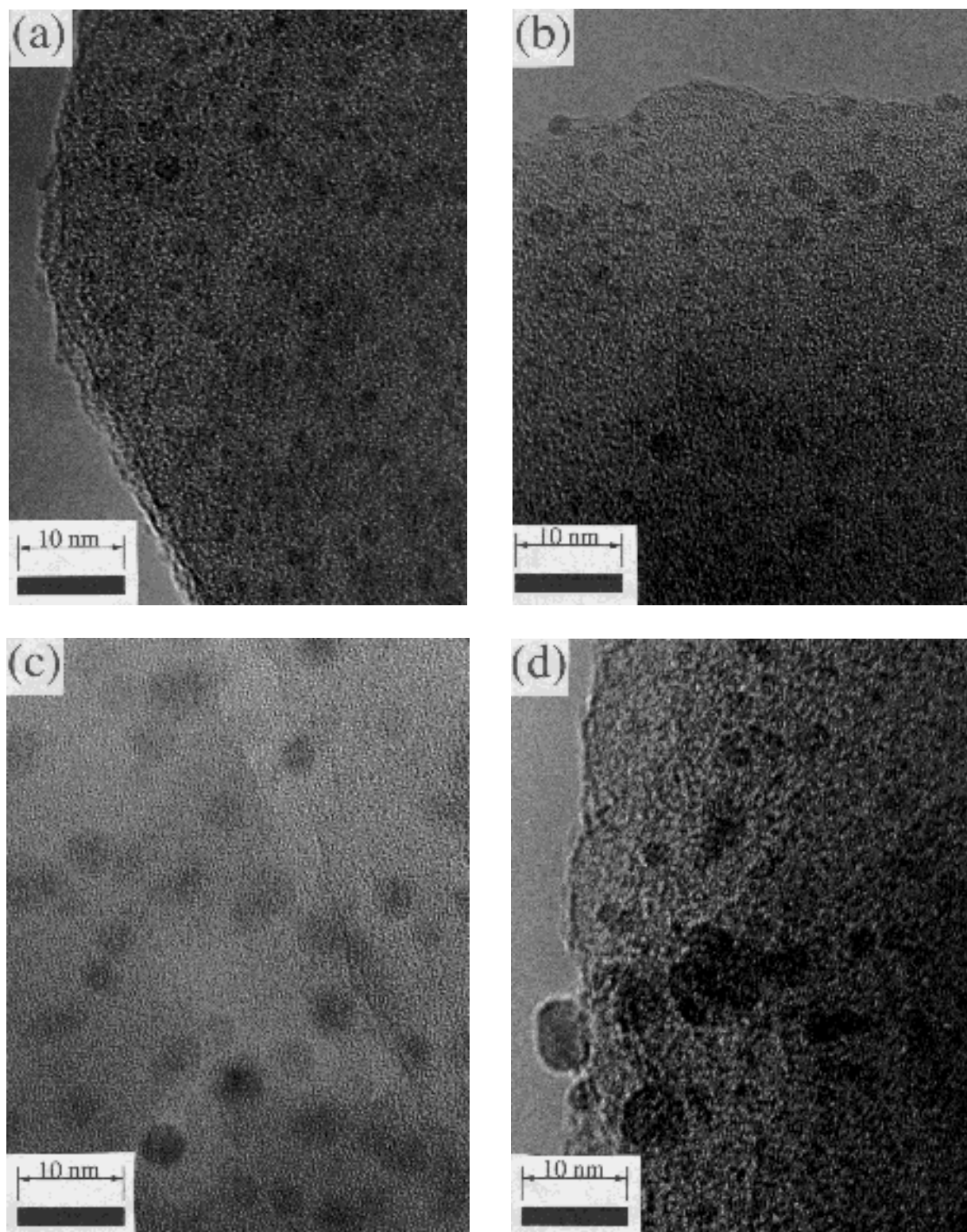


Figure 2. The TEM images observed for (a) RuY, (b) Ru<sub>3</sub>/NaY, (c) Ru<sub>3</sub>/FSM, and (d) Imp-Ru/NaY.

found in the promotion of CO formation rather than that of oxygenates. From the fact that CO addition to reactant gas decreased the total activity of Co–RuY like in the case of RuY, it is suggested that CO addition switched the reaction from CO<sub>2</sub> hydrogenation to CO hydrogenation in Co–RuY.

## 4. Discussion

### 4.1. Catalytic reactivity and particle size

Initially we tried to prepare supported Ru catalysts with uniform Ru metal particles. For this purpose, we used metal

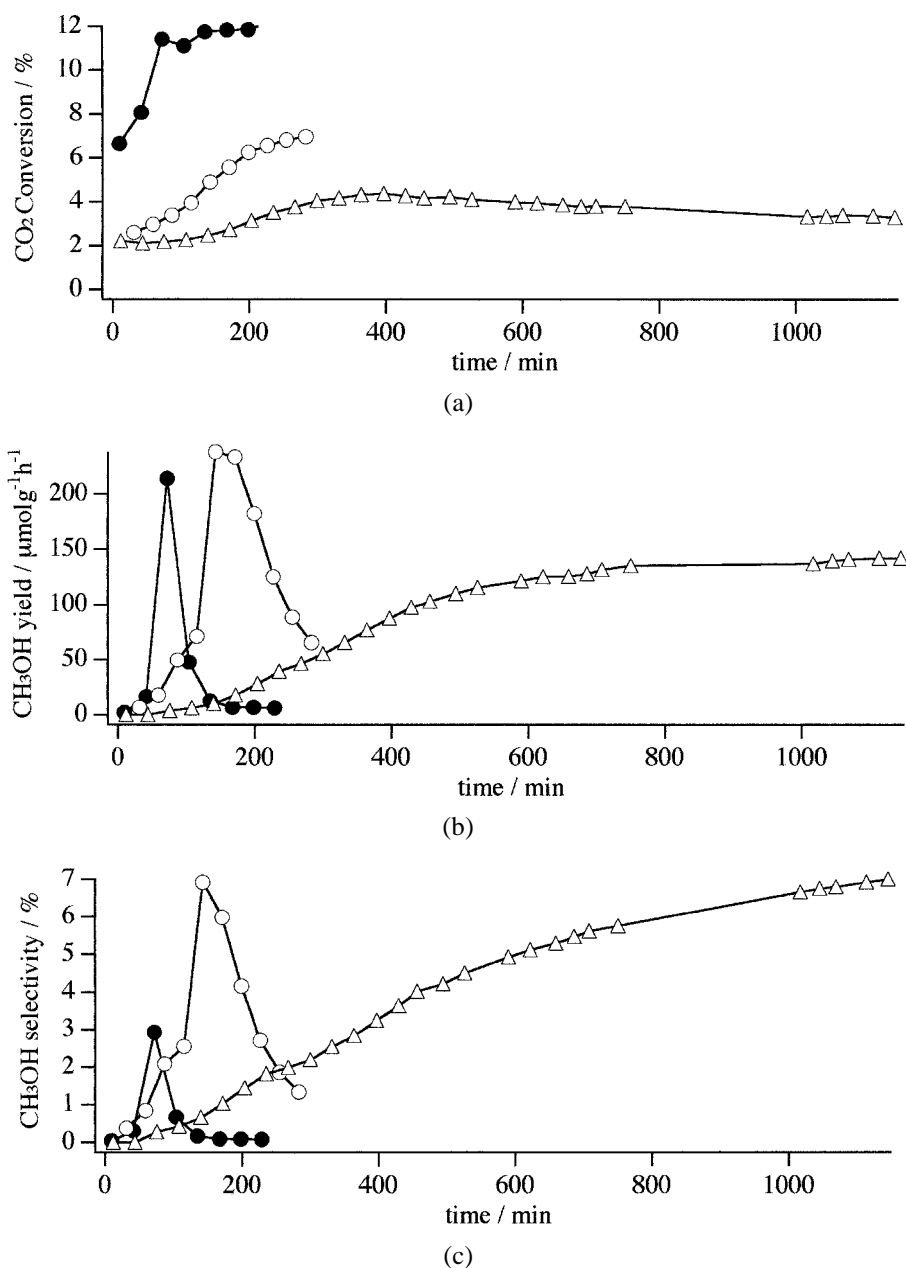


Figure 3. The results of CO<sub>2</sub> hydrogenation over RuY (●), Co–RuY(3) (○), and Co–RuY(1) (Δ): (a) CO<sub>2</sub> conversion, (b) CH<sub>3</sub>OH yield, and (c) CH<sub>3</sub>OH selectivity. Reaction conditions: H<sub>2</sub>/CO<sub>2</sub> = 3, total pressure = 3 MPa, temperature = 423 K, flow rate = 100 ml/min, catalyst = 1 g.

Table 3  
The results of CO<sub>2</sub> + CO hydrogenation.<sup>a</sup>

Sample	Loading		CO <sub>2</sub> conversion (%)	Selectivity (%)						
	Ru (wt%)	Co/Ru <sup>b</sup>		CH <sub>4</sub>	CO	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	Hydrocarbons		
								C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
RuY	3	—	0.54	60.7	0.0	9.0	2.7	4.9	10.3	12.2
Co—RuY(5)	3	5	0.39	65.5	11.8	1.6	0.0	6.9	9.5	4.5

<sup>a</sup> Reaction conditions: catalyst = 1 g, H<sub>2</sub>/CO<sub>2</sub> = 3, CO = 1.8%, total pressure = 3 MPa, flow rate = 100 ml/min, temperature = 423 K.

<sup>b</sup> Atomic ratio.

oxides with regular pore structures and tried to build metal particles inside the cage, so that the size of metal particles could be controlled by the pore diameter. In order to embed

metal atoms inside the pores, ion-exchange and CVD methods were adopted. For determination of the particle size, we examined the used (already used for CO<sub>2</sub> hydrogenation)

tion reaction) catalysts. It is reported that in some catalyst, aggregation of metal sites occurred during reaction [19]. A similar behavior was also observed in RhY catalysts [2]. So we think, we had better compare particle sizes by those observed after reaction. The Ru metal particles in Y-type zeolite were found to be located outside the cage because the diameter of Ru particles (2.2–2.6 nm) was larger than that of the pores (1.3 nm), regardless of the method of preparation (table 2, figure 2 (a) and (b)). Though the particles on the Y-type zeolite were not formed inside the cage, these particles were relatively uniform (figure 2 (a) and (b)). For Ru<sub>3</sub>/FSM, judging from the particle size deduced from the dispersion and TEM, the particles existed inside the channels because the diameter of pores (straight channels) in FSM-16 was about 3.9 nm (calculated from XRD data) and that of Ru particles was about 3.3–3.6 nm (H<sub>2</sub> adsorption, TEM). Moreover, from TEM observation, it is found that the Ru particles formed in Ru<sub>3</sub>/FSM were so uniform (figure 2(c)) that it is clear that the size of these particles was controlled by pores. As a reference, we prepared conventionally impregnated catalysts and observed TEM. As shown in figure 2(d), the size of Ru particles in Imp-Ru/NaY was not uniform. It included various sizes of Ru particles. So not only the structure of the support but also the preparation method influences the particle size distribution of metal sites. Conventionally, the size of supported metal particles was controlled by varying the concentration of the metal in the catalyst [4]. But in this work, we controlled the particle size by varying the size of pores of the substrate for almost the same metal loading.

Concerning the reactivity, we have obtained a couple of new aspects in this work. One is about the reactivity of RuY and Ru<sub>3</sub>/NaY. Both catalysts exhibited very high activity. When we compare by TOF, they also showed similar total activity. The main product was methane for both catalysts. The most distinct difference was found in the formation of methanol. Compared by the highest TOF for methanol production, RuY showed more than five times higher activity than Ru<sub>3</sub>/NaY. As mentioned above, the particle size was almost the same for RuY and Ru<sub>3</sub>/NaY. So the difference in methanol formation activity was not attributed to the difference in the average particle size. We also carried out CO<sub>2</sub> hydrogenation over Imp-Ru/NaY. Imp-Ru/NaY included different sizes of particles, most of which are thought to be located on the outer surface of the zeolite. The total TOF was comparably high for Imp-Ru/NaY, but the selectivity for methanol was low like for Ru<sub>3</sub>/NaY. Therefore, it is expected that the ion-exchange method can produce very specific sites on the surface where methanol formation was promoted. As we reported in the previous paper [2], the Rh-ion-exchanged zeolite catalysts (RhY) had an ability to produce methanol. In that case, the main product was methane and the Rh metals after reaction were as large as 3.3 nm. Although the total activity was proportional to the surface area of Rh particles, the activity for methanol was rather independent of the metal surface area. We concluded that the active Rh sites for methanol were

located either on defects of the substrate or in some specific sites inside the cage. In the supported Ru catalysts case, methanol was produced exclusively on RuY. Taking into account the RhY case, we concluded that it was the preparation method that brought about the difference in productivity of methanol. In other words, in the process of ion exchange, the metal precursors were atomically adsorbed on the ion-exchange sites or defects of the substrate. The majority of Ru atoms formed large particles by subsequent reduction. However, the Ru species adsorbed on defects remained still in a highly dispersed form. On the other hand, in the course of CVD preparation, the metal atoms were attached in the form of clusters and generation of such atomically dispersed Ru sites could not happen. If we assume that methanol was formed on such specific sites, it is understandable that only RuY showed high ability toward methanol formation.

In spite of the large difference in total productivity, the specific activity (TOF) was similar among three kinds of Y-zeolite supported Ru catalysts (RuY, Ru<sub>3</sub>/NaY, and Imp-Ru/NaY). The TOF of Ru<sub>3</sub>/FSM was low compared with Y-zeolite supported Ru catalysts. We think that it is due to the difference of the support, rather than difference in intrinsic activity of Ru particles. If we compared TOF between Ru<sub>3</sub>/FSM and Imp-Ru/FSM, the former showed two times higher activity for CO<sub>2</sub> hydrogenation than the latter. We can think of two explanations for this phenomenon. One is the difference in dispersion. In the literature, it is reported that in some cases, the activity is influenced by dispersion [5]. The second explanation is that the location of Ru particles affected the activity. Judging from dispersion, Ru particles in Ru<sub>3</sub>/FSM were expected to be formed inside the pore, meanwhile, most of Ru particles in Imp-Ru/NaY were thought to be formed on the outer surface. We think that the pores and embedded Ru particles formed reaction sites where activation of CO<sub>2</sub> was promoted.

#### 4.2. Effect of Co addition

As mentioned above, the supported Ru catalysts had a high ability toward methane formation from CO<sub>2</sub> + H<sub>2</sub>, but the active sites for methanol production were rather specific sites. It was strongly suggested that interaction between Ru and the support modified the catalytic activity. So it is probable that addition of other metals into Ru catalysts can modify the reactivity. In the literature, it is reported that addition of Co into Ru sites is effective for oxygenate production from CO + H<sub>2</sub> as well as for hydroformylation [9–11]. And CO<sub>2</sub> hydrogenation over Ru catalysts is expected to proceed through adsorbed CO intermediates [12]. Therefore, addition of Co was expected to be effective for modification of the reactivity. In fact, Co addition promoted the selectivity for methanol as high as 7% in Co–RuY(1) and the absolute amount of formed methanol was kept high for a long period (figure 3). For the CO hydrogenation reaction and hydroformylation, it is reported that doped Co

atoms formed Co–Ru bimetallic sites and on these sites, associative hydrogenation of adsorbed CO species, as well as insertion of CO species into alkyl groups were promoted. For CO<sub>2</sub> hydrogenation, we expect a similar effect, that is, adsorbed CO intermediates formed on Ru–Co sites associatively hydrogenated and methanol was formed. When enough amount of Co was added (Co/Ru = 3), such bimetallic sites were formed at the initial stage of the reaction, so the highest activity for methanol was observed at 150 min. On the other hand, if the amount of Co was comparable to that of Ru (Co/Ru = 1), interaction between Ru and Co was incompletely formed at the initial stage. The bimetallic sites gradually formed as the reaction proceeded, accompanied by the promotion of methanol formation.

In some cases, additives have an effect to promote adsorption of CO<sub>2</sub> [3]. In the case of Co–RuY, it is found that addition of carbon monoxide to the reactant gas switched the reaction path from CO<sub>2</sub> hydrogenation to CO hydrogenation. This result also suggests that addition of Co is not so effective for CO<sub>2</sub> conversion to adsorbed CO. The effect of Co additive is rather found in stabilization of adsorbed CO during reaction. The precise reaction mechanism is now under investigation.

## 5. Conclusion

We studied the CO<sub>2</sub> hydrogenation reactivity of various supported Ru catalysts, in order to elucidate the relationship between metal particle size and reactivity. A Ru-ion-exchanged zeolite catalyst (RuY) showed high activity for CO<sub>2</sub> hydrogenation and it also produced methanol. A catalyst prepared by CVD (Ru<sub>3</sub>/NaY) also exhibited high activity but it formed little methanol. An impregnated Ru catalyst (Imp-Ru/NaY) did not produce so much methanol either. It is concluded that preparation method rather than metal particle size influenced the reactivity.

We succeeded to prepare relatively uniform metal particles in the channels of FSM-16 by CVD (Ru<sub>3</sub>/FSM).

Compared with an impregnated catalyst (Imp-Ru/FSM), it is suggested that pores and embedded metal particles formed some active sites for reaction.

We found that Co addition to RuY is effective for methanol production from CO<sub>2</sub> and H<sub>2</sub>. It is suggested that the effect of Co was to stabilize adsorbed CO during the reaction.

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