Water gas shift reaction of reformed fuel over supported Ru catalysts

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Abstract

Precious metal catalysts (Ir, Pd, Pt, Rh and Ru) supported on Al_2O_3 and Ru catalysts on CeO_2, La_2O_3, MgO, Nb_2O_5, Ta_2O_5, TiO_2, V_2O_5 and ZrO_2 were investigated for water gas shift reaction of reformed gas. Ru/V_2O_3 catalyst reduced at $400\,°C$ in H_2 demonstrated the highest activity for the shift reaction without producing methane. The activities for the shift reaction over Ru catalysts supported on different oxides were not correlated with BET surface area or Ru dispersion, but the activity depended on the chemical character of oxide supports. The catalyst supported on a strongly basic or acid oxide is not effective for the shift reaction. In the same series of catalysts like Ru/V_2O_3, the activity systematically changed with BET surface area and Ru dispersion.
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1. Introduction

Water gas shift reaction (reaction (1)) has been studied as a CO removal technique of reformed fuels for application to fuel cells. The reformed fuel generally contains a large amount of CO, which can be significantly reduced with the shift reaction at low temperatures:

$$CO + H_2O \leftrightarrows CO_2 + H_2, \quad \Delta H_{298} = -41\,kJ/mol \tag{1}$$
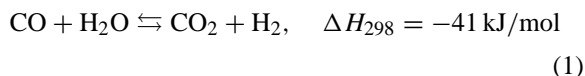
Although Cu catalysts have been well known as active catalysts for the shift reaction [1,2], precious metal catalysts are also evaluated frequently owing to their potential stability in oxidizing atmospheres. Recently,

small-scale hydrogen production units have been increasingly requested for applications to fuel cell systems. Such applications involve frequent start-ups and shut-downs. The catalysts for the shift reaction are, therefore, sometimes exposed to water and/or oxygen containing atmospheres at low temperatures. Copper-based catalysts are generally more active for the shift reaction, but are more unstable to oxidant gases than precious metals. It is, therefore, important to develop highly stable Cu-based catalysts or highly active precious metal catalysts. It is reported that Au supported on TiO_2, Fe_2O_3 and ZrO_2 [3–5], Pt supported on ZrO_2 [6] and Ru supported on Fe_2O_3 and La_2O_3 [7–10], demonstrated high activity for the shift reaction. Precious metal catalysts supported on CeO_2 are also reported for the shift reaction [11–13]. However, Zalc et al. [14] reported that a large amount of H_2 leads to the irreversible reduction of CeO_2 and to catalyst deactivation. It is necessary to improve

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the activity for the shift reaction and to decrease the loading weight of costly precious metals on supports. Although these precious metal catalysts have been often evaluated in gaseous mixtures of CO and H_2O, the activity is also influenced by coexisting H_2 or CO_2 in reformed fuels. In this study, we investigated precious metal catalysts supported on several kinds of oxides for the shift reaction in a model gas of reformed methanol or reformed methane fuels. The behavior of the Ru-based catalysts for the shift reaction in reformed gas has been discussed in relation with the support interaction.

2. Experimental

2.1. Catalyst preparation

Supported precious metal catalysts were prepared by the impregnation method. Alumina (γ-Al_2O_3) support was impregnated with each aqueous solution of $IrCl_4$, $Pd(NH_3)_2(NO_2)_2$, $Pt(NH_3)_2(NO_2)_2$, $Rh(NO_3)_3$ and $Ru(NO_3)_3$. Other supports (CeO_2, La_2O_3, MgO, Nb_2O_5, Ta_2O_5, TiO_2, V_2O_5 and ZrO_2) were impregnated with an aqueous solution of $Ru(NO_3)_3$. These materials were dried at $120\,^\circ$C and then calcined at $500\,^\circ$C for 3 h in air. Other Ru catalysts supported on V_2O_5 were also prepared by the same method and were reduced at 400, 500, 650 and $800\,^\circ$C for 3 h in 10% H_2/He flow. Each loading weight of precious metals was 2 wt.%.

2.2. Characterization

The specific surface area of each catalyst was evaluated by the BET method using nitrogen adsorption and the crystalline phase of each catalyst was determined by X-ray diffraction (XRD). Dispersion of Ru was determined by adsorption of CO to Ru species at $25\,^\circ$C after reduction at $400\,^\circ$C for 1 h in 10% H_2/N_2. Morphologies of the Ru particles on catalysts were monitored by transmission electron microscopy (TEM).

2.3. Catalytic activity

The catalytic activities for the water gas shift reaction were measured in a conventional fixed bed flow reactor at atmospheric pressure after reduction at $400\,^\circ$C

for 1 h in 10% H_2/N_2. Ru/V_2O_5 in the working state is expressed as Ru/V_2O_3, since V_2O_5 was completely reduced to V_2O_3. The feed gas for the shift reaction was model gas of reformed methanol or reformed methane with steam (CO, CO_2, H_2, H_2O and N_2 balance). The gas composition was analyzed by on-line TCD and FID gas chromatography. CO and H_2 conversions and CH_4 yield from CO and CO_2 were defined as follows:

$$CO \text{ conversion } (\%) = \frac{(F_{CO\,in} - F_{CO\,out}) \times 100}{F_{CO\,in}} \quad (2)$$

$$H_2 \text{ conversion } (\%) = \frac{(F_{H_2\,in} - F_{H_2\,out}) \times 100}{F_{H_2\,in}} \quad (3)$$

$$CH_4 \text{ yield } (\%) = \frac{F_{CH_4\,out} \times 100}{F_{CO\,in} + F_{CO_2\,in}} \quad (4)$$

where $F_{i\,in}$ and $F_{i\,out}$ denote flow rates of ith species at the inlet and outlet of the reactor, respectively.

3. Results and discussion

3.1. Thermodynamic consideration of the shift reaction

The equilibrium of the shift reaction is easily achieved in the presence of an active catalyst around $250\,^\circ$C or higher temperatures [2]. The equilibrium gas composition of the reaction system was estimated by considering CO, CO_2, H_2 and H_2O with or without methane production. Base metal catalysts like Cu are not active for methane formation, so they are controlled by the partial equilibrium without methane. Fig. 1 shows CO and H_2 conversions and CH_4 yield from CO and CO_2. The CO conversion decreased and H_2 conversion increased with a rise in temperature, since the reaction is exothermic, as shown in reaction (1). The shift reaction at low temperatures is effective for conversion of CO and H_2O to CO_2 and H_2. On the other hand, the production of methane in the equilibrium evaluation significantly changes the picture of the gas composition. Though the CO conversion was 100% below $350\,^\circ$C, large amounts of CO and CO_2 were converted to CH_4, since methane is one of the stable species at low temperatures. This result reveals that the methane production is dominant over catalysts having activity for the methanation and that a large amount of H_2 is consumed even if catalysts
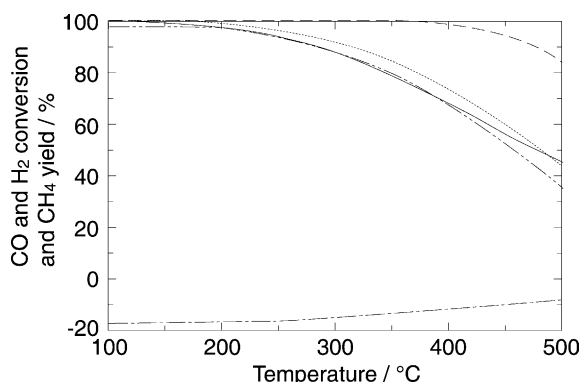
Fig. 1. Equilibrium conversion of CO and H_2 and yield of CH_4: (line 1) CO conversion and (line 2) H_2 conversion without CH_4 formation; (line 3) CO conversion, (line 4) H_2 conversion and (line 5) CH_4 yield with CH_4 formation. Initial gas composition: CO, 5%; CO_2, 3.1%; H_2, 28.1%; H_2O, 13.8%; N_2, balance; S.V., $6400\,h^{-1}$. (—) Line 1; (- · -) line 2; (- - -) line 3; (- · · -) line 4; (· · ·) line 5.

have high activity for the shift reaction. Some of the precious metal catalysts such as Ru-based ones tend to have high activity for the methanation. Therefore, it is important to inhibit the methanation with high activity for the shift reaction.

### 3.2. Water gas shift reaction over supported precious metal catalysts

Cu-based catalysts have been popularly employed for the water gas shift reaction. However, the disadvantage of the Cu catalysts is the deactivation of catalytic activity upon oxidation or hydration of the active component. The adsorption of oxygen and/or water is weaker for the precious metal catalysts than for the base metal catalysts. Thus, stable operation could be possible by using precious metal catalyst systems even when frequent start-ups and shut-downs are executed.

The conversion of CO was evaluated for the various precious metal catalysts supported on Al_2O_3 in a model gas of reformed methanol. The conversion of CO does not only lead to the shift reaction but also to the methanation. Fig. 2(a–e) summarizes CO conversion and CH_4 yield over these catalysts. The conversion of CO on the Ir/Al_2O_3 catalyst was very low. A small amount of CO was produced by reverse water gas shift reaction (reverse direction of reaction (1)) over Pd/Al_2O_3 at around 250 °C. The Pt/Al_2O_3 cat-

alyst converted CO of ca. 40% without methanation. Though Ru and Rh catalysts had similar catalytic characters with high activities, the Ru catalyst had high activity at lower temperature, 250 °C. The CO conversion of the Ru/Al_2O_3 was the highest, while it was active for the methanation reaction. However, we consider that high activity of the Ru catalyst will become attractive for the shift reaction if methanation is inhibited.

3.3. Water gas shift reaction over supported Ru catalysts

Activities of precious metal catalysts are often significantly changed by chemical interaction with support oxides. Modification of catalytic characteristics has been investigated by using several support oxides. Fig. 3(a–h) summarizes CO conversion and CH_4 yield over the Ru catalysts in a model gas of reformed methane. Every supported Ru catalyst converted large amounts of CO and CO_2 above 400 °C, but the catalyst was characterized generally by high activity for the formation of CH_4. The Ru catalysts were not suitable for shift reactions above 400 °C. The Ru catalysts supported on CeO_2 and Ta_2O_5 commonly demonstrated steep rises in CO conversion and CH_4 yield from 250 °C to the levels over 99 and 75%, respectively, where the principle reaction was methanation from CO and CO_2 (reactions (5) and (6)). The CH_4 yield gradually decreased from 330 °C:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{5}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{6}$$
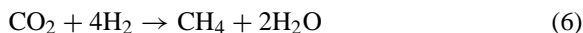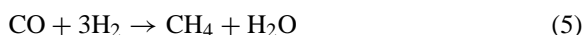
The CO conversion over Ru/La_2O_3 and Ru/MgO was low below 300 °C, while the high conversion above 400 °C again led to high CH_4 yields over 40%. The CO conversion and CH_4 yield over Ru/Nb_2O_5 increased from 300 °C to the level over 90 and 40% at 425 °C, respectively. The above-mentioned Ru catalysts were active only for the methanation. On the other hand, Ru catalysts supported on TiO_2, V_2O_3 and ZrO_2 had some activity for the shift reaction while producing little amounts of methane in the limited reaction temperature region. The shift reaction proceeded at 150 and 200 °C over Ru/ZrO_2, though the CO conversion was low. The production of methane increased with reaction temperatures above 200 °C. The Ru/TiO_2 catalyst
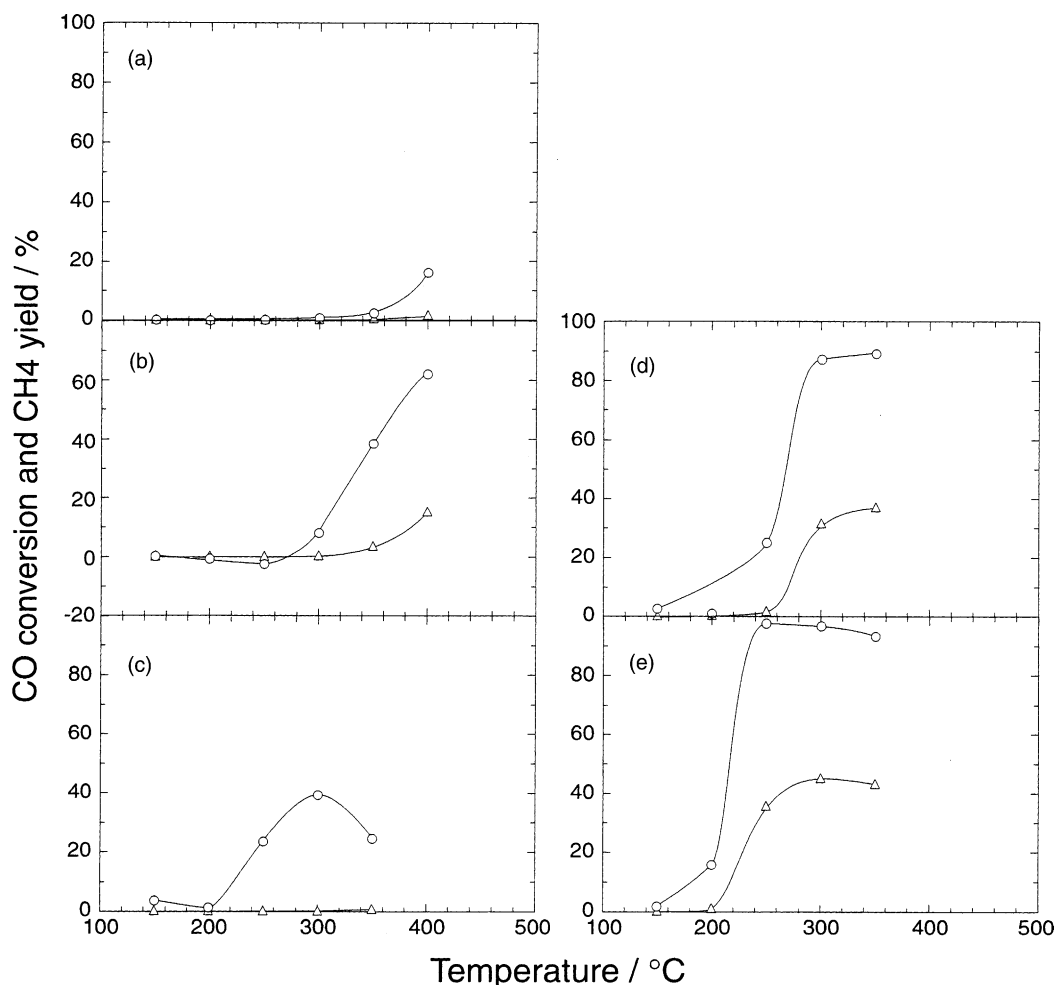
Fig. 2. (○) CO conversion and (△) CH₄ yield over: (a) Ir; (b) Pd; (c) Pt; (d) Rh; and (e) Ru catalysts supported on Al_2O_3. Reaction conditions: CO, 1.3%; CO_2, 12.5%; H_2, 37.5%; H_2O, 25%; N_2, balance; S.V., $6400\,h^{-1}$.

converted CO (2–16%) by the shift reaction, producing little amount of methane (<1000 ppm) below 350 °C. The Ru/V_2O_3 catalyst demonstrated a high activity for the shift reaction without methane production. Though the CO conversion was low (<3%) below 200 °C, the conversion increased with little methane production (<1500 ppm) until 350 °C. A large amount of methane was produced only above 350 °C. The deviation of CO conversion and CH₄ yield was the largest among the Ru-based catalysts investigated in the present study, indicating the promising activity for the shift reaction.

Table 1 summarizes BET surface area and Ru dispersion over supported Ru catalysts. The Ru disper-

sion for Ru/La_2O_3 is not listed, since this catalyst did not adsorb CO. The Ru/ZrO_2 catalyst had the largest BET surface area and the highest dispersion of Ru. However, the catalytic activity for the water gas shift reaction was not correlated with the surface area and Ru dispersion. The Ru/V_2O_3 catalyst with high activity for the shift reaction possessed low surface area and low Ru dispersion. This implies that the catalytic activity for the shift reaction is not related with the microstructural dispersion of Ru but may result from strong chemical interaction with the support.

In Fig. 4, the CO conversion at 1% CH₄ yield is taken as a measure of the effective progress of the shift
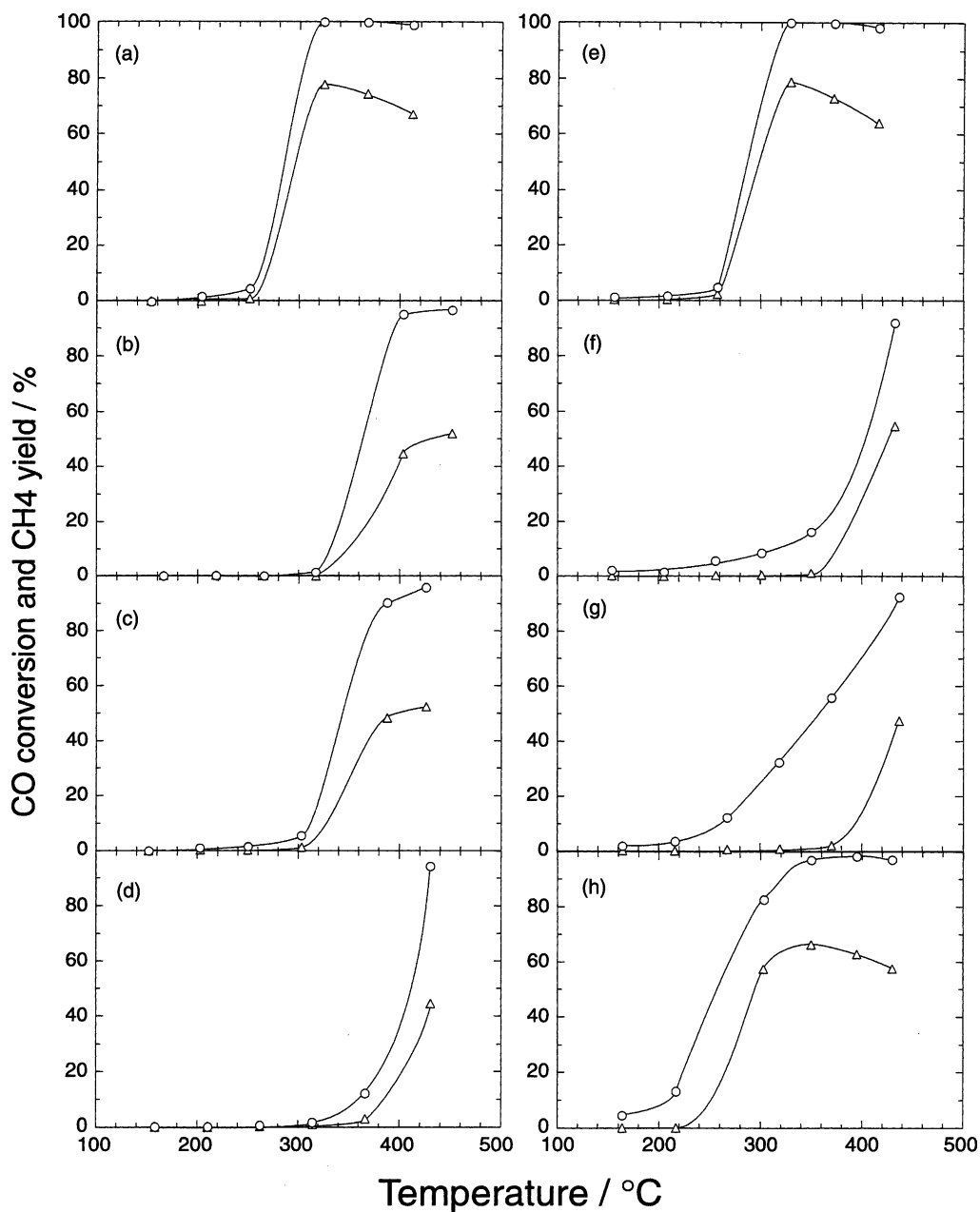
Fig. 3. (○) CO conversion and (△) CH_4 yield over Ru catalysts supported on: (a) CeO_2; (b) La_2O_3; (c) MgO; (d) Nb_2O_5; (e) Ta_2O_5; (f) TiO_2; (g) V_2O_5; and (h) ZrO_2. Reaction conditions: CO, 5%; CO_2, 3.1%; H_2, 28.1%; H_2O, 13.8%; N_2, balance; S.V., 6400 h^{-1}.

reaction with reference to methanation. The value is plotted as a function of an electronegativity of support oxides over supported Ru catalysts. The electronegativity of oxides is the geometric mean value of

Pauling's electronegativities of the metal and oxygen atoms. The catalysts with high or low electronegativity have little activity for the shift reaction. The catalysts with intermediate electronegativity around 2.45

Table 1
BET surface area and Ru dispersion over supported Ru catalysts

Catalyst	BET surface area ($m^2 g_{cat}^{-1}$)	Ru dispersion (%)
Ru/CeO_2	6	2.4
Ru/La_2O_3	14	–
Ru/MgO	56	2.4
Ru/Nb_2O_5	7	0.3
Ru/Ta_2O_5	0.05	1.0
Ru/TiO_2	56	6.2
Ru/V_2O_5	7	0.8
Ru/ZrO_2	68	45.9
Ru/V_2O_5 (at 400 °C)[a]	26	3.6
Ru/V_2O_5 (at 500 °C)[a]	14	1.7
Ru/V_2O_5 (at 650 °C)[a]	12	0.6
Ru/V_2O_5 (at 800 °C)[a]	8	0.4

[a] Reduced in 10% H_2/N_2.

demonstrated the high activity. A. Basińska et al. [8] have reported that Ru/La_2O_3 catalyst had high activity for the shift reaction. However, our Ru/La_2O_3 catalyst demonstrated low activity for the shift reaction. This difference is attributed to two reasons. Firstly, our catalyst was reduced in H_2 before the shift reaction. It is reported that precious metal catalysts supported on CeO_2 have high activity for the shift reaction [11–13]. However, CeO_2 is irreversibly reduced in H_2 during long operation and the catalysts are deactivated [14]. It is necessary to stabilize the catalyst activity in a reducing atmosphere for the supports with variable valence. Secondly, we fed a model reformed gas containing four components (CO, CO_2, H_2 and H_2O), while the

reactant gas used in the report consisted of only CO and H_2O. Therefore, it is considered that some kinds of reactions, i.e. the forward or reverse shift reaction and CO and CO_2 hydrogenation, contributed more in our system than in their system. The second reason also causes some difference in activity over Ru/MgO (our catalyst had higher activity by CO hydrogenation). It is sometimes possible that hydrogenation of CO and/or CO_2 proceeds in reformed gas even over a shift catalyst. If we consider an application of catalysts to CO removal for fuel cell systems, precious metal catalysts with high activity for hydrogenation and the catalysts with easily reduced support should be carefully evaluated as regards the activity for the shift reaction in reformed gas. We conclude that the catalysts supported on strongly basic or acid oxide are not effective for only shift reaction.

3.4. Water gas shift reaction over Ru/V_2O_3

Fig. 5 shows XRD patterns of Ru/V_2O_3 reduced at 400–800 °C. The catalyst after reduction consisted of the phases of only Ru and V_2O_3. The crystallinity of the catalyst reduced at 400 °C was low and the Ru particles were unobservable due to their small size. The diffraction pattern of the oxide phase is attributed to
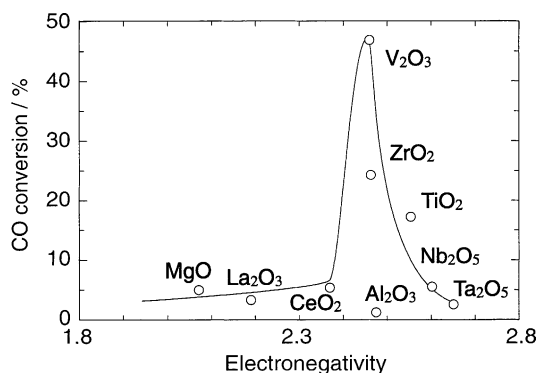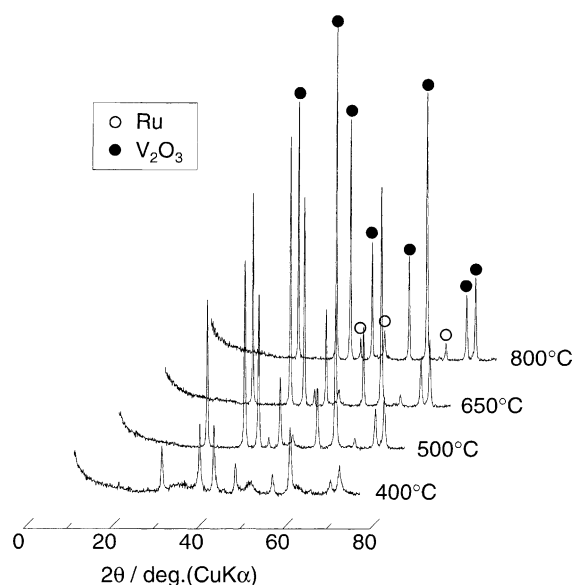

Fig. 4. CO conversion at 1% CH_4 yield for electronegativity of support oxides over supported Ru catalysts. Reaction conditions: CO, 5%; CO_2, 3.1%; H_2, 28.1%; H_2O, 13.8%; N_2, balance; S.V., 6400 h^{-1}.

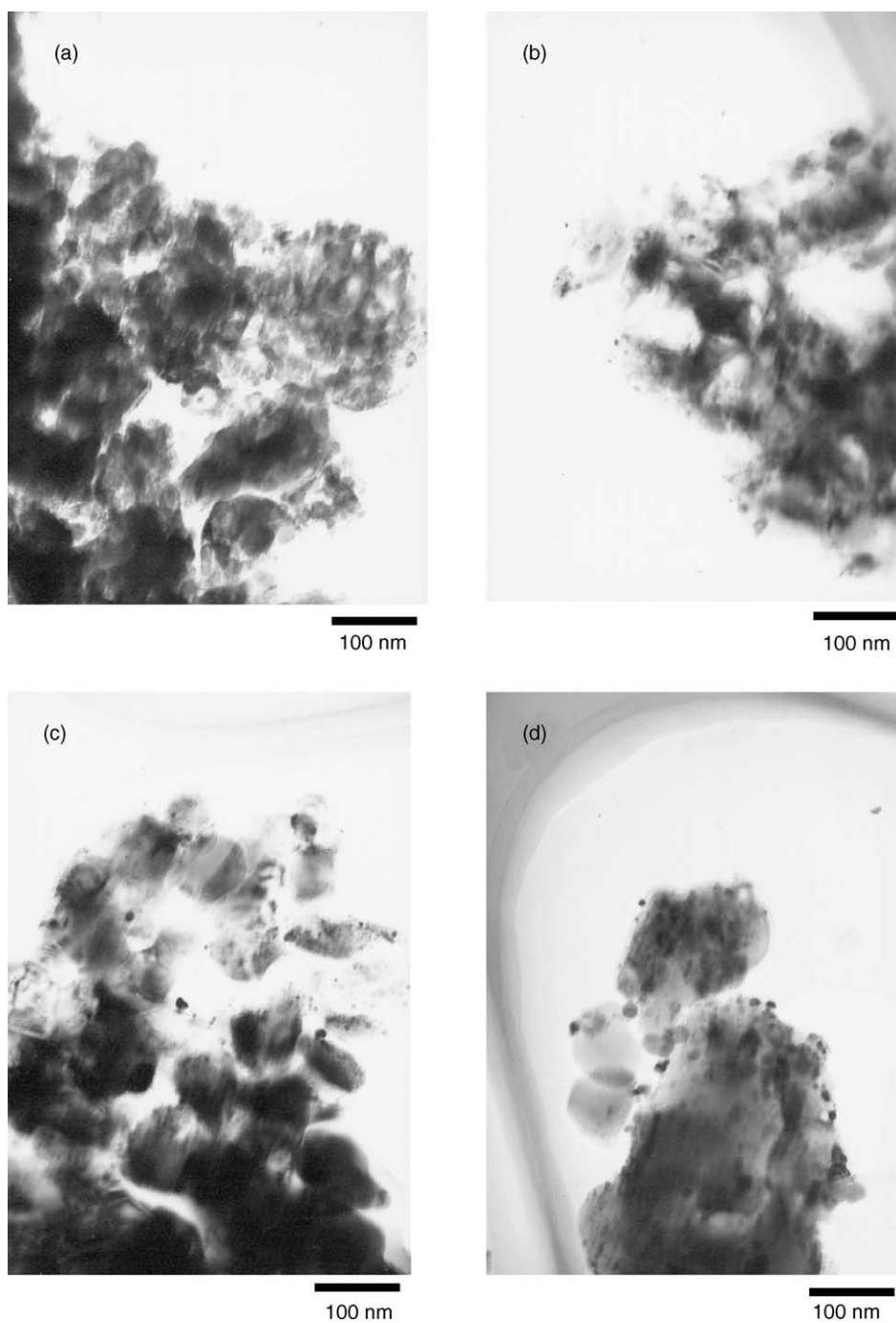Fig. 5. XRD patterns of Ru/V_2O_3 reduced at 400–800 °C.

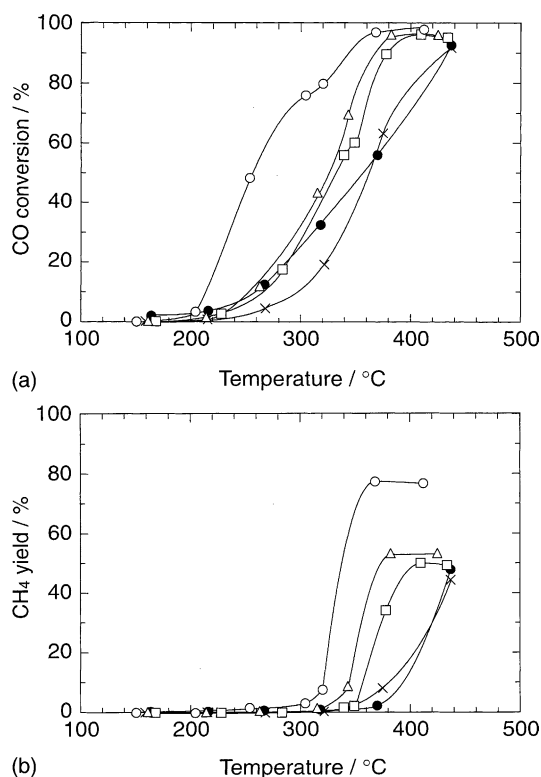Fig. 6. TEM images of Ru/V$_2$O$_3$ reduced at (a) 400 °C, (b) 500 °C, (c) 650 °C and (d) 800 °C.

Fig. 7. (a) CO conversion and (b) CH_4 yield over Ru/V_2O_5 calcined in air at (●) 500 °C and reduced in 10% H_2/N_2 at (○) 400 °C, (△) 500 °C, (□) 650 °C and (×) 800 °C. Reaction conditions: CO, 5%; CO_2, 3.1%; H_2, 28.1%; H_2O, 13.8%; N_2, balance; S.V., 6400 h^{-1}.

V_2O_3. Therefore, the catalyst in the working state is denoted as Ru/V_2O_3. The Ru and V_2O_3 phases gradually crystallized with increasing reduction temperatures, judging from the intense and sharp diffraction lines. TEM photographs of the Ru/V_2O_3 catalyst reduced at 400–800 °C are shown in Fig. 6. The Ru particles grew with a rise in reduction temperature, as is confirmed from the photographs. The Ru/V_2O_3 catalysts had the highest activity for the shift reaction without producing methane. These catalysts were reduced in 10% H_2/N_2 at 400–800 °C to check the activity for the shift reaction. Fig. 7(a) and (b) shows CO conversion and CH_4 yield over the Ru/V_2O_3 catalysts reduced at various temperatures. These figures also show results of Ru/V_2O_3 calcined at 500 °C in air. Table 1 summarizes the BET surface area and Ru dispersion. The catalyst reduced at 500 °C in H_2 attained CO con-

version of 45% at lower temperature (330 → 310 °C) than the Ru/V_2O_3 calcined in air. The BET surface and Ru dispersion of reduced catalyst were twice as large as those of the catalyst calcined in air, indicating that the number of active sites increased. The catalyst reduced at 400 °C demonstrated the highest activity for the shift reaction without methane formation (45% CO conversion and 1% CH_4 yield at 250 °C). The activity for the shift reaction became low with increasing reduction temperature, since the BET surface area and Ru dispersion decreased. These results indicate that high BET surface area and Ru dispersion determine the availability of active sites. The catalytic activity was related to this microstructural property when the catalyst system is fixed.

4. Conclusion

We investigated supported precious metal catalysts for the water gas shift reaction in reformed gas. The Ru/V_2O_3 catalyst reduced at 400 °C had the highest activity for the shift reaction without producing methane. The activity for the shift reaction was not correlated with BET surface area and Ru dispersion and depended on the chemical character of oxide supports. The catalysts supported on strongly basic or acid oxide were not effective for the shift reaction, but the methanation was dominant. For the catalysts with the same composition, like Ru/V_2O_3, BET surface area and Ru dispersion are simply related with the activity.

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