Enhancement of selectivity for preferential CO oxidation over SO$_2$-pretreated Ru/Al$_2$O$_3$ catalyst by the presence of sulfur compounds

Hidenobu Wakita [a,*], Tatsuya Takeguchi [b], Wataru Ueda [b]

[a] *Living Environment Development Center, Matsushita Electric Industrial Co. Ltd., Moriguchi, Osaka 570-8501, Japan*
[b] *Catalysis Research Center, Hokkaido University, N21-W10 Sapporo 001-0021, Japan*

Abstract

The preferential CO oxidation on a monolith Ru/Al$_2$O$_3$ catalyst pretreated with SO$_2$ in the reactant gas was investigated in the presence/absence of 0.21–20 ppm sulfur compounds (SO$_2$ or H$_2$S). In the presence of 2.1 ppm sulfur compound, CO was preferentially oxidized over the SO$_2$-pretreated catalyst at 150 °C. On the other hand, in the absence of sulfur compounds, the H$_2$ oxidation was promoted. By in situ IR measurements, multicarbonyl species and SO$_4{}^{2-}$ species were found on Ru in the presence of SO$_2$. The presence of multicarbonyl species at a high frequency (2154 cm^{-1}) and that of SO$_4{}^{2-}$ species on Ru suggested that Ru was oxidized. Since the rate of CO oxidation was low on oxidized Ru, the selectivity for CO oxidation was low over the SO$_2$-pretreated catalyst in the absence of sulfur compounds. On the other hand, the increase in the selectivity in the presence of sulfur compounds suggested that weakly adsorbed sulfur compounds suppressed the migration of dissociatively adsorbed H atom on Ru or decreased the H atoms next to adsorbed O atom for the H$_2$ oxidation.
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1. Introduction

H$_2$ is expected to be one of the clean energy resources, if it can be produced from the solar energy, natural energy, and bioenergy without CO$_2$ evolution. However, the infrastructure for domestic use of H$_2$ has not been developed. To consume energy effectively, residential polymer electrolyte fuel cell (PEFC) co-generation systems using natural gas, liquefied petroleum gas, or kerosene as H$_2$ sources have attracted much attention. The fuel processor of the system normally comprises a desulfurizer, a steam reformer, a shift converter, and a preferential CO oxidation (PROX) unit. Since just a small amount of CO poisons the anode catalyst for PEFC, the CO concentration in the reformed fuel gas must be reduced to less than 10 ppm by the water–gas shift reaction and the PROX. The stoichiometric [O$_2$]/[CO] ratio is 0.5 for the CO oxidation; however, it is necessary to supply excess O$_2$ to achieve high CO conversion for the PROX in H$_2$-rich gas [1,2]. Thus the PROX is usually conducted at the [O$_2$]/[CO] ratio of 1.5–2.5, though excess O$_2$

consumes H$_2$ and the selectivity for CO oxidation is as low as 20–33%.

For residential use, long-term durability over 10 years is required [3]; however, it has not been ensured yet. In addition, only a few studies on the deactivation of the PROX catalyst have been reported [4–6], since the PROX is not needed for phosphoric acid fuel cell systems. For the PROX, contaminants in air, such as SO$_2$ and H$_2$S, may deactivate the catalyst. In addition, for autothermal reforming of liquid fuels, which usually contain sulfur compounds, H$_2$S is supplied to the subsequent catalysts [7]. Though Cu–ZnO catalysts for the water–gas shift reaction have large absorption capacity for H$_2$S, some catalysts cannot absorb H$_2$S. Therefore, we have investigated the influence of sulfur compounds (SO$_2$ and H$_2$S) over the monolith Ru/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts [8]. The supply of 4.3–48 ppm sulfur compounds to the Ru/Al$_2$O$_3$ catalyst for 100–350 min decreased the CO conversion. Most of the sulfur compounds were oxidized to SO$_4{}^{2-}$ species, which migrated to the support. During the SO$_2$ poisoning, parts of the Ru sites strongly adsorbed the SO$_4{}^{2-}$ species, and the CO oxidation was suppressed.

In some cases of practical use, contaminated air is supplied to the PROX catalysts for a long term. In addition, the composition of the contaminants is not always the same. From this

* Corresponding author. Tel.: +81 6 6906 2430; fax: +81 6 6906 2875.
E-mail address: wakita.h@jp.panasonic.com (H. Wakita).

point of view, the Ru/Al_2O_3 catalyst was employed for the reaction in the presence of SO_2 for a long term (SO_2 pretreatment), and then the sulfur compound was intermittently supplied to the SO_2-pretreated catalyst. In this work, the first SO_2 poisoning is designated as the SO_2 pretreatment, though the reaction conditions of the pretreatment are the same as those for the PROX, except for the coexistent SO_2. Interestingly, the SO_2-pretreated catalyst showed significant changes in the selectivity for CO oxidation caused by sulfur compounds. In this study, the catalytic behavior after the pretreatment is reported in detail, and the mechanisms are discussed on the basis of in situ IR spectra.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by the impregnation method described in detail elsewhere [8]. By impregnating a θ-Al_2O_3 support with an aqueous solution of $RuNO(NO_3)_x$, 2.0 wt% Ru/Al_2O_3 catalyst powder thus obtained was supported on cordierite honeycombs (20 mm diameter; 10 mm thickness; 400 cell/in.^{2}) with an Al_2O_3–sol binder. The prepared monolith Ru/Al_2O_3 catalyst with Ru loading of 1.6 g/l was employed for transient response tests in a fixed bed reactor.

For the in situ IR measurements, 3.8 wt% Ru/Al_2O_3 catalyst powder was prepared.

2.2. Reaction tests

Catalytic activities were measured in a fixed bed reactor. The reactant gas was 51.5 vol.% H_2, 0.3 vol.% CO, 12.9 vol.% CO_2, 0.5 vol.% O_2, 6.0 vol.% N_2, and 28.8 vol.% H_2O at an [O_2]/[CO] ratio of 1.5, which simulates the steam-reformed natural gas after the shift converter. The pretreatment reaction was conducted in the presence of 20 ppm SO_2 in the reactant gas at GHSV = $9260\,h^{-1}$ and ca. 150 °C for 60 h.

After the pretreatment, the above-mentioned reactant gas without sulfur compounds was continuously fed to the SO_2-pretreated Ru/Al_2O_3 catalyst at ca. 150 °C for 15–23 h. Then 5.0–500 ppm SO_2 or H_2S diluted with N_2 was intermittently added to the reactant gas. The concentration of the sulfur compound was 0.21–20 ppm in the reactant gas, which was corresponding to 8.7–830 ppm in air. When the sulfur compound was not added to the reactant gas, N_2 was fed instead. The reaction was usually conducted at GHSV = $9260\,h^{-1}$ and ca. 150 °C. The reaction temperatures were measured with a thermocouple in contact with the top of the catalyst bed. When the [O_2]/[CO] ratio was changed, the air flow rate was changed. The method of the gas composition analysis was described in detail earlier [8]. The selectivity for CO oxidation was defined by the following equation: $S = \{(\text{inlet CO concentration} - \text{outlet CO concentration} - \text{outlet CH}_4 \text{ concentration})/2\} \times 100/(\text{inlet O}_2 \text{ concentration} - \text{outlet O}_2 \text{ concentration})$. However, the outlet CH_4 concentration was negligible under any conditions in this study.

The temperature dependence of catalytic activities was also measured in the presence/absence of 2.1 ppm sulfur compounds by lowering the catalyst temperature stepwise from 200 to 90 °C.

2.3. Catalyst characterization

IR spectra were obtained with an FTIR spectrometer (FTIR 8200, Shimadzu Corp.) equipped with a DRIFT apparatus (model 0030-103, Spectra-Tech Inc.) having CaF_2 windows. The 3.8 wt% Ru/Al_2O_3 catalyst without the SO_2 pretreatment was reduced at 200 °C for 30 min in a 5 vol.% H_2/He flow, and cooled to 150 °C. After the background spectrum was taken in a He flow, a spectrum was taken at 150 °C in a reactant gas flow (gas composition (I): 75.5 vol.% H_2, 0.5 vol.% CO, 19.0 vol.% CO_2, 0.7 vol.% O_2, 2.7 vol.% N_2, and 1.6 vol.% H_2O). Next, SO_2 diluted with N_2 was added to the reactant gas for 150 min (SO_2 pretreatment), and the IR spectra were recorded. The gas composition during the SO_2 pretreatment was 65.6 vol.% H_2, 0.4 vol.% CO, 16.5 vol.% CO_2, 0.6 vol.% O_2, 15.5 vol.% N_2, 1.4 vol.% H_2O, and 66 ppm SO_2 (gas composition (II)). After the SO_2 pretreatment, the reaction (gas composition (I)) was continuously carried out for 70 min. Then SO_2 was re-supplied to the SO_2-pretreated catalyst (gas composition (II)).

The CO adsorption on the pretreated/fresh catalysts was also conducted at 50 °C by the pulse method on an automatic gas adsorption apparatus (R6015, Okura Riken Co. Ltd.). Before the measurements, the catalysts were reduced at 200 °C for 15 min in a H_2 flow.

3. Results

3.1. Changes in the catalytic activity caused by SO_2

As shown in Table 1, the fresh monolith Ru/Al_2O_3 catalyst without SO_2 pretreatment showed ~100% conversions of both CO and O_2 at the [O_2]/[CO] ratio of 1.5 and 155 °C (I), and neither of conversions changed 0.5 h after the start of the pretreatment with 20 ppm SO_2 (II) even in the presence of SO_2. However, the CO and O_2 conversions decreased to 75.0% and 37.7% at 60 h, respectively (III). In addition, the temperature of the top of the catalyst bed decreased from 155 to 142 °C at 60 h due to the suppression of the oxidations of CO and H_2. As described above, the SO_2 pretreatment for 60 h was conducted.

Then the supply of SO_2 was interrupted and the reaction was continuously conducted over the SO_2-pretreated catalyst in the absence of SO_2 for 22 h. The O_2 conversion increased to 99.4% at 22 h, though the CO conversion decreased further to 65.5% (IV). The catalyst temperature increased to 151 °C with an increase in the O_2 conversion. Therefore, the interruption of SO_2 promoted the H_2 oxidation. Next, 20 ppm SO_2 was re-supplied, which increased the CO conversion with a decrease in the O_2 conversion. A high CO conversion (95.7%) was attained with a low O_2 conversion (56.0%) (V) 1.5 h after the resumption of the SO_2 supply. Thus the selectivity for CO oxidation significantly increased to 52.2%. However, a long-term supply of 20 ppm SO_2 (24 h) gradually decreased the CO and O_2 conversions to 77.1% and 45.4%, respectively (VI). Interestingly, the selectivity was very high (56.2%) even at this moment. The interruption of SO_2 promoted the H_2 oxidation again. Next, SO_2 of low concentration (2.1 ppm) was supplied. A high CO conversion (95.1%) and a high selectivity (46.0%) were attained in

Table 1
Changes in the catalytic activity in the presence/absence of SO_2

Condition	SO_2 in the reaction gas	CO conversion (%)	O_2 conversion (%)	Selectivity for CO oxidation (%)
Before SO_2 pretreatment (I)	None	99.8	99.7	33.1
At 0.5 h after the start of SO_2 pretreatment (II)	20 ppm	99.8	99.8	33.1
At 60 h after the start of SO_2 pretreatment (III)	20 ppm	75.0	37.7	65.8
At 22 h after the SO_2 pretreatment for 60 h (IV)	None	65.5	99.4	21.8
At 1.5 h after the start of SO_2 supply to the SO_2-pretreated catalyst (V)	20 ppm	95.7	56.0	52.2
At 24 h after the start of SO_2 supply to the SO_2-pretreated catalyst (VI)	20 ppm	77.1	45.4	56.2
At 33 h after the start of SO_2 supply to the SO_2-pretreated catalyst (VII)	2.1 ppm	95.1	68.4	46.0

Reaction conditions: feed, 51.5 vol.% H_2, 0.3 vol.% CO, 12.9 vol.% CO_2, 0.5 vol.% O_2, 6.0 vol.% N_2, 28.8 vol.% H_2O; $[O_2]/[CO] = 1.5$; temperature, ca. 150 °C; GHSV = 9260 h^{-1}; SO_2 pretreatment, 20 ppm SO_2 under the reaction condition for 60 h.

the presence of SO_2 even 33 h after the start of the supply of SO_2 of low concentration (VII).

In summary, the H_2 oxidation was promoted in the absence of SO_2 over the SO_2-pretreated catalyst (IV), while CO was preferentially oxidized in the presence of SO_2 and unreacted O_2 was exhausted without consuming H_2, which gave high selectivities (V, VII). However, the CO conversion decreased little by little with high selectivities kept, when SO_2 of high concentration (20 ppm) was supplied for a long term (V, VI). On the other hand, in the presence of SO_2 of low concentration (2.1 ppm), the high CO conversion was kept for a long term (VII).

To elucidate the effect of the Al_2O_3 support (θ or α), a Ru/α-Al_2O_3 catalyst with Ru loading of 1.6 g/l was pretreated with SO_2. The interruption of SO_2 promoted the H_2 oxidation, and CO was selectively oxidized in the presence of 20 ppm SO_2. The point is that the catalytic behavior did not depend on the support, but on the catalyst metal of Ru.

3.2. Influence of sulfur compounds on the activities of the SO_2-pretreated catalyst

To investigate the influence of the SO_2 concentration on the activities of the catalyst pretreated with SO_2 for 60 h, 0.21–20 ppm SO_2 was intermittently added to the reactant gas for a short term (50–100 min). The reaction was conducted over the SO_2-pretreated catalyst at the $[O_2]/[CO]$ ratio of 1.5 and 150 °C and the results are shown in Table 2 and Fig. 1. Table 2 shows the catalytic activities 90 min after the start of sulfur compound supply, except those in the presence of 0.21 ppm sulfur compound supply.

Table 2
Changes in the activity of the SO_2-pretreated catalyst by the presence of SO_2 or H_2S

Sulfur compound in the reaction gas	CO conversion (%)	O_2 conversion (%)	Selectivity for CO oxidation (%)
None	65.5	99.4	21.8
0.21 ppm SO_2	89–98	87–98	30–37
2.1 ppm SO_2	98.4	62.4	52.2
20 ppm SO_2	95.7	56.0	56.6
0.21 ppm H_2S	95–99	79–98	32–41
2.1 ppm H_2S	97.4	60.8	53.1

The activities at 1.5 h after the start of sulfur compound supply were shown, except for the poisoning with 0.21 ppm sulfur compound. Reaction conditions and pretreatment conditions are the same as those shown in Table 1.

pounds. Some tests were repeated, and the high reproducibility was confirmed. In the presence of SO_2 of very low concentration (0.21 ppm), the CO conversion increased and the O_2 conversion slightly decreased (Table 2) although conversions were unstable and fluctuated. Thus, the selectivity for CO oxidation showed relatively high value of 30–37%. In the presence of SO_2 of low concentration (2.1 ppm), the CO conversion was as high as 98.4%, and the O_2 conversion was as low as 62.4% (Table 2 and Fig. 1(a)). As a result, the selectivity for CO oxidation increased to 52.2%. After SO_2 was stopped, the CO conversion immedi-
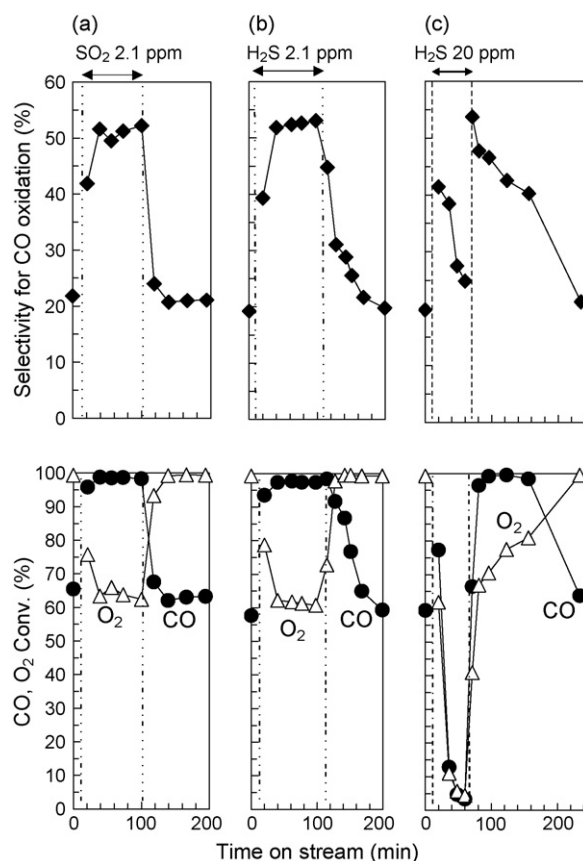

Fig. 1. Changes in the catalytic activity of the SO_2-pretreated Ru/Al_2O_3 catalyst in the presence/absence of (a) 2.1 ppm SO_2, (b) 2.1 ppm H_2S, and (c) 20 ppm H_2S. (●) CO conversion, (△) O_2 conversion, and (◆) selectivity for CO oxidation. Reaction conditions and pretreatment conditions are the same as those shown in Table 1.

ately decreased to ~60% with an increase in the O_2 conversion to ~100%, which showed that the H_2 oxidation was promoted. The presence of SO_2 of high concentration (20 ppm) also led to similar behavior within a short period of 90 min (Table 2).

Next, the influence of the H_2S concentration (0.21–20 ppm) on the activity of the SO_2-pretreated catalyst was examined. The results are also shown in Table 2 and Fig. 1. As shown in Fig. 1(b), H_2S of low concentration (2.1 ppm) increased the CO conversion and the selectivity as was the case of SO_2 of low concentration (2.1 ppm) (Fig. 1(a)). However, the interruption of H_2S supply resulted in a slower decrease in the CO conversion than the interruption of SO_2. We have already reported that the sulfur compounds were oxidized to SO_4^{2-} species, which migrated to the support [8]. Therefore, these results indicate that H_2S was oxidized more slowly to SO_4^{2-} species than SO_2. In the presence of H_2S of very low concentration (0.21 ppm), the CO conversion also increased with a decrease in the O_2 conversion, though they fluctuated as was the case of SO_2 of very low concentration (0.21 ppm) (Table 2). In the presence of H_2S of high concentration (20 ppm), however, both CO and O_2 conversions significantly decreased (Fig. 1(c)), unlike in the case of SO_2 of high concentration (20 ppm) (Table 2). This also indicates that weakly adsorbed H_2S or S^{2-} species was more slowly oxidized to SO_4^{2-} species than SO_2 and accumulated on Ru, resulting in the rapid deactivation. After H_2S of high concentration was stopped, the O_2 conversion gradually increased, and the CO conversion once increased and then decreased. Both CO and O_2 conversions returned to the same as those before the H_2S supply, 170 min after the interruption of H_2S supply. The changes in the CO conversions after the interruption of H_2S of high concentration suggest that the CO conversion and the selectivity strongly depended on the coverage of the weakly adsorbed sulfur compounds, which were slowly oxidized after the interruption of H_2S supply.

The pretreatment was also conducted by H_2S instead of SO_2. The interruption of H_2S supply promoted the H_2 oxidation, and the sulfur compound re-supply enhanced the selectivity [9]. This also suggests that H_2S was oxidized to SO_4^{2-} species.

3.3. Dependence of the catalytic activities on the SO_2 pretreatment condition

The dependence of the activities of SO_2-pretreated catalysts in the absence of sulfur compounds on the amount of supplied SO_2 for the pretreatment was investigated by changing the period of pretreatment. In Fig. 2, the abscissa presents the molar ratio of supplied SO_2 to the Ru loading, where 30 mol_S/mol_{Ru} of SO_2 corresponds to the pretreatment with 20 ppm SO_2 for 60 h. The reaction was carried out at the $[O_2]/[CO]$ ratio of 1.5 and 150 °C. The activities were measured at 15–23 h after the SO_2 pretreatment. The catalyst pretreated with 0.5 mol_S/mol_{Ru} of SO_2 showed the same activity as the fresh one. However, the CO conversion significantly decreased to 86% at 2.0 mol_S/mol_{Ru}, and decreased further to 70% at 9.1 mol_S/mol_{Ru}. However, the CO conversion of the catalyst at 30 mol_S/mol_{Ru} was slightly lower than that at 9.1 mol_S/mol_{Ru}. On the other hand, the O_2 conversion remained ~100% irrespective of the amount of SO_2.
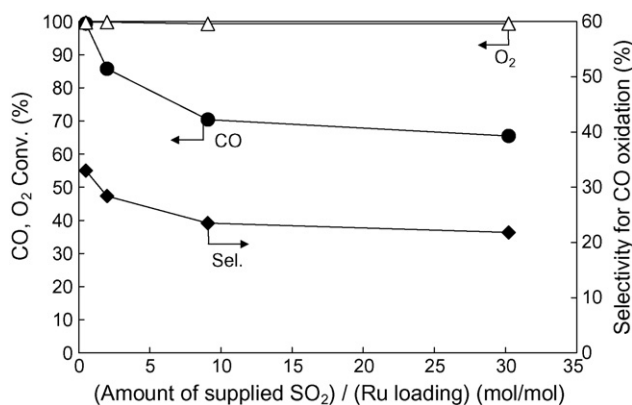

Fig. 2. Dependence of the activities of the Ru/Al_2O_3 catalysts in the absence of sulfur compounds on the amount of supplied SO_2 for the pretreatment. (●) CO conversion, (△) O_2 conversion, and (◆) selectivity for CO oxidation. Reaction conditions and pretreatment conditions are the same as those shown in Table 1, except for the period of the pretreatment.

Thus, the changes in the selectivity strongly depended on the CO conversion.

Fig. 3 shows the dependence of the activities of the SO_2-pretreated catalyst in the presence of SO_2 of low concentration (2.1 ppm) on the amount of supplied SO_2 for the pretreatment. After the pretreatment followed by the reaction for 15–23 h in the absence of SO_2, SO_2 was re-supplied and the activity 1.5 h after the start of SO_2 was plotted against the molar ratio of supplied SO_2 to the Ru loading. The catalyst at 2.0 mol_S/mol_{Ru} showed the same activity as that of the fresh one. The O_2 conversion decreased to 60% at 30 mol_S/mol_{Ru}, though the CO conversion remained higher than 98%. Thus, the changes in the selectivity depended on those in the O_2 conversion. At more than 9.1 mol_S/mol_{Ru}, both CO and O_2 conversions changed by the presence/absence of SO_2 of low concentration (Figs. 2 and 3).

Fig. 4 shows the dependence of the nominal Ru dispersion estimated by the CO adsorption on the amount of supplied SO_2 for the pretreatment. In this paper, the Ru dispersion was defined as the molar ratio of the amount of CO adsorbed to the amount of Ru loaded. The Ru dispersion after the reduction at 400 °C
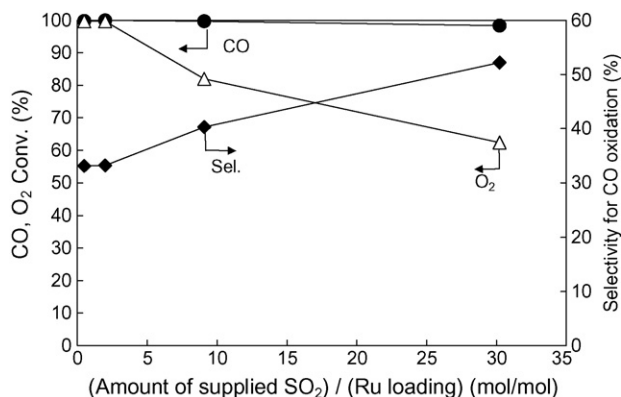

Fig. 3. Dependence of the activities of the Ru/Al_2O_3 catalysts in the presence of 2.1 ppm SO_2 on the amount of supplied SO_2 for the pretreatment. (●) CO conversion, (△) O_2 conversion, and (◆) selectivity for CO oxidation. The activity at 1.5 h after the start of SO_2 supply was plotted. Reaction conditions and pretreatment conditions are the same as those shown in Table 1, except for the period of the pretreatment.
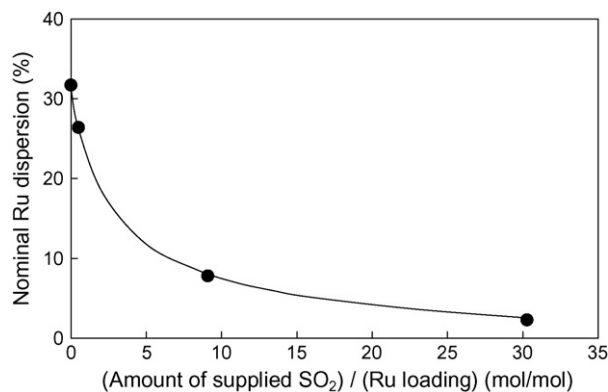
Fig. 4. Dependence of the nominal Ru dispersion estimated by the CO adsorption on the amount of supplied SO_2 for the pretreatment. Pretreatment conditions are the same as those shown in Table 1, except for the period of the pretreatment.

in a H_2 flow was lower than that after the reduction at 200 °C, since SO_4^{2-} species reversely spilled over from the support to Ru above 220 °C as reported in our previous study [8]. Therefore, the Ru dispersion after the reduction at 200 °C is shown in Fig. 4. Though the supplied SO_2 at 0.5 mol_S/mol_{Ru} was 1.6 times as much as the surface Ru, the Ru dispersion slightly decreased from 31.7% to 26.4%. The Ru dispersion at 9.1 mol_S/mol_{Ru} decreased to 7.8%; however, the catalyst at 30 mol_S/mol_{Ru} maintained 2.3% of the Ru dispersion. Thus, even though a large amount of SO_2 was supplied, migration of SO_4^{2-} species to the support retained some active sites, and the Ru catalyst showed high tolerance to SO_2. In addition, the rate of oxidation was fast enough to achieve 100% of O_2 conversion over small numbers of active sites after the pretreatment. We have already reported that the mean size of Ru particles of a Ru catalyst (Ru loading, 3.1 g/l) increased from 1.7 to 2.7 nm by the poisoning with 48 ppm SO_2 for 8 h from TEM images, though the nominal Ru dispersion significantly decreased from 34.3% to 1.8% [8]. The XPS for the catalyst at 9.1 mol_S/mol_{Ru} showed only S^{6+} species, which also supports the presence of SO_4^{2-} species on Al_2O_3 and Ru. Therefore, it is implied that the decrease in the Ru dispersion was mainly caused by the SO_4^{2-} species strongly adsorbed on the Ru surface. Figs. 2 and 4 indicate that a small amount of SO_4^{2-} species strongly adsorbed on Ru selectively promoted the H_2 oxidation in the absence of sulfur compounds. On the other hand, in the presence of SO_2, the O_2 conversion decreased when the number of active sites further decreased by the weakly adsorbed sulfur compounds.

We also checked the amount of residual sulfur on the catalyst at 9.1 mol_S/mol_{Ru}, and 28% of the total SO_2 supplied was detected. Though the quantitative analysis of sulfur compounds in the effluent gas was difficult due to a high dew point (70 °C), only SO_2 was detected in the effluent gas when the dew point was low as in the case of in situ IR measurements to be given later (the dew point, 15 °C).

3.4. Temperature dependence of the catalytic activities

For practical use, it is preferable to reduce CO concentration in a wide temperature range. Thus the temperature dependence of the catalytic activities was investigated in the
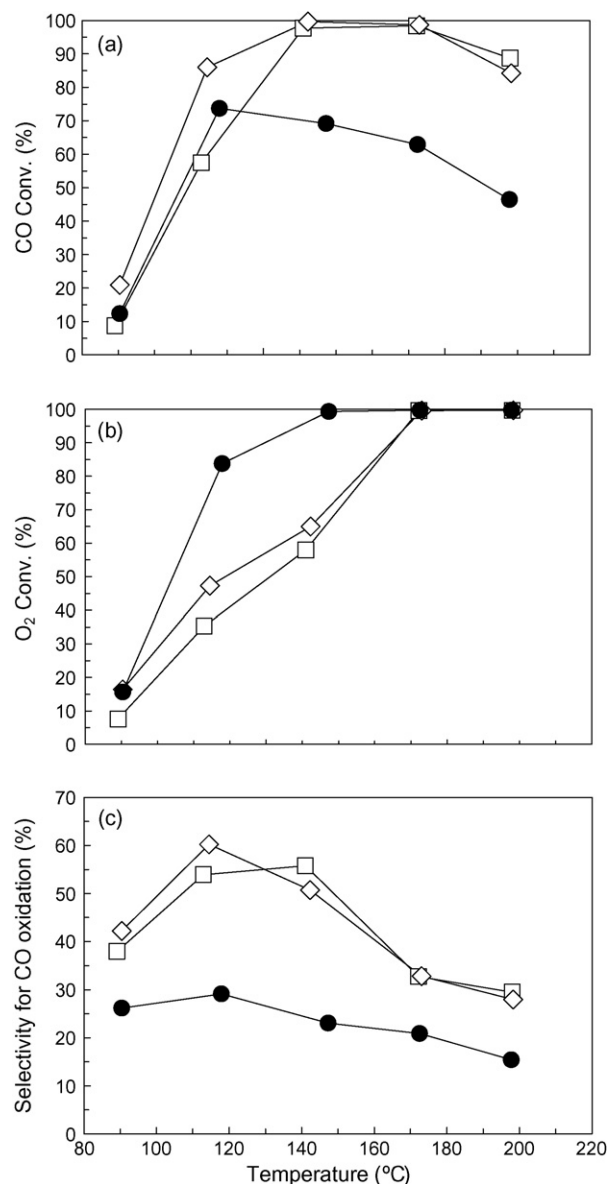

Fig. 5. Temperature dependence of the activities of the SO_2-pretreated Ru/Al_2O_3 catalyst in the presence/absence of sulfur compounds: (a) CO conversion, (b) O_2 conversion, and (c) selectivity for CO oxidation. (●) In the absence of sulfur compounds, (◇) in the presence of 2.1 ppm SO_2, and (□) in the presence of 2.1 ppm H_2S. Reaction conditions and the pretreatment conditions are the same as those shown in Table 1.

presence/absence of sulfur compounds of low concentration (2.1 ppm) (Fig. 5). The catalyst pretreated for 60 h showed low CO conversions in the absence of sulfur compounds at the $[O_2]/[CO]$ ratio of 1.5 (Fig. 5(a)), which indicates that the CO oxidation was suppressed by the SO_4^{2-} species strongly adsorbed on the Ru particles. Though the fresh catalyst without the pretreatment showed constant selectivities (32–33%) at the temperature range between 120 and 190 °C due to high CO conversions (>97%) and high O_2 conversions (∼100%), the SO_2-pretreated catalyst showed the maximum CO conversion and selectivity at 120 °C in the absence of sulfur compounds. When we examined the activity of the SO_2-pretreated catalyst for the reverse water–gas shift reaction in a reactant gas flow

without CO and air (52.1 vol.% H_2, 13.0 vol.% CO_2, 4.1 vol.% N_2 and 30.8 vol.% H_2O), CO was not detected even at 200 °C. Therefore, the reverse water–gas shift reaction did not cause the decrease in the CO conversion above 120 °C. Therefore, supposedly the activation of CO was suppressed in the absence of sulfur compounds, and the H_2 oxidation was enhanced with an increase in temperature, which consumed O_2 in the upper stream of the catalyst bed.

However, the SO_2-pretreated catalyst showed very high CO conversions in the presence of sulfur compounds of low concentration (2.1 ppm) especially between 145 and 175 °C. At 145 °C, O_2 was not completely consumed (Fig. 5(b)), since the H_2 oxidation was suppressed by the sulfur compounds weakly adsorbed on Ru. Above 175 °C, O_2 was completely consumed due to the increased rate of the H_2 oxidation, so that the selectivity decreased. However, the CO conversions and selectivities in the presence of sulfur compounds were higher than those in the absence of sulfur compounds, which indicates that the weakly adsorbed sulfur compounds suppressed the H_2 oxidation even at high temperature.

3.5. Dependence of the catalytic activities on the [O₂]/[CO] ratios

Fig. 6 shows the dependence of the catalytic activities at 150 °C on the $[O_2]/[CO]$ ratios. Over the fresh catalyst without the SO_2 pretreatment, the CO conversion significantly decreased at the $[O_2]/[CO]$ ratio of 0.8, though the O_2 conversion was ∼100% at any $[O_2]/[CO]$ ratios (Fig. 6(a)). The selectivity increased with a decrease in the $[O_2]/[CO]$ ratios. Over the SO_2-pretreated catalyst, the O_2 conversion was also ∼100% in the absence of sulfur compounds at any $[O_2]/[CO]$ ratios; however, the selectivity was nearly constant (Fig. 6(b)). In other words, the ratio of the CO oxidation to the H_2 oxidation in the upper stream of catalyst bed was constant irrespective of the changes in the O_2 concentration. In the presence of 2.1 ppm SO_2, the O_2 conversion of the SO_2-pretreated catalyst was low at the $[O_2]/[CO]$ ratio of 1.5; however, it largely increased with a decrease in the $[O_2]/[CO]$ ratio from 1.5 to 1.1 (Fig. 6(c)). The CO conversion slightly decreased with a decrease in the $[O_2]/[CO]$ ratio from 1.5 to 1.1 and significantly decreased at the $[O_2]/[CO]$ ratio of 0.8.

At the $[O_2]/[CO]$ ratio of 1.5, the selectivity for CO oxidation on the SO_2-pretreated catalyst in the presence of 2.1 ppm SO_2 was the highest at 115 °C as shown in Fig. 5(c). Similar tendency was also observed at the $[O_2]/[CO]$ ratio of 1.1 (Table 3). In the presence of 2.1 ppm SO_2, the O_2 conversion at 120 °C was lower than that at 150 °C, keeping relatively high CO conversions. So a very high selectivity (50.7%) was attained at 120 °C at the low $[O_2]/[CO]$ ratio of 1.1. It was five points higher than that (45.5%) of the fresh catalyst without the pretreatment under the same conditions, though the CO conversion was a little smaller than that of the fresh catalyst.

3.6. In situ IR measurements

In the in situ IR apparatus, the 3.8 wt% Ru/Al_2O_3 catalyst powder was pretreated with 66 ppm SO_2 at ca. 150 °C in the
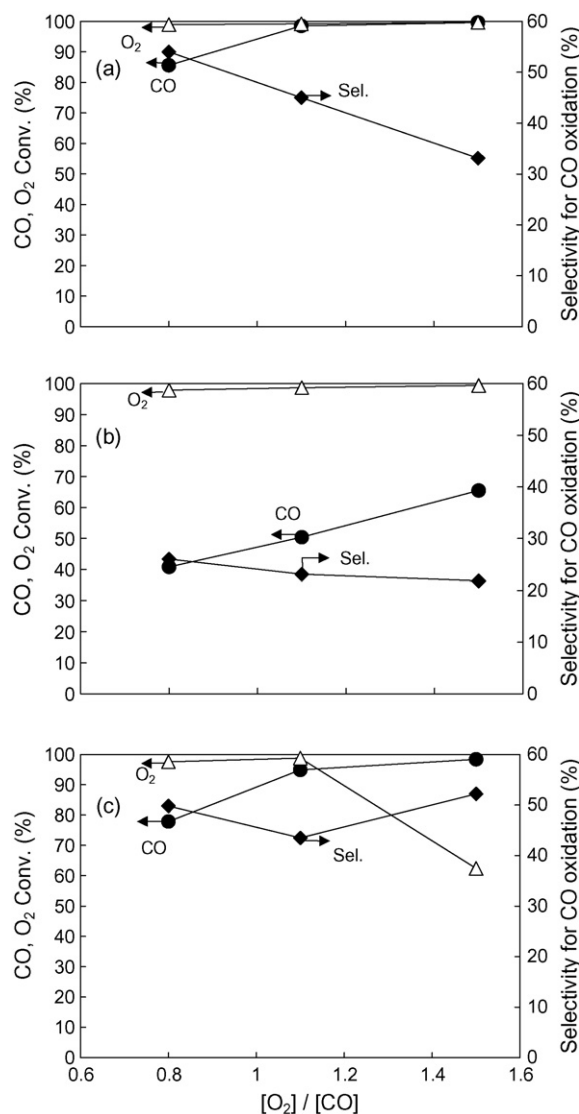

Fig. 6. Dependence of the catalytic activities at 150 °C on the $[O_2]/[CO]$ ratio: (a) in the absence of sulfur compounds over the fresh catalyst, (b) in the absence of sulfur compounds over the SO_2-pretreated catalyst, and (c) in the presence of 2.1 ppm SO_2 over the SO_2-pretreated catalyst. (●) CO conversion, (△) O_2 conversion, and (◆) selectivity for CO oxidation. Reaction conditions are the same as those shown in Table 1, except for the O_2 and N_2 concentrations (0.3–0.5 vol.% O_2, 5.2–6.0 vol.% N_2). Pretreatment conditions are the same as those shown in Table 1.

reactant gas flow. Fig. 7(a) shows the in situ IR spectra over the regions of the C–O stretching vibrations and the S–O stretching vibrations before the SO_2 pretreatment (gas composition (I)). The CO bands arising from carbonyls adsorbed on Ru are generally divided into three groups: HF_1 (high-frequency 1) bands at 2156–2133 cm^{-1}, HF_2 bands at 2100–2060 cm^{-1}, and LF (low-frequency) bands at 2080–2000 cm^{-1} [8–21]. It has been reported that the monocarbonyl species linearly adsorbed on Ru^0 was characterized by the LF band at 2040 cm^{-1} [12,19]. As shown in Fig. 7(a), the bands were observed at different frequencies of ca. 2030, 2000 and 1970 cm^{-1} due to the differences in the oxidation states of Ru sites [19–23]. The band at

Table 3
Catalytic activity in the presence/absence of 2.1 ppm SO_2 at the $[O_2]/[CO]$ ratio of 1.1

Catalyst	Temperature (°C)	SO_2 in the reaction gas	CO conversion (%)	O_2 conversion (%)	Selectivity for CO oxidation (%)
SO_2-pretreated catalyst	120	2.1 ppm	95.5	85.3	50.7
SO_2-pretreated catalyst	150	2.1 ppm	94.9	98.8	43.5
Fresh catalyst	120	None	99.7	99.2	45.5

Reaction conditions are the same as those shown in Table 1, except for the $[O_2]/[CO]$ ratio and reaction temperature. $[O_2]/[CO] = 1.1$. The pretreatment conditions are the same as those shown in Table 1.

ca. 1970 cm^{-1} might also arise from bridge-adsorbed carbonyl species [22].

As shown in Fig. 7(b)–(d), broad absorption bands appeared at 1180 and 1260 cm^{-1} during the SO_2 pretreatment, and the band intensities increased with time on stream. As reported in our previous study [8], the band at 1180 cm^{-1} was assigned to the SO_4^{2-} species in bulk $Al_2(SO_4)_3$, while the band at 1260 cm^{-1} was attributed to the surface SO_4^{2-} species on the Al_2O_3 support and the Ru particles.

During the SO_2 pretreatment, the HF_2 band, which lay as a shoulder peak before the SO_2 pretreatment, clearly appeared at 2068 cm^{-1} with a decrease in the LF band intensities at ca. 1970 and 2030 cm^{-1}. It has been reported that the $Ru^{n+}(CO)_2$ dicarbonyls were characterized by a pair of the HF_2
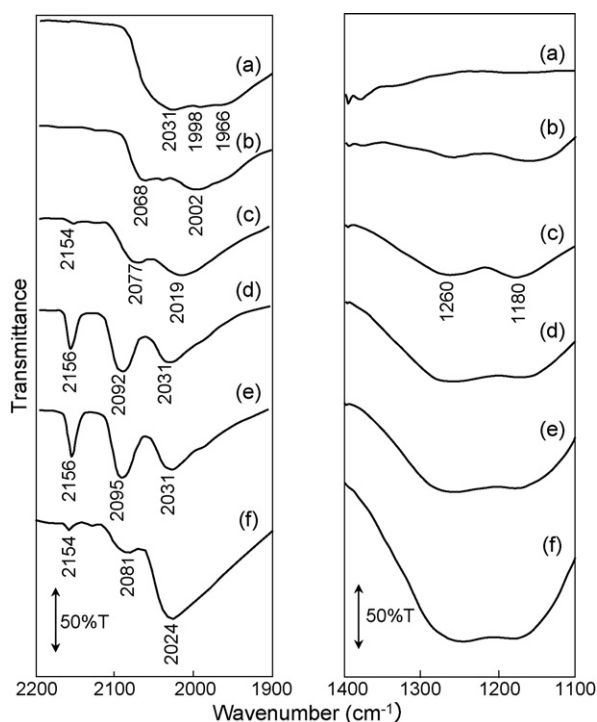

Fig. 7. In situ IR spectra over the regions of the C–O and S–O stretching vibrations at ca. 150 °C: (a) before the SO_2 pretreatment, (b) at 10 min after the start of SO_2 pretreatment (66 ppm), (c) at 30 min, (d) at 150 min, and (e) at next 60 min after the SO_2 pretreatment. (a)–(e) The spectra during the in situ SO_2 pretreatment over the 3.8 wt% Ru/Al_2O_3 catalyst. (f) The spectra in the absence of sulfur compounds (gas composition (I)) over the 2.0 wt% Ru/Al_2O_3 catalyst pretreated with SO_2 for 139 h in the fixed bed reactor. Feed, 75.5 vol.% H_2, 0.5 vol.% CO, 19.0 vol.% CO_2, 0.7 vol.% O_2, 2.7 vol.% N_2, 1.6 vol.% H_2O (gas composition (I)) or 65.6 vol.% H_2, 0.4 vol.% CO, 16.5 vol.% CO_2, 0.6 vol.% O_2, 15.5 vol.% N_2, 1.4 vol.% H_2O, 66 ppm SO_2 (gas composition (II)).

band at 2092–2045 cm^{-1} and the LF band at 2038–1970 cm^{-1} [21,24–35]. Therefore, it is considered that the presence of SO_2 increased the band intensity of dicarbonyls and decreased the band intensity of monocarbonyls adsorbed on Ru at 2030 cm^{-1}. In addition, the HF_1 band appeared at 2154 cm^{-1} at 30 min and the intensity increased with time on stream (Fig. 7(c)–(d)). It has been reported that $Ru^{m+}(CO)_3$ tricarbonyls were characterized by a pair of the HF_1 and HF_2 bands [20,21,35–37] and that multicarbonyls were formed by the disruption of the Ru–Ru bonding by anionic groups [19,20]. Thus, the band at 2154 cm^{-1} was characterized by the tricarbonyls on the Ru sites oxidized by SO_4^{2-} species. Thus, it has been found that the SO_2 supply decreased the linearly adsorbed monocarbonyls, increased the dicarbonyls and developed the tricarbonyls.

The IR spectrum of the catalyst pretreated with SO_2 for 150 min did not change even after the interruption of SO_2 supply (Fig. 7(d) and (e)). When SO_2 was re-supplied to the catalyst, the IR spectrum did not change. This indicates that the reactivity of carbonyls on the SO_2-pretreated catalyst hardly changed by the interruption of SO_2 supply and the SO_2 re-supply.

To check the influence of a long-term SO_2 pretreatment on the IR spectra, the pellet 2.0 wt% Ru/Al_2O_3 catalyst was pretreated with 21 ppm SO_2 for 139 h in the fixed bed reactor. After it was confirmed that the catalyst showed changes in the selectivity in the presence/absence of sulfur compounds similar to those shown in Fig. 1, the catalyst was grounded, and the in situ IR spectrum was taken in the absence of sulfur compounds (gas composition (I)) (Fig. 7(f)). The dicarbonyls and tricarbonyls were observed as in the case of the in situ short-term SO_2 pretreatment. Thus, the IR spectrum for the long-term SO_2 pretreatment was essentially identical to those for the in situ short-term SO_2 pretreatment, though it differed in the degree of poisoning.

4. Discussion

Yokomizo et al. reported that the linearly adsorbed monocarbonyls were the most active species for the CO oxidation over a Ru/SiO_2 catalyst [20]. In this study, the SO_2 pretreatment decreased the linearly adsorbed monocarbonyls, disrupted the Ru–Ru bonding, and decreased the interaction between CO and Ru with a little higher oxidation state of Ru sites, which suppressed the activation of CO. As shown in Fig. 7(d) and (e), the interruption of SO_2 supply did not restore the IR spectra over the region of the C–O stretching vibrations. This indicates that the oxidized Ru was not reduced after the interruption of SO_2 supply and that the activation of CO was not restored.
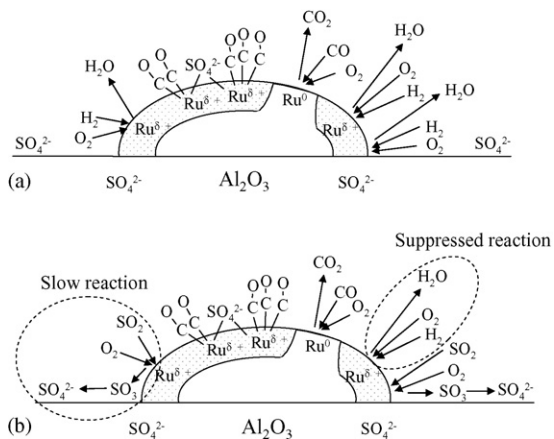
Fig. 8. Reaction models on the SO_2-pretreated catalyst (a) in the absence of sulfur compounds and (b) in the presence of SO_2.

In other words, SO_4^{2-} species strongly adsorbed on the oxidized Ru sites, which accumulated little by little during the SO_2 pretreatment, were not removed even after the interruption of SO_2 supply. Thus the CO oxidation was suppressed in the absence of SO_2, and O_2 was consumed in the upper stream of the catalyst bed by the H_2 oxidation. The proposed reaction model in the absence of sulfur compounds is shown in Fig. 8(a). The SO_2 pretreatment decreased the linearly adsorbed carbonyls on Ru^0 and decreased the CO coverage to promote the H_2 oxidation, which had been suppressed on the fresh catalyst with high CO coverage [38]. The H_2 oxidation might occur even over the partially oxidized Ru sites. Thus, the selectivity for CO oxidation decreased in the absence of sulfur compounds. In this case, CO was oxidized on the slightly remaining reduced Ru sites; however, the consumption of O_2 in the upper stream of the catalyst bed resulted in a decrease in the CO conversion.

On the other hand, in the presence of sulfur compounds, the sulfur compounds weakly adsorbed on the SO_2-pretreated catalyst were slowly oxidized to SO_4^{2-} species, most of which migrated to the support. The weakly adsorbed sulfur compounds probably covered the active sites, on which the H_2 oxidation could occur in the absence of sulfur compounds. For the H_2 oxidation on Ru catalysts, it has been reported that an H atom of an adsorbed H_2 molecule formed an OH group with an adsorbed O atom and then the OH group reacted with a dissociatively adsorbed H atom to form H_2O [39]. Assuming that the OH group reacts with an H atom adsorbed on another Ru site, two vacant Ru sites, both of which are located next to the adsorbed O atom, are needed for the H_2 oxidation. On the other hand, only one vacant Ru site next to the adsorbed O atom is needed for the CO oxidation. If the coverage with the weakly adsorbed sulfur compounds is high, it is probably difficult to give two vacant sites next to the adsorbed O atom for the H_2 oxidation. In addition, the high coverage with the weakly adsorbed sulfur compounds likely suppressed the migration of the H atom, though the CO oxidation occurs without the migration of CO. As a result, the H_2 oxidation was strongly suppressed and the selectivity for CO oxidation increased.

Fig. 8(b) shows the proposed reaction model in the presence of SO_2 over the catalyst. The active sites for the CO oxidation were hardly affected by the presence of sulfur compounds in the reactant gas. When sulfur compounds of high concentration were fed for a long term (Table 1(V and VI)), the weakly adsorbed sulfur compounds accumulated on the Ru particles and then suppressed the CO oxidation, keeping high selectivities for the CO oxidation. On the other hand, in the presence of SO_2 of low concentration, high CO conversions were kept for a long term (Table 1(VII)), since the weakly adsorbed sulfur compounds were also slowly oxidized to migrate to the support. However, sulfur compounds of very low concentration (0.21 ppm) slightly increased the selectivity (Table 2). After the interruption of sulfur compound supply, they were oxidized to SO_4^{2-} species, most of which migrated to the support. Therefore, the H_2 oxidation was promoted again.

5. Conclusions

The reaction behavior of the SO_2-pretreated Ru/Al_2O_3 catalyst for the PROX was investigated in the presence/absence of sulfur compounds. The following conclusions are drawn:

1. After the catalyst was pretreated with SO_2 for a long term, the H_2 oxidation was promoted at ca. 150 °C in the absence of sulfur compounds. On the other hand, in the presence of 2.1 ppm sulfur compounds, the catalyst showed high selectivities (46–53%) with high CO conversions (>95%) at the $[O_2]/[CO]$ ratio of 1.5.
2. The in situ IR results showed that coexistent SO_2 decreased the linearly adsorbed monocarbonyls, increased the dicarbonyls and developed the tricarbonyls. This suggests that the CO oxidation was suppressed by the SO_4^{2-} species strongly adsorbed on Ru, which oxidized Ru. Thus, the H_2 oxidation was promoted in the absence of sulfur compounds. In the presence of sulfur compounds, the H_2 oxidation was suppressed by the weakly adsorbed sulfur compounds, which were slowly oxidized and migrated to the support.

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