New reaction pathway in the selective oxidation of carbon monoxide over Ru/Al_2O_3

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Introduction

Selective oxidation of CO in a hydrogen-rich atmosphere (PROX) has attracted great attention in recent years because of its potential for removing CO contaminations from hydrogen-rich fuel gases for polymer electrolyte fuel cells (PEFC), which are produced by reforming of liquid fuels such as methanol or hydrocarbons. Various catalysts have been studied for this purpose, and among them supported Pt, Ru and Au catalysts are well recognized to have high activity and selectivity for this reaction. However, little is known about the structure of the active sites as well as the intrinsic mechanism for this reaction. In the present study, we have applied kinetic analysis together with in-situ FT-IR spectroscopy and isotopic tracer technique for the PROX reaction and found new reaction pathways, which can elucidate the selective oxidation of CO at lower temperatures in the presence of excess H_2.

Materials and Methods

Ru/Al_2O_3 catalysts were prepared by usual incipient wetness method employing K_2RuO_4 and $RuCl_3$ as precursors which were pore-filled into spherically molded Al_2O_3 support. After drying the catalysts were reduced *in situ* under H_2 flow at 573K, prior to the reaction. The catalytic reaction was carried out in a fixed-bed flow-type system. The input gas composition for PROX reaction was $H_2/CO/O_2/N_2$ = 70%/0.7%/1.4%/28%, and O_2/CO ratio was 2.0(space velocity =12,000h^{-1}). For IR measurement, the catalyst was pressed into a disk and put in an in-situ IR cell, which was connected to a closed gas circulation system. After the pretreatment, similar composition of mixed gases was introduced into the system and the spectra were taken during the PROX reaction as well as CO adsorption.

Results and Discussion

Fig. 1 demonstrates the temperature profiles of the typical PROX reaction (H_2/CO = 100) together with the addition effect of H_2 (H_2/CO=0, 2, 15, 30) and H_2O (3.2 vol.%) to the $CO-O_2$ reaction over 4 wt% Ru/SiO_2 catalysts. In the case of PROX reaction. CO conversion reached to 100% at around 363-373 K. On the other hand in the case of CO oxidation without H_2 (H_2/CO=0), 100% CO conversion was obtained only at 433-443 K. By adding H_2 to $CO-O_2$ reaction, the rate of CO oxidation increased significantly, approaching to the typical PROX reaction rate. The addition effect was pronounced even more in the case of H_2O as shown by the broken line in Fig.1, and 100% conversion was obtained even at 333K. These results strongly suggest that H_2 and H_2O enhance the rate of CO oxidation.

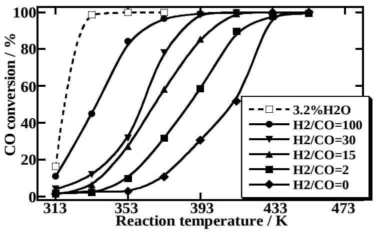

Fig. 1 Temperature profile of $CO-O_2$ reaction

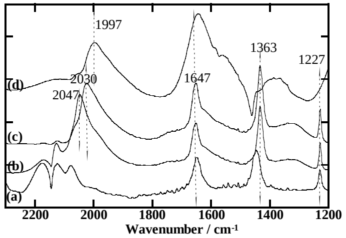

Fig.2 FT-IR spectra (a)PROX at 373K (b)CO intro.at R.T.(c)evac.at R.T. (d) H_2O added at R.T.

The FT-IR spectrum of adsorbed species during PROX reaction at 373K was shown in Fig. 2(a). Three characteristic peaks were observed at 1647, 1363 and 1227 cm^{-1}, which can be assigned to adsorbed carbonate species at the vicinity of Ru and Al_2O_3 support. The same peaks were observed when only CO was introduced onto the reduced Ru/Al_2O_3 at R.T. as shown in Fig.2 (b) & (c). These results suggest that the carbonate species may be formed by the disproportionation of CO and that formed CO_2 may react with surface OH to form C(a) and carbonate. When the gaseous CO was replaced by H_2O, the adsorbed carbonate peaks disappeared completely even at R.T, indicating a rapid reaction between carbonate and H_2O as shown in Fig.2 (d). The large enhancement effect of H_2O vapor addition for $CO-O_2$ reaction in Fig. 1 may be explained by this rapid removal of carbonate by H_2O.

In order to estimate the amount of C (a) formed by disproportionation of CO, adsorbed CO and carbonate species were removed by higher temperature evacuation (500k), and remained C(a) was titrated by the reaction with O_2. The amount of formed CO_2 was only 2/3 of the amount of CO_2 formed during disproportionation step. This result strongly suggests that there exists third CO_2 formation pathway during CO disproportionation through the oxidation of CO with the support -OH group, which possesses strong oxidation ability.

To confirm the participation of support-OH groups for this reaction, $C^{18}O$ was employed for the disproportionation process mentioned above. More than 85% of formed CO_2 was $C^{16}O^{16}O$ with 15% of $C^{16}O^{18}O$, while only trace amount of $C^{16}O$ was detected. These results clearly indicate the participation of support oxygen in the formation process of CO_2.

Fig. 3 summarizes the reaction pathways proposed in the present study. Scheme-I is the CO oxidation over Ru metal through CO (a) and O (a), which may become a predominant pathway at higher temperatures. Scheme-II represents the CO dispropartionation step to form C (a) and $CO_3H(a)$ which is formed by the reaction between CO_2 and OH. Formed carbonates easily react with H_2O formed by $H_2–O_2$ reaction and give CO_2 and surface OH group. Formed C (a) may also react with O_2 to form CO_2. Scheme-III represents the CO oxidation by special surface OH to form CO_2 and H_2. The latter two reaction pathways may be predominant at lower temperatures, where Ru surface is still saturated by adsorbed CO species.

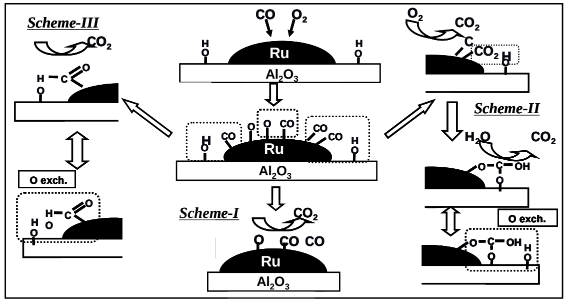

Fig. 3 Proposed reaction pathways