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CO adsorption and correlation between CO surface coverage and activity/selectivity of preferential CO oxidation over supported Ag catalyst: an *in situ* FTIR study

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In situ IR measurements for CO adsorption and preferential CO oxidation in H_2-rich gases over Ag/SiO_2 catalysts are presented in this paper. CO adsorbed on the Ag/SiO_2 pretreated with oxygen shows a band centered around 2169 cm^{-1}, which is assigned to CO linearly bonded to Ag^+ sites. The amount of adsorbed CO on the silver particles (manifested by an IR band at 2169 cm^{-1}) depends strongly on the CO partial pressure and the temperature. The steady-state coverage on the Ag surface is shown to be significantly below saturation, and the oxidation of CO with surface oxygen species is probably *via* a non-competitive Langmuir–Hinshelwood mechanism on the silver catalyst which occurs in the *high-rate branch* on a surface covered with CO below saturation. A low reactant concentration on the Ag surface indicates that the reaction order with respect to Pco is positive, and the selectivity towards CO_2 decreases with the decrease of Pco. On the other hand, the decrease of the selectivity with the reaction temperature also reflects the higher apparent activation energy for H_2 oxidation than that for CO oxidation.

KEY WORDS: FTIR; preferential CO oxidation; silver catalyst; CO coverage; selectivity.

1. Introduction

Supported silver catalysts are well-known for low temperature oxidation of carbon monoxide, epoxidation of ethylene, as well as for formaldehyde synthesis [1–4]. Many researchers have examined the effects of different preparation methods, supports and the reaction kinetics for CO oxidation on Ag/metal oxide catalysts (e.g. Ag/Cu,Mn/ reducible oxides) [5–7]. Recently, silver catalysts have gained attention for preferential oxidation of CO in H_2-rich gases (PROX), which is used for the purification of H_2 feed-gas streams from a methanol reforming for polymer electrolyte membrane (PEM) fuel cells [8–11]. The general suitability of the Ag/SiO_2 catalyst for the PROX reaction has been extensively investigated in our research group. The silver catalyst showed a relatively high activity and selectivity for CO selective oxidation at low temperatures ($<60°$ C). This, in principle, improves the cold-start properties in a fuel cell system, and also allows for a thermal integration of the PROX unit with the PEM fuel cell stack in the form of a thin second layer placed on top of the anode-side of the membrane electrode assembly [12]. It was also found that the selectivity for CO oxidation over silver catalyst decreased with the reaction temperature, which was drastically different from $Pt/\gamma\text{-}Al_2O_3$ catalyst in reaction properties, the selectivity for $Pt/\gamma\text{-}Al_2O_3$ catalyst remained constant for operating temperatures $\leq 200°$ C [13]. *Recently Mavrikakis et al. reported that both Au and Cu were more selective than Pt catalyst for CO selective oxidation in H_2 and the PROX selectivity was determined by the coverages of CO and H on the metal surfaces* [14]. Thus it is reasonable to assume that the higher activity and selectivity for CO selective oxidation over silver catalyst at low temperatures may be related with the steady state CO converges on the silver surface during the reaction. The studies for silver catalyst on this respect, which are crucial for mechanistic understanding of the reactions, are still lacking.

In this paper, we present results and discussion of a spectroscopic study of CO adsorption and its coverage on the surface of a silver catalyst by means of the *in situ* FTIR technique.

2. Experimental

The Ag/SiO_2 catalyst was prepared by an incipient wetness impregnation method, and the as-prepared $AgNO_3/SiO_2$ sample was aged at RT and dried at 80° C for 12 h [8,11].

The Ag/SiO_2 sample was pressed into a self-supporting wafer of approximately 15 mg/cm^2. The wafer was placed in a quartz IR cell equipped with CaF_2 windows, in which *in situ* pretreatments could be performed, and then pretreated in a flowing 30% O_2/He

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mixture at 500° C, and followed by H_2 at 100° C. The pretreated sample was evacuated to 10^{-5} Torr at the treatment temperature for 1 h, subsequently cooled to −120° C, then exposed to CO (or CO/O_2) for IR study. All IR spectra were recorded on a Fourier transform infrared spectrometer (Nicolet Impect 410) with a resolution of 4 cm^{-1} and 64 scans in the region of 4000–1000 cm^{-1}. All the spectra were subtracted by the spectrum of the sample recorded before adsorption.

Reaction tests were conducted in a conventional flow reactor with on-line gas chromatograph analysis. [10,11] The reactants were fed with a volume ratio of $H_2/CO/O_2 = 98.5/1/0.5$, and the selectivity toward CO oxidation was calculated from the oxygen mass balance.

3. Results and discussion

3.1. Kinetic comparison of Ag with Pt, Au catalysts

In microkinetic studies of the PROX over Pt/γ-Al_2O_3 at 150–250° C, the reaction orders with respect to Pco and Po_2 were determined to be −0.4 and +0.8, respectively [13]. Mechanistically, this is consistent with the selective CO oxidation reaction occurring in the so-called *low-rate branch* [15]. In this reaction regime, the Pt surface is thought to be completely covered by CO, with dissociative O_2 adsorption being the rate limiting step [16]. Thus CO and H_2 oxidation rates are coupled, giving an essentially constant selectivity of ca. 40% on the Pt/γ-Al_2O_3 catalyst over the entire range of CO (0.02–1.5 kPa) and O_2 partial pressures at temperatures below 250° C [13].

However the rate of the reaction in the presence of both oxygen and carbon monoxide in the ambient gas was first order with respect to carbon monoxide, and zero order with respect to oxygen gas on silver catalyst at 0–100° C (Pco = 30–60 Torr; Po_2 *= 10–30 Torr)* [17]. And it was found that the rate of CO oxidation over silver catalyst was proportional to the pressure of CO and independent of that of the oxygen [18]. *The similar results have also been obtained over gold catalyst, and the reaction orders with respect to Pco and* Po_2 *were 0.55 and 0.27 at 80 °C, respectively* [19]. In terms of a mechanistic model, the positive CO reaction order suggests that there is no self-poisoning of the CO oxidation reaction by the adsorbed CO. *A low CO coverage on the gold particles under reaction conditions (40–80°* C) has been found. Burghaus *et al.* proposed that the reaction for CO oxidation follows a Langmuir–Hinshelwood mechanism [20]. Thus in this case, it is reasonable to suggest that a decrease of the CO partial pressure on silver surface will decrease the reaction probability for CO oxidation. *Figure* 1 *shows the selectivity of CO selective* oxidation in H_2 *over Ag/*SiO_2 *catalyst under a real* reaction condition ($\lambda = 1$, $\lambda = 2Po_2/Pco$, H_2 *balances*) *as a function of reaction temperature*. The relatively high selectivity of the Ag catalyst, particularly at low temperatures, indicates that the activity for CO selective oxidation may be related to the higher CO coverage at low temperatures, as compared with that at elevated temperatures. The following *in situ* FTIR experiments will give further credence for the assumption of the existence of a low CO coverage condition during the PROX reaction on Ag/SiO_2 catalyst.

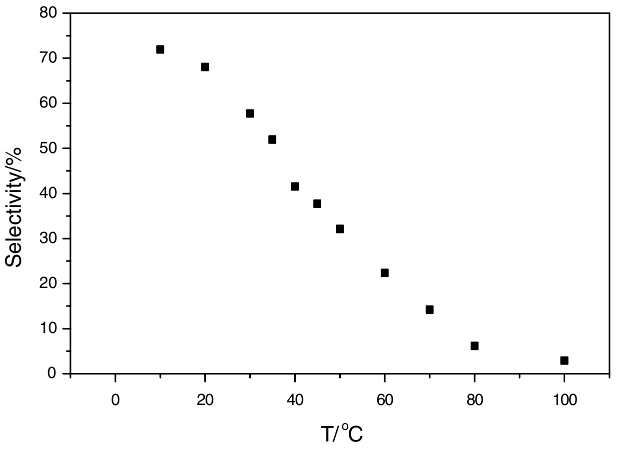

Figure 1. Variation of selectivity to CO oxidation in H_2 over Ag/SiO_2 with reaction temperature under real reaction system (1% CO, 0.5% O_2, H_2 balances). The composition of the effluent gas is monitored by an on-line GC-14B gas chromatograph equipped with a Molsieve 5 Å column and a Porapak Q column.

3.2. CO coverage on Ag/SiO₂ catalyst

3.2.1. CO adsorption at ambient temperature on Ag/SiO₂

Introduction of CO (26 mbar) to the activated Ag/SiO_2 catalyst (pretreated with oxygen at 500° C) resulted in the appearance of one main band with a maximum at 2169 cm^{-1} and a high-frequency shoulder at 2187 cm^{-1}, which are assigned to linearly adsorbed Ag^+–CO species [21–23]. These bands decreased in intensity with the decrease in equilibrium pressure and disappeared completely after evacuation (not shown here). Generally, the CO adsorption species on the silver surface are moderately unstable [21,22,24]. When silver catalyst was reduced with H_2, the band for CO adsorption disappeared quickly after slight evacuation.

3.2.2. Low temperature CO adsorption on Ag/SiO₂

Usually adsorption is favored at low temperatures, and those adsorption species that are not stable at ambient temperature can thus be detected. Two main bands still developed in the ν(CO) stretching region after adsorption of CO (26 mbar) at −120° C on the Ag/SiO_2 catalyst pretreated with oxygen at 500° C, as shown in figure 2a. The bands at 2169 and 2187 cm^{-1}, although exhibiting a decrease in intensity with the CO pressure, did not disappear after evacuation. These bands are caused by the same Ag^+–CO species that had been already detected at ambient temperature. The position

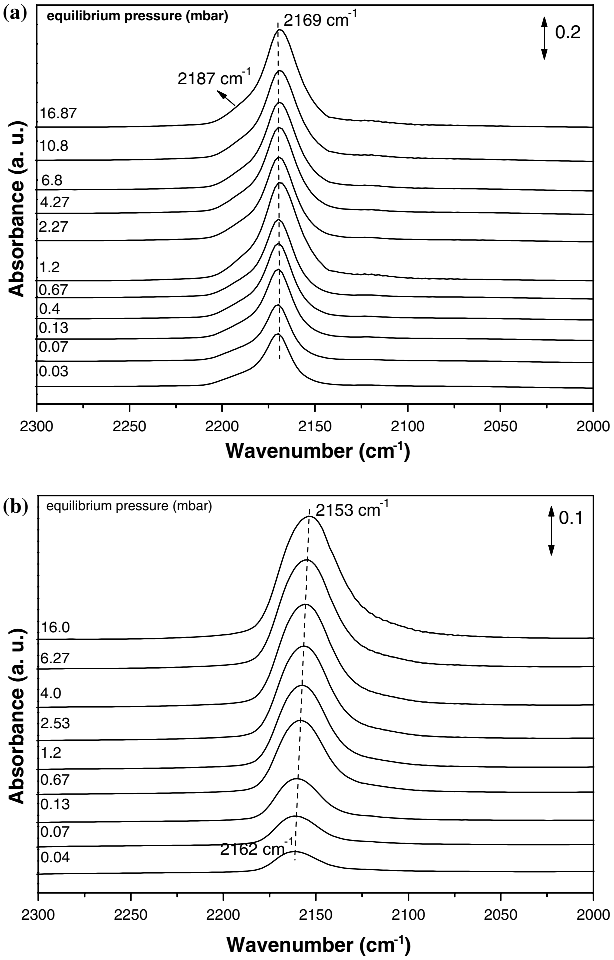

Figure 2. FTIR spectra of CO adsorbed at −120° C on Ag/SiO_2 treated with oxygen at 500° C (a), and followed by in situ H_2 treatment at 100° C (b). CO equilibrium pressure changes from 0.03 to 16 mbar.

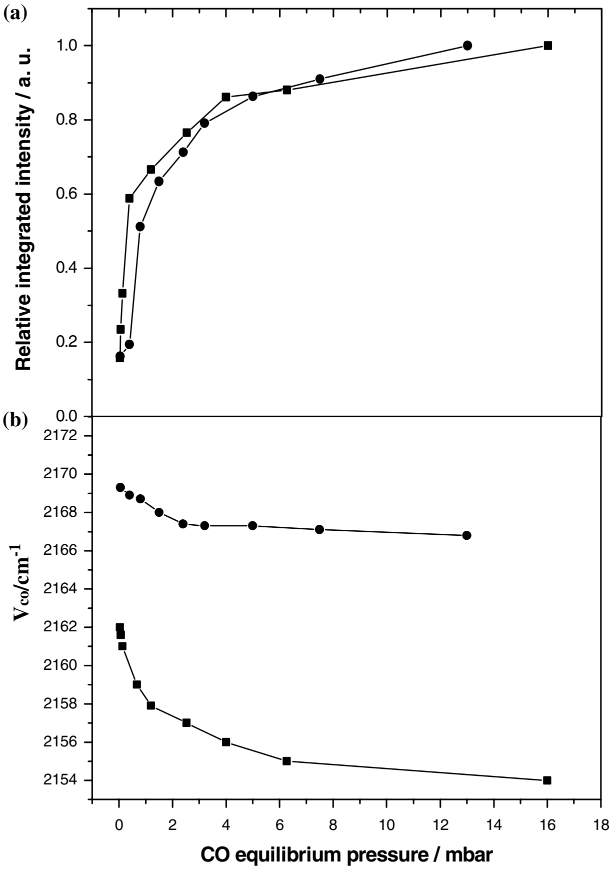

Figure 3. IR intensities of linearly bonded CO on Ag/SiO_2 (a) and corresponding band position (b) during pure CO adsorption (■) and CO oxidation (●) at −120° C.

of the 2169 cm^{-1} band on the silver catalyst pretreated with oxygen was coverage independent, which implies that the respective Ag^+ adsorption sites were isolated cations. The frequency of CO adsorption on the Ag/SiO_2 sample reduced with H_2 at 100° C following O_2 pretreatment shifted to a lower frequency (2162 cm^{-1}), which is assigned to $Ag^{\delta+}$–CO species (figure 2b, $0 < \delta < 1$). *Even if the reduction temperature increases to 500 °C, there is still no significant IR features associated with CO adsorbed on metallic silver sites (2020–2060 cm^{-1}) due to the formation of subsurface oxygen species resulted for oxygen pretreatment at high temperatures* [11]. The resulting CO adsorption intensities and the corresponding IR frequencies are plotted in figure 3 as a function of CO equilibrium pressure. The CO_{ad} intensity increased with the CO equilibrium pressure (from 0.03 to16 mbar), which represented a significant increase of the CO coverage on the silver particles. The decrease of the υ_{CO} on the silver surface from 2162 to 2153 cm^{-1} with the increasing of θ_{CO} (figure 3b) indicated that there existed slight interaction between the adsorbed molecules, and also suggested that the band corresponded to the CO located on associated Ag^+ cations. This kind of blue-shift with the decreasing in coverage was enhanced with the reduction temperature.

The IR intensity of CO adsorbed on the silver catalyst also decreased with the temperature, as shown in figure 4. It suggests that CO adsorption on the silver surface under the real reaction temperature is rather weak. The details will be discussed in the following part, which concerns the low CO coverage on the silver surface under the reaction condition.

Influence on the mechanistic aspect of the selective CO oxidation may be drawn from what is known for the CO oxidation reaction on single crystals and supported catalysts. In early reviews by Engel and Ertl [15,25], concerning CO oxidation on both single crystals and polycrystalline materials under UHV conditions, a distinction has been made between two reaction regimes: (a) a *high rate branch* where the CO surface concentration is very small; (b) a *low rate branch* in which the surface is predominantly covered with adsorbed CO. Both branches belong to the Langmuir–Hinshelwood mechanism. From the FTIR measurements of CO adsorption on Ag/SiO_2, one would expect the reaction to occur in the *high rate branch*. i.e., the CO

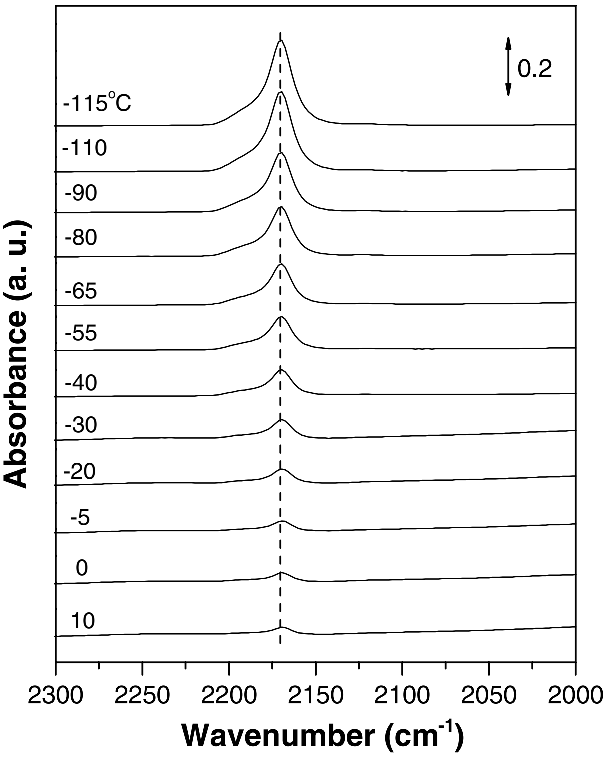

Figure 4. Variation of the intensity of linearly bonded CO on silver catalyst with the temperature. The temperature of CO adsorption is at −120° C, and all spectra are taken after 10 min of of equilibrium.

concentration is low on the silver surface at conditions which prevail in the PROX process. *Similarly, the steady-state coverage on the Au surface was found to be significantly below saturation and the low reactant surface concentrations explain the positive reaction order with respect to Pco, owing to a reduced reaction probability at reduced* θ_{CO} [26].

3.2.3. *CO and O_2 co-adsorption on Ag/SiO_2*

The P_{CO}-dependence of the CO vibration frequency during CO oxidation on Ag/SiO_2 catalyst reduced with H_2 is shown in figure 3b, and the associated FTIR spectra are displayed in figure 5. Compared the case of CO adsorption with pure CO, the CO frequency under oxidation conditions is now shifted to significantly higher wavenumbers and barely changes (2169–2167 cm^{-1}) with the decrease of the CO equilibrium pressure (similar to CO adsorbed on the silver catalyst pretreated with oxygen). This increase in ν_{CO} is assigned to the effect of co-adsorption oxygen on the decreasing of the electron density in the silver particles.

Two types of Lewis acid sites may be distinguished by their preferential bonding nature to ligands, namely, electrostatic and covalent [27]. Silver cations are considered to be covalent acids, that is to say, they form a covalent bond with the ligands. In general, CO can be bonded to covalent Lewis acid sites by both σ-donation and π-back-donation. Many data indicate that the π-back-donation in the Ag^{+}–CO complexes is negligible and the σ-donation bond is predominantly formed [28]. Under the CO oxidation condition, the presence of oxygen species near the silver decreases the electron density on the silver, and therefore the back donation from the silver to the anti bonding π orbital of CO is decreased, resulting in the consequent insignificant increase of the CO frequency. The nearly-zero shift under CO oxidation condition observed in figure 3b can be understood as a result of these two counteracting effects (decreasing ν_{CO} with increasing θ_{CO}, but increasing wavenumber ν_{CO} with increasing $P_{CO/O2}$).

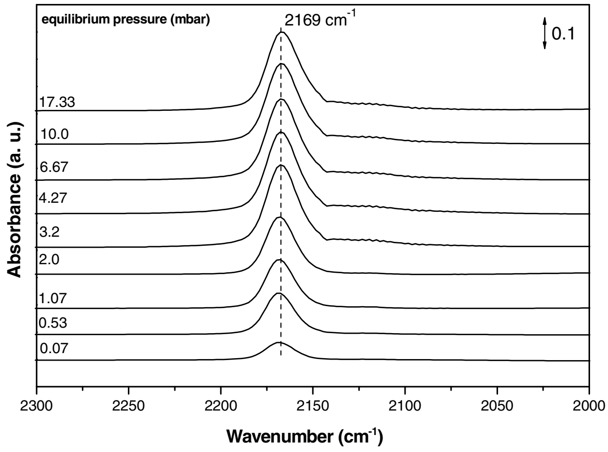

Figure 5. FTIR spectra of CO oxidation at −120° C on Ag/SiO_2 reduced by H_2 at 100° C following oxygen treatment at 500° C. CO is exposed to the O_2-covered silver surface, and its equilibrium pressure changes from 0.07 to 17 mbar.

FTIR spectra after CO adsorption on O-covered Ag/SiO_2, or O_2 adsorption on CO-covered Ag/SiO_2, exhibited similar CO vibration frequency, as shown in figure 6. The CO frequency under these two conditions also significantly shifted to higher wavenumbers

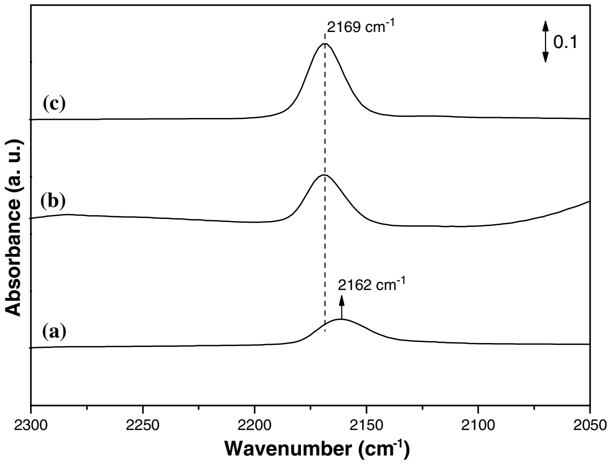

Figure 6. CO-FTIR spectra after CO directly adsorbed on Ag/SiO_2 catalyst (a), O_2 adsorbed on CO-covered sample (b) and CO adsorbed on O_2-covered Ag catalyst (c) at −120° C.

(2169 cm^{-1}). From these results, it can also be concluded that the existing of oxygen does not block the adsorption of CO on the silver surface, and it does only change the adsorption properties of the silver surface. Meanwhile the low CO coverage on the Ag surface does not influence the dissociative adsorption of O_2 as well as the oxidation of H_2 with the adsorbed O_2 at low temperatures. Thus, it is reasonable to think that there exists a non-competitive adsorption for CO and O_2 over the silver surface. *Ag is known to incorporate oxygen and form subsurface oxygen species under oxygen exposure at elevated pressures or pretreatment with oxygen at high temperatures. Rocca et al. have found that the subsurface oxygen species affects the catalytic properties of silver surface, and that CO adsorption can be stabilized up to crystal temperatures of 160 K under ultra high vacuum conditions* [29]. *In a recent study we have found the crucial role of subsurface oxygen species for the CO oxidation* [11]. *A possible reaction pathway for CO selective oxidation catalyzed by silver catalysts and the possible roles of oxygen in the feed gas were suggested. However the detailed reaction mechanism of CO with subsurface and surface oxygen species on the silver catalyst is still unclear, and further* [18] *O isotope experiment will be required to get more detailed information in the future.*

3.3. Temperature dependence

Figure 7 shows the *in situ* FTIR spectra of the oxidation reaction on the Ag/SiO_2 catalyst at varying temperatures, which will provide further evidence for the hypothesis that the CO coverage under PROX conditions at low temperatures (e.g. RT) is far below saturation. CO was injected to the O_2-covered Ag catalyst at −120° C, and then the temperature was increased. All spectra were taken after 10 min of equilibrium. Clearly, the amount of linearly adsorbed CO decreased with the increasing in temperature, and adsorbed CO_2 resulted from CO oxidation yielded a peak of 2348 cm^{-1} at −75° C. The detailed reaction results obtained by *in situ* FTIR will be presented elsewhere. The remarkable decrease in the CO coverage with temperature resembles the behavior expected in the steep, middle regime of a Langmuir adsorption–desorption isobar, in which the CO coverage is far below saturation. This gives further evidence to the hypothesis that the CO coverage under PROX reaction conditions (RT-60° C) is rather low on the Ag/SiO_2 catalyst. The large variation of the CO_{ad} concentration on the silver surface fits well to the reaction scheme in which CO supply is dominantly rate limiting, which allows one to understand well the reason of the decrease in selectivity for CO oxidation with the increase in reaction temperature. The increase in selectivity with decreasing temperature also reflects higher apparent activation energy for H_2 oxidation than that for CO oxidation.

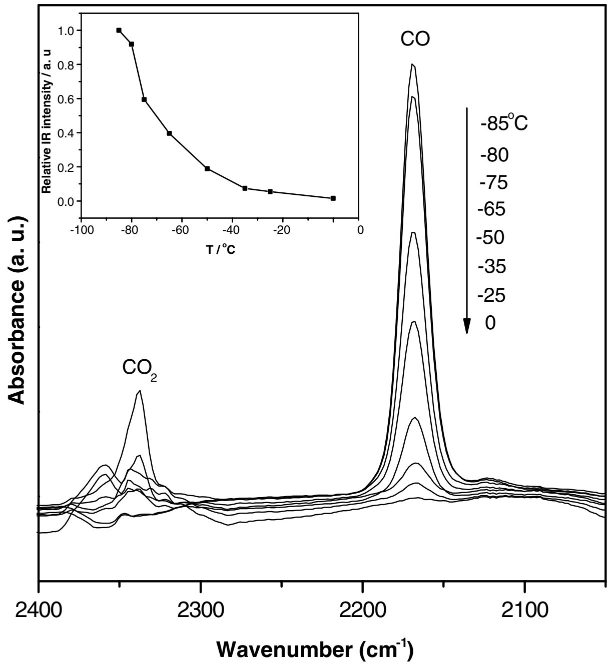

Figure 7. *In situ* FTIR spectra on Ag/SiO_2 during CO oxidation at different temperatures. Inset shows the integrated IR intensities of linearly bound CO versus temperature. All spectra are taken after 10 min of equilibrium. Adsorbed CO_2 on silver surface yields a peak of 2348 cm^{-1} at −75° C, and gas CO_2 shows a drouble peaks with increasing the temperature.

4. Conclusions

Linearly bonded CO is the dominant species on silver catalysts, and the electronic effect of O_2 is also observed. Adsorbed CO gives a higher frequency for oxygen-existing system due to a decrease in the electron density on atoms of the Ag surface. It is suggested that the reaction kinetics and the selectivity in the PROX reaction on an Ag/SiO_2 catalyst are largely determined by the steady-state CO coverage on the catalyst surface, and the CO coverage on the silver surface changes significantly with the temperature and CO pressure. *There exists a non-competitive adsorption for CO and oxygen on the silver surface, and the oxidation of CO with surface oxygen species occurs in the high-rate branch on a surface covered with under-saturation CO*. The facts that low CO coverage does not limit the adsorption of O_2 and the oxidation of H_2 indicate that the reaction rates of CO and H_2 oxidation are not interrelated. The lower CO coverage on the silver surface and the higher apparent activation energy for H_2 oxidation will lead to the decrease of selectivity for CO oxidation at higher reaction temperatures.

Acknowledgments

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