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# Temperature-programmed FT-IR study of the adsorption of CO and co-adsorption of CO and H<sub>2</sub> on Ni/Al<sub>2</sub>O<sub>3</sub>

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## Abstract

The adsorption of CO and co-adsorption of CO and H<sub>2</sub> on Ni/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by a distinct procedure were studied by means of FT-IR technique. The study shows that only one kind of CO adsorption site – the linear CO adsorption site – exists on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst used in present work. Temperature-programmed heating of CO adspecies in CO atmosphere reveals that the disproportionation of linearly adsorbed CO may occur at above 473 K. In H<sub>2</sub> + CO atmosphere, a new IR band centered near 1910 cm<sup>-1</sup> emerges, the intensity of which increases and decreases concomitantly with that of the band centered about 2050 cm<sup>-1</sup> with increasing temperature, indicating the occurrence of a new adspecies in the dynamic process of CO hydrogenation under reaction conditions. This new adspecies is tentatively ascribed to nickel carbonyl hydride species. The methanation of CO on Ni/Al<sub>2</sub>O<sub>3</sub> may occur via a mechanism involving the formation of nickel carbonyl hydride species.

*Keywords:* FT-IR spectroscopy; Adsorption; Carbon monoxide; Nickel; Alumina

## 1. Introduction

The adsorption of CO and co-adsorption of CO and H<sub>2</sub> on nickel-based catalysts is of significant theoretical and practical importance. A wealth of work has been performed in order to ascertain the surface structure of the catalyst and the reaction mechanism of CO hydrogenation [1–8]. The IR bands of CO adsorption on Ni/Al<sub>2</sub>O<sub>3</sub> in the region of near 2080 cm<sup>-1</sup>, 2040–2070 cm<sup>-1</sup>, 1900–1975 cm<sup>-1</sup>, and 1800–1900 cm<sup>-1</sup> are generally attributed to

multiple- (subcarbonyl), mono- (linear), bridged and multicentered CO adspecies respectively [1,2,6,9–11]. Since the true catalyst is the solid which spontaneously forms under reaction conditions [12], dynamic studies have attracted growing interest. Working with a 20% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and using TP-IR method, Lu et al. [2] found that both the linear and bridged CO adspecies were involved in the hydrogenation reaction, and the dissociation of CO might not surely be the rate-controlling step in CO methanation, Stockwell et al. [4] and Underwood et al. [13] proposed that the global rate of CO methanation on Ni/Al<sub>2</sub>O<sub>3</sub> was controlled by a competition between the formation and the hydrogenation of CH<sub>x</sub> species. Study of the

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dynamic behavior of CO adspecies on a distinct adsorption site may enable us to catch a glimpse of the related catalytic reaction at molecular level. This paper investigates the adsorption of CO and the coadsorption of CO and H<sub>2</sub> on Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with only one kind of CO adsorption site – the linear CO adsorption site – in an attempt to understand the molecular aspects of the mechanism of CO methanation.

## 2. Experimental

### 2.1. Preparation of catalyst

The catalyst was prepared by wet impregnation using nickel nitrate solution. The support was degassed at 283 K before impregnation. The nickel concentration of the solution was controlled to make the final nickel content of the catalyst to be less than 5%. The support was impregnated for 24 h and the excess solution was poured out. Then the supported nickel nitrate was dried in a vacuum system, and then calcined in air flow at 673 K for 4 h. The nickel content of the finished catalyst was detected to be 3.34 wt.-% by atomic absorption spectroscopy.

### 2.2. Infrared spectroscopy measurement

The IR studies were performed with a Perkin Elmer 599B type Fourier-transform infrared (FT-IR) spectrometer.

### 2.3. Pretreatment of the sample

The precursor was compressed under 7 tons/cm<sup>2</sup> pressure in order to obtain disks. The sample disk was installed in an heatable absorption cell coupled to a vacuum system and reduced at 673 K in H<sub>2</sub> flow for 2 h. After that, the system was evacuated to 10<sup>-4</sup> Torr at 673 K and then cooled to 283 K in vacuum prior to

adsorption, and IR spectrum of the catalyst was recorded.

### 2.4. Desorption of CO adspecies on Ni/Al<sub>2</sub>O<sub>3</sub> in vacuum

The pretreated sample was exposed to CO at 22 Torr, and adsorption spectrum of CO was recorded after 15 min CO exposure, and the system was evacuated and again a spectrum was recorded. Then heating with a temperature ramp of 8 K/min in vacuum was performed and another spectrum was recorded at 323 K.

### 2.5. Temperature-programmed heating in CO ambience

The pretreated sample was exposed to CO at 18 Torr. IR spectrum was recorded after a contact of 15 min at 283 K. Then the system was subjected to a temperature-programmed heating with a ramp of 8 K/min in CO atmosphere, and IR spectra were recorded at different temperatures.

### 2.6. Temperature-programmed reaction in CO + H<sub>2</sub> atmosphere

1. The pretreated sample was exposed to CO at 20 Torr, and IR spectrum was recorded after 15 min. Then H<sub>2</sub> at 20 Torr was introduced in the system and IR spectra were recorded under temperature-programmed heating with a temperature ramp of 8 K/min in a CO + H<sub>2</sub> mixture.

2. A reverse order of the introduction of the adsorbates was also performed using H<sub>2</sub> at 15 Torr and CO at 20 Torr, and IR spectra were recorded under the same temperature-programmed heating described above in CO + H<sub>2</sub> ambience

3. Premixed CO (25 Torr) and H<sub>2</sub> (45 Torr) were introduced to the pretreated sample, and then the system was heated with a temperature ramp of 8 K/min in H<sub>2</sub> + CO ambience. IR spectra were recorded at given temperatures.

### 3. Results and discussion

#### 3.1. The desorption of CO adspecies on Ni/Al<sub>2</sub>O<sub>3</sub> in vacuum

As shown in Fig. 1, the IR spectrum of the catalyst exposed to CO at 22 Torr and at 283 K shows three absorption peaks centered at 2180 cm<sup>-1</sup>, 2111 cm<sup>-1</sup>, and 2058 cm<sup>-1</sup> with a shoulder at 2075 cm<sup>-1</sup>, which can be ascribed to linear CO adspecies on Ni<sup>δ+</sup> and Ni<sup>0</sup> [6]. No peak in the region from 1900 cm<sup>-1</sup> to 1975 cm<sup>-1</sup> indicates the absence of bridge CO adspecies. After the removal of weakly bounded species by evacuation at 283 K, only the peak at 2075 cm<sup>-1</sup> remains with remarkable decrease in intensity. Subsequent rise in temperature makes further decrement in intensity with frequency shift to lower values, but no band in the region from 1900 cm<sup>-1</sup> to 1975 cm<sup>-1</sup> is observed. These facts indicate the existence of only one kind of CO adsorption site – the linear CO adsorption site – on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst prepared and treated in present study. Many factors influence the CO adsorption behavior of Ni/Al<sub>2</sub>O<sub>3</sub>. The Ni source, the predrying temperature in preparation, the reduction temperature and the Ni loading significantly alter CO adsorption on Ni/Al<sub>2</sub>O<sub>3</sub> [2,5]. In fact, Peri observed the unique linear adsorption of CO on

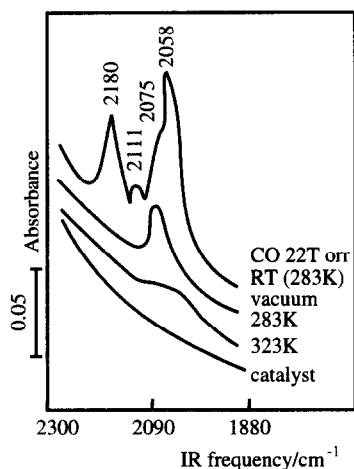


Fig. 1. Vacuum desorption of adsorbed CO.

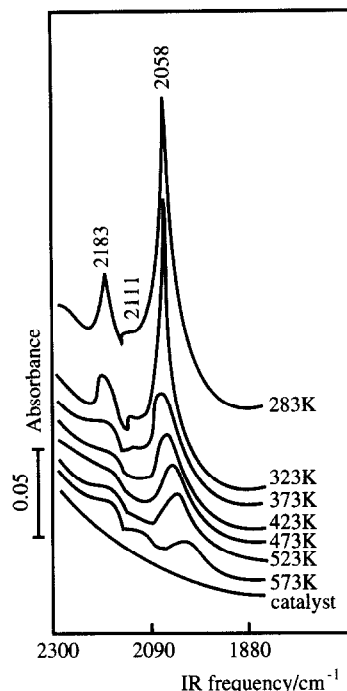


Fig. 2. Temperature programmed heating of adsorbed CO in CO atmosphere  $P_{\text{CO}} = 18$  Torr.

Ni/Al<sub>2</sub>O<sub>3</sub> with very low Ni concentration [6], but the dynamic behavior has not yet been investigated. In the present case, the observation of only one kind of CO adsorption site may be caused by the low nickel loading, the low predrying temperature and the low reduction temperature.

#### 3.2. Temperature-programmed heating in CO atmosphere

Fig. 2 shows the temperature dependence of IR intensities in CO atmosphere. The intensity of the band at 2058 cm<sup>-1</sup> decreases with increasing temperature from 283 K to 373 K with little shift in frequency, but there is little change in IR intensity from 373 K to 473 K while the frequency shifts to lower values. Further increase in temperature (above 473 K) results in a remarkable decrease in intensity and the shift of IR frequency to lower values continues. It should be emphasised that no band in the region of 1900–1975 cm<sup>-1</sup> is observed in the whole heat-

ing process in CO atmosphere. Temperature-programmed desorption of adsorbed CO showed that the desorption of adsorbed CO started at rather low temperature with maximum desorption rate at about 373 K, but the disproportionation of adsorbed CO could only occur above 400 K with maximum CO<sub>2</sub> formation rate at about 523 K [14–17]. Thus the decrease in intensity of IR band at 2058 cm<sup>-1</sup> in the temperature region from 283 K to 373 K may indicate the thermal desorption of linearly bounded CO on Ni/Al<sub>2</sub>O<sub>3</sub> and the disproportionation of CO on the specific linear CO adsorption site may occur above 473 K, which is in good agreement with the literature.

### 3.3. Temperature-programmed IR measurement of preadsorbed CO linearly bounded to Ni/Al<sub>2</sub>O<sub>3</sub> in CO + H<sub>2</sub> mixture

When H<sub>2</sub> is contacted with the catalyst with preadsorbed CO, the IR spectrum varies little, as shown in Fig. 3, indicating that the preadsorbed CO is not displaced by H<sub>2</sub> at room temperature, which is in good agreement with the result of previous work [14]. The intensity of the IR band at 2057 cm<sup>-1</sup> decreases with increasing temperature from 283 to 373 K, which is similar to what observed in TP-IR measurement in CO atmosphere. It indicates the thermal desorption of CO adspecies. The fact that neither CH<sub>4</sub> nor CO<sub>2</sub> was detected in this temperature range in previous studies [14–16] carried out under similar conditions, supports this assignment. The intensity of the IR band centered at 2057 cm<sup>-1</sup> increases from 373 to 473 K and reaches a maximum at about 473 K, further increase in temperature decreases the intensity. It is remarkable that a new band centered near 1912 cm<sup>-1</sup> appears and the variation in both the intensity and frequency of the new band is concomitant with the band centered near 2057 cm<sup>-1</sup> with increasing temperature, which indicates the formation of new adsorption species. The ascription of this band will be discussed later.

### 3.4. Temperature-programmed IR measurement for preadsorbed H<sub>2</sub> and co-adsorbed CO + H<sub>2</sub> in H<sub>2</sub> + CO mixture

In the case of H<sub>2</sub> preadsorption or H<sub>2</sub> + CO co-adsorption, the band centered near 2057 cm<sup>-1</sup> disappears at 283 K. However, with increasing temperature, two bands centered near 2057 cm<sup>-1</sup> and 1912 cm<sup>-1</sup> reappear and the intensity of the two bands changes concomitantly to reach maximum at about 473 K, with frequency shift to lower values, as shown in Figs. 4 and 5. When H<sub>2</sub> is preadsorbed (Fig. 4), the two bands emerge and vanish at a lower temperature than the corresponding ones when CO is preadsorbed (Fig. 3) or coadsorbed (Fig. 5).

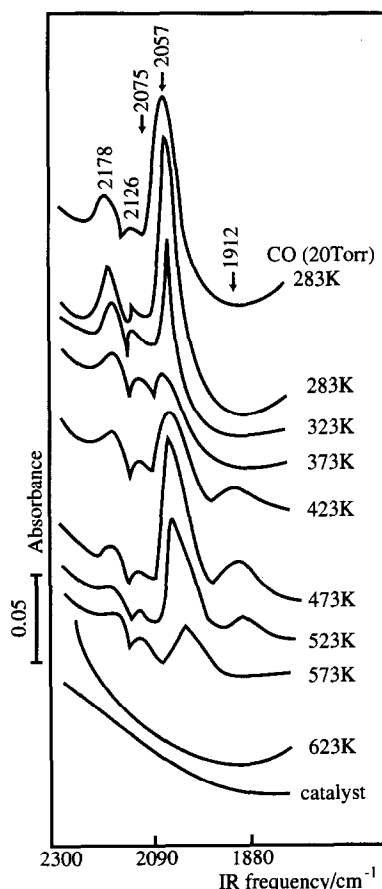


Fig. 3. Temperature programmed reaction of adsorbed CO in CO (20 Torr) + H<sub>2</sub> (20 Torr) mixture.

The coadsorption of CO and H<sub>2</sub> on Ni/Al<sub>2</sub>O<sub>3</sub> has been examined in several studies [2,4,14,15]. It was tentatively proposed that preadsorption of H<sub>2</sub> did not affect the amount of CO that would be adsorbed subsequently [14]. Our IR results indicate that the preadsorption of H<sub>2</sub> on the distinct linear CO adsorption site may inhibit the adsorption of CO, and the adsorption of H<sub>2</sub> is superior to that of CO in the competition adsorption in CO + H<sub>2</sub> mixture at 283 K. The discrepancy may be caused by the following reasons: (i) In the present study the adsorption occurs on the distinct site, the coverage does not alter the adsorption state of CO, and in previous works the adsorption sites were not separated thus the results obtained from adsorption measurement reflected the overall effects of the

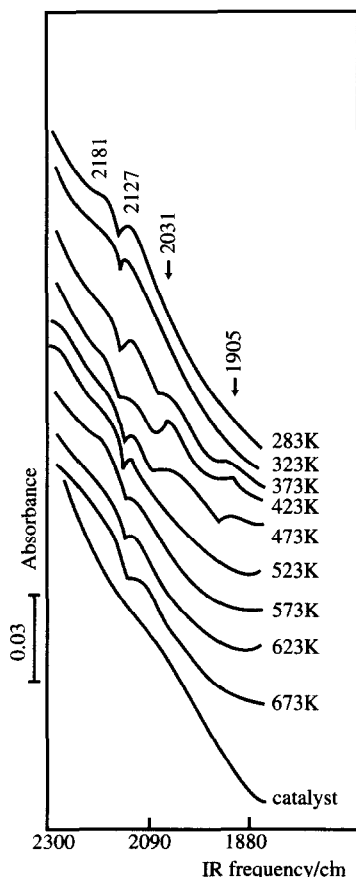


Fig. 4. Temperature programmed reaction of adsorbed H<sub>2</sub> in CO (20 Torr)+H<sub>2</sub> (15 Torr) mixture.

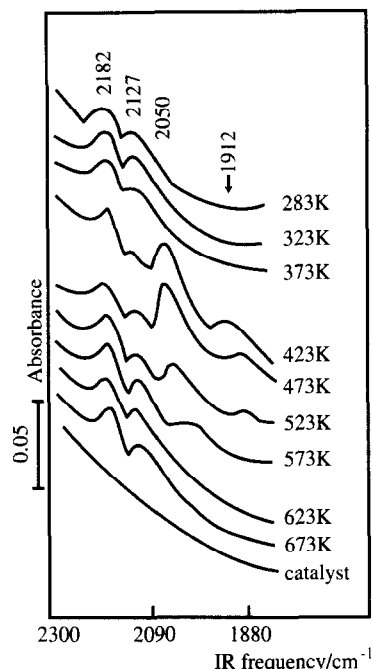


Fig. 5. Temperature programmed reaction of coadsorbed CO in CO (25 Torr)+H<sub>2</sub> (45 Torr) mixture.

catalyst. (ii) Different adsorption temperatures are used.

### 3.5. Nickel carbonyl hydride species

The band near 1912 cm<sup>-1</sup>, emerges in the region of bridge-CO adsorption. Nevertheless, there is reason in ascribing the two concomitantly appearing bands at 1912 and 2058 cm<sup>-1</sup> to nickel carbonyl hydride species. The band at 1912 cm<sup>-1</sup> is not observed in the absence of H<sub>2</sub>. The evacuation and the subsequent heating which significantly change the coverage prevent its appearance. It is also not observed in the temperature-programmed heating in CO atmosphere. These facts do not support the assignment of bridge CO adspecies initiated by CO coverage or adsorption temperature, but indicate the formation of new adspecies. Metal carbonyl hydride species with IR bands near 2000 cm<sup>-1</sup> have been proposed on rhodium and ruthenium catalysts by theoretical and experimental investigations on the interaction of CO + H<sub>2</sub> or CO<sub>2</sub>

+ H<sub>2</sub> over these catalysts [18–20]. The infrared spectrum of hydrogen adsorbed on Ni/Al<sub>2</sub>O<sub>3</sub> was observed at 1880 cm<sup>-1</sup> with a half width of about 50 cm<sup>-1</sup> by Nakata [26]. Thus nickel carbonyl hydride species may form when CO + H<sub>2</sub> mixture interacts with a nickel catalyst. The concomitant appearance and concomitant temperature dependence of the two bands centered near 2050 cm<sup>-1</sup> and 1912 cm<sup>-1</sup> in the presence of H<sub>2</sub> confirm the above reasoning.

There are some contention on the methanation mechanism of CO in the literature. The C–O bond breaking mechanism was widely proposed and thought to be the rate-determining step [14,15,21,22]. The rate-determining step was also proposed to be linked to the hydrogenation of surface carbon via dissociative adsorption of CO and the possibility of collision between gaseous hydrogen and the active surface carbon [23]. The direct disproportionation mechanism [24], the hydrogen assisted dissociation mechanism [3,25], and other mechanisms with no unequivocal rate-determining step [4,13] have also been reported. From our results, we tentatively propose a nickel carbonyl hydride intermediate mechanism on the linear CO adsorption site for the following reasons: (i) The direct disproportionation of CO in CO atmosphere occurs at a much higher temperature than that for the methanation reaction to occur in CO + H<sub>2</sub> mixture, as observed by others [14–17]. The two concomitantly appearing bands which also emerge at much lower temperature than that for the disproportionation to start in CO atmosphere in the present study may indicate the reaction of CO with H<sub>2</sub>. (ii) The temperature range for the two concomitantly appearing bands to emerge, vary in intensity and disappear, is in accord with that for CH<sub>4</sub> formation [14,15,17].

#### 4. Conclusion

Distinct adsorption site – the linear CO adsorption site on Ni/Al<sub>2</sub>O<sub>3</sub> – could be obtained

by a specific procedure. The realization of one kind of distinct adsorption site facilitates the dynamic study of adsorbed CO species.

On the linear CO adsorption site, the disproportionation starts at above 473 K. The concomitantly appearing IR bands centered near 2057 cm<sup>-1</sup> and 1912 cm<sup>-1</sup> may be ascribed to nickel carbonyl hydride species formed on the linear CO adsorption site under the methanation reaction conditions. The methanation of CO on Ni/Al<sub>2</sub>O<sub>3</sub> may involve the formation of nickel hydride species.

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