JOURNAL OF CATALYSIS 131, 234–242 (1991)

# Infrared Studies of CO and/or NO Adsorption on Reduced $W/Al_2O_3$ Catalysts

YUSHAN YAN, QIN XIN,[1] SHAOCONG JIANG, AND XIEXIAN GUO

*National Laboratory for Fundamental Research in Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

Received September 4, 1990; revised April 29, 1991

Infrared spectroscopy (IR) has been used to investigate CO and/or NO adsorption on reduced $W/Al_2O_3$ catalysts. The effect of reduction temperature and tungsten-loading was studied. Three different kinds of surface W-sites were identified according to the IR spectra (possibly $W^{5+}$, $W^{4+}$ (I), and $W^{4+}$ (II)). Up to three IR bands at 2198, 2176, and 2154 $cm^{-1}$ for adsorbed CO, which are best assigned to $W^{5+}$ (CO), $W^{4+}$ (I) (CO), and $W^{4+}$ (II) (CO), respectively, were observed. Only two kinds of surface complexes, $W^{5+}$ (NO) with a single band at 1843 $cm^{-1}$ and $W^{4+}$ (I and II) $(NO)_2$ with coupled bands at 1780 and 1691 $cm^{-1}$, were formed upon NO contact. In the case of CO + NO and NO + CO (added in sequence) coadsorption, a surface complex in the form of (CO) $W^{4+}$ (I) $(NO)_2$, which gave three IR bands at about 2117, 1801, and 1725 $cm^{-1}$, was evidenced in the spectra in addition to $W^{5+}$ (CO) and $W^{4+}$ (II) $(NO)_2$ on the surface. These observations suggest that $W^{4+}$ (I)-sites differ from $W^{4+}$ (II)-sites in the coordination state and the coadsorption of CO + NO or NO + CO allows more information about the surface W-sites to be achieved than the corresponding CO or NO single adsorption in IR studies. The adsorption and desorption mechanisms are discussed for the surface complex of (CO) $W^{4+}$ (I) $(NO)_2$. Laser Raman spectroscopy (LRS) and temperature-programmed reduction (TPR) were also employed as complementary techniques to characterize the $W/Al_2O_3$ catalysts. The results from these two measurements are in good agreement with our IR results. © 1991 Academic Press, Inc.

## INTRODUCTION

$W/Al_2O_3$ and catalysts derived from this system are very important for many industrial reactions such as metathesis, hydrodesulfurization (HDS), and hydrodenitrogenation (HDN) (*1, 2*). To search for more active and more selective catalysts, much attention has been paid to the characterization of the active sites. The most popular method used is the chemisorption of gaseous probes which is expected to titrate the active sites and elucidate their chemical nature. Among all these probes, CO and NO are attractive because they are usually stable and can be followed by IR spectroscopy. CO or NO is usually used individually in IR studies as probe, but in some cases coadsorption of CO and NO proves to be more powerful and has received increasing attention (*3*). A recent review by Kung and Kung (*4*) has shown that CO and NO have widely been used to characterize reduced $Cr/Al_2O_3$ and $Mo/Al_2O_3$ catalysts, but applied less often for $W/Al_2O_3$ catalysts possibly because $W/Al_2O_3$ is very difficult to reduce (*5, 6*). To avoid this difficulty, Kazusaka and Howe (*6*) have used supported tungsten hexacarbonyl as a new route to a low valent state of tungsten. Using NO as probe, they find that NO can oxidize $W^0$ to $W^{4+}$ as evidenced spectroscopically by the formation of $W^{4+}$ $(NO)_2$ complex. Recently Duchet *et al.* (*7*) reported CO adsorption on $W/Al_2O_3$ catalysts in the oxidized and sulfided states. No studies on either CO or NO adsorption, especially CO and NO coadsorption, to our knowledge, have appeared for the hydrogen-reduced $W/Al_2O_3$ catalysts. In this paper, we describe the infrared study of CO and/or NO adsorption on hydrogen-reduced $W/Al_2O_3$ catalysts. The objective

---

[1] To whom correspondence should be addressed.

0021-9517/91 $3.00
Copyright © 1991 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TABLE 1

Compositions and Codes of the Tungsten Catalysts

| Catalyst | $WO_3$ wt% | W wt% | W atoms/nm$^2$ |
|---|---|---|---|
| $TA_{11.4}$ | 14.4 | 11.4 | 1.6 |
| $TA_{17.0}$ | 21.4 | 17.0 | 2.6 |
| $TA_{23.4}$ | 29.5 | 23.4 | 3.9 |
| $TA_{25.8}$[a] | 32.5 | 25.8 | 4.6 |

[a] Calculated monolayer coverage based on an oxide concentration of $9.1 \times 10^{18}$ O ions/m$^2$ of γ-alumina (110) surface (Ref. (*11*)).

is to elucidate the nature of the surface W-sites.

## EXPERIMENTAL

### *Catalyst Preparation*

Catalysts were prepared by impregnation of γ-$Al_2O_3$ ($S_{BET}$ = 275 m$^2$/g) with ammonium metatungstate solution followed by drying at 393 K overnight and calcination at 773 K for 2 h in air. The compositions of the tungsten catalysts and their codes are shown in Table 1. Tungsten-loading in terms of W atoms/nm$^2$ is also given in order to facilitate results comparison.

### *Raman Spectroscopy*

Raman spectra were recorded on a Jobin Yvon spectrometer. A Spectra Physics Model 2000 argon-ion laser was used as the excitation source, with 200 mW of radiation using the 418-nm line. Samples were pressed (4.5 ton/cm$^2$) into a disc 13 mm in diameter. The sample disc was rotated to avoid thermal decomposition by the laser beam. A typical spectral slit width of 4 cm$^{-1}$ was employed.

### *Infrared Spectroscopy*

The sample was ground and pressed (4.5 ton/cm$^2$) into self-supporting wafer 15 mm in diameter. The wafer was mounted in a quartz sample holder and placed in a quartz *in situ* infrared cell which allowed treatments of the sample either under vacuum or in a flowing gas at temperature between 300 and 1300 K. The sample holder was easily shifted by an external magnet between the sample beam and the oven where the temperature was controlled by a programmed temperature controller.

The pretreatment procedures of the sample before adsorption experiments are described in the following. The oxide sample was heated *in situ* in flowing hydrogen (50 ml/min) from room temperature to 773 K (873 or 973 K) at a constant heating rate of 20 K/min, maintained at 773 K (873 or 973 K) for 2 h and then cooled in hydrogen to 673 K for evacuation ($10^{-5}$ Torr). The sample was always cooled to room temperature before adsorption experiments.

The adsorption of CO or NO and the coadsorption were performed at room temperature. The pressure of CO or NO (partial pressure in the case of coadsorption) was 30 Torr. The coadsorption was performed by adding the second gas after exposing the sample to the first gas for a period of time. Infrared spectra were recorded by using a Perkin–Elmer 580B spectrophotometer with a 3600 data station.

Hydrogen and carbon monoxide (Dalian Gas Prod. Co. 99.99%) were further purified by passage through a 5A molecular sieve column (Shanghai Chem.) and a 401 deoxyagent column (Dalian Inst. of Chem. Phys.). Nitric oxide (Dalian Gas Prod. Co. 99%) was purified by repeated freezing–evaporation cycles and only a portion of the middle fraction was used.

### *Temperature-Programmed Reduction*

The catalyst sample in the size of 20–40 mesh was reduced in a stream of hydrogen/argon mixture (13% $H_2$–Ar, flowing rate 40 ml/min) from 300 to 1300 K at a constant heating rate 10 K/min. The decrease in hydrogen concentration was detected by a thermal conductivity cell. Before each measurement the sample was preheated in flowing argon at 773 K for 2 h in order to eliminate the possible surface contamination. The weight of each sample of different tungsten-loading was chosen in such a way that

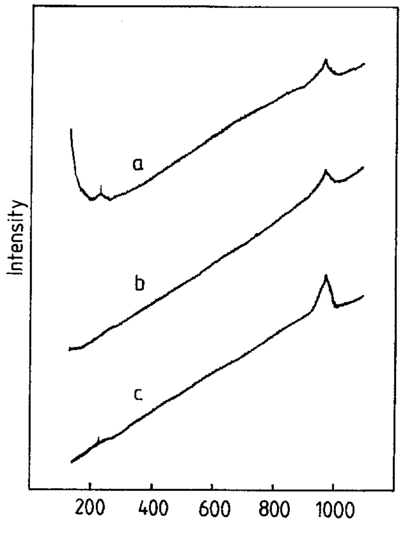


FIG. 1. Raman spectra of (a) $TA_{11.4}$, (b) $TA_{17.0}$, (c) $TA_{23.4}$.

the amount of tungsten in different runs was approximately the same.

## RESULTS AND DISCUSSION

### RAMAN SPECTROSCOPY

Raman spectroscopy has been proven to be valuable in studies of supported $W/Al_2O_3$ catalysts (*8–10*) notwithstanding that the assignments of the observed bands still conflict each other. Thomas *et al.* (*8, 9*) attributed the band at about 970 $cm^{-1}$ to a polymeric, octahedrally coordinated tungsten compound and the bands at about 715 and 805 $cm^{-1}$ to $WO_3$, but Salvati, Jr. *et al.* (*10*) proposed that the occurrence of both bands around 973 and 333 $cm^{-1}$ is the indication of the presence of a tetrahedrally coordinated tungsten species and the bands around 807, 715, and 272 $cm^{-1}$ with ill-defined bands in the lattice band region (100–400 $cm^{-1}$) are due to a octahedrally coordinated tungsten species. The Raman spectra of our $W/Al_2O_3$ catalysts are shown in Fig. 1. Catalysts in the concentration range from 11.4 to 23.4 wt% W are characterized by a broadband at about 970 $cm^{-1}$. Regardless of the assignments of the bands, we can conclude from the absence of the bands at about 805, 715 $cm^{-1}$ that no bulk $WO_3$ is formed on the alumina support after calcination. This conclusion conforms with the calculated monolayer coverage which is 25.8 W wt% for the $\gamma$-$Al_2O_3$ applied in this study (Table 1) using a method proposed in Ref. (*11*).

### INFRARED SPECTROSCOPY

### (*A*) *Oxide W/Al₂O₃ Catalysts*

It is reported (*7*) that $W^{6+}$–CO was formed with a weak band at about 2208 $cm^{-1}$ on oxide and sulphided $W/Al_2O_3$ catalysts. Topsøe and Topsøe (*12*) studied oxide Mo/$Al_2O_3$ catalysts by NO adsorption and found that the adsorption of NO is highly dependent on the evacuation temperature. An evacuation temperature as high as 773 K was reported to be necessary to achieve IR bands of appropriate intensity and they proposed that a small fraction of the Mo atoms at the surface of the alumina was reduced by the high temperature pretreatment to a state capable of adsorbing NO. In our IR studies, however, no bands were observed for adsorbed CO and NO on oxide $W/Al_2O_3$ catalysts which had been preevacuated for 2 h at 673 K. This evacuation procedure is typically employed to remove the adsorbed hydrogen after reduction treatments. It is known (*5*) that $WO_3$ interacts strongly with $\gamma$-alumina and $W/Al_2O_3$ catalysts are difficult to reduce. Thus the absence of IR bands due to adsorbed NO and CO in our studies is quite understandable since lower evacuation temperature (673 K vs 773 K) and shorter period of evacuation (2 h vs 16 h) are used. We can, therefore, suggest that surface W-sites, which are accessible to CO and NO as shown in the following, have a formal charge lower than 6+.

### (*B*) *Reduced W/Al₂O₃ Catalysts*

(*a*) *CO adsorption.* As shown in Fig. 2, CO adsorption on the reduced $W/Al_2O_3$ catalysts gives rise to as many as three IR bands at 2198, 2176, and 2154 $cm^{-1}$ (Fig. 2c). Re-

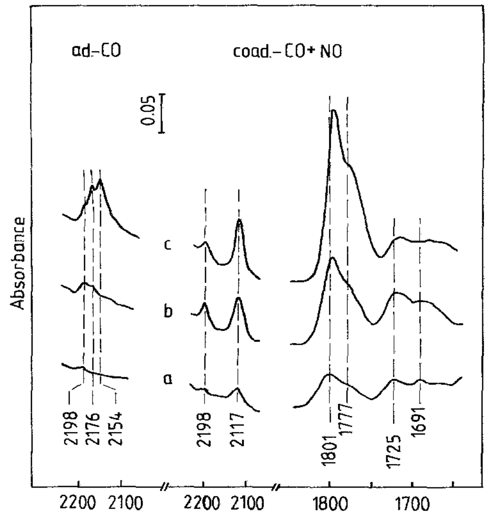


FIG. 2. IR spectra of CO and CO + NO on TA$_{23.4}$ reduced at (a) 773 K, (b) 873 K, (c) 973 K.

duction at increasing temperature increases the intensity of the bands at 2176 and 2154 cm$^{-1}$ while the band at 2198 cm$^{-1}$ remains almost unchanged. Zecchina *et al.* (*13*) observed three overlapped IR bands at 2191, 2186, and 2181 cm$^{-1}$ for CO adsorbed on CO-reduced Cr/SiO$_2$ catalysts. According to their interpretation, the band at 2191 cm$^{-1}$ is due to Cr$^{3+}$–CO complex and the bands at 2186 and 2181 cm$^{-1}$ come from two kinds of Cr$^{2+}$–CO complexes differing in coordination state. Similarly, we assign the band at 2198 cm$^{-1}$ to W$^{5+}$ (CO) complex and the bands at 2176 and 2154 cm$^{-1}$ to W$^{4+}$ (CO) complexes of different coordination states.

It is generally accepted that Mo$^{5+}$ and Mo$^{4+}$ are the dominant specis on hydrogen-reduced Mo/Al$_2$O$_3$ catalysts (*14–19*). Mo metal is formed only under extreme reduction condition (reduction temperature 1173 K) as reported by Peri (*20*) in a CO adsorption study. Considering the fact that W/Al$_2$O$_3$ catalyst is more difficult to reduce than Mo/Al$_2$O$_3$ catalyst, it seems reasonable to suppose that only W$^{5+}$ and W$^{4+}$ are present as CO and NO accessible sites on the hydrogen-reduced W/Al$_2$O$_3$ catalysts.

For surface cations with the same formal charge, the stretching frequency of CO adsorbed on them is highly dependent on their coordination state (before adsorption of CO), i.e., number of oxygen ligands, nature and strength of metal–oxygen bonds (*21*). We, therefore, suggest that the bands at 2176 and 2154 cm$^{-1}$ come from W$^{4+}$ (I) (CO) and W$^{4+}$ (II) (CO) complexes with W$^{4+}$ (I) and W$^{4+}$ (II) in different coordination states.

(*b*) *CO + NO coadsorption.* Drastic changes in the spectra are produced as NO is introduced into the IR cell following CO adsorption (Fig. 2). The bands at 2176 and 2154 cm$^{-1}$ disappear while the band at 2198 cm$^{-1}$ remains unchanged. Simultaneously five new bands at about 2117, 1801, 1777 (shoulder), 1725, and 1691 cm$^{-1}$, respectively, are observed in the spectra (Fig. 2c). The relative stability of the IR bands is examined by heating the coadsorbed sample *in vacuo*. An example of this treatment is presented in Fig. 3. Coadsorption of CO + NO for 8 h gives six bands at about 2198,

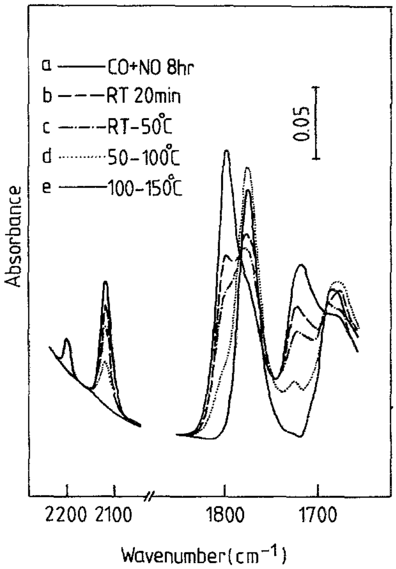


FIG. 3. TPD–IR spectra of CO + NO on TA$_{23.4}$ reduced at 873 K.

2117, 1801, 1777 (shoulder), 1725, and 1691 $cm^{-1}$, respectively (Fig. 3a). The band at 2198 $cm^{-1}$ is readily pumped out at room temperature for 5 min. Evacuation at room temperature for 20 min causes a parallel decrease of the bands at about 2117, 1801, and 1725 $cm^{-1}$ along with a parallel growth of the bands at 1780 and 1691 $cm^{-1}$. Subsequent heating *in vacuo* at elevated temperature has the same effect on the spectra. After heating the sample *in vacuo* at 373–423 K, the bands at 2117, 1801, and 1725 $cm^{-1}$ are totally eliminated and only two bands at about 1780 and 1691 $cm^{-1}$, respectively, are left (Fig. 3e). On evacuation at temperature higher than 423 K, the bands at 1780 and 1691 $cm^{-1}$ decrease in parallel with the appearance of a band at about 1280 $cm^{-1}$. Many investigators (*3, 12, 20, 22–24*) have used infrared spectroscopy to study the NO adsorption on $Cr/Al_2O_3$ and $Mo/Al_2O_3$ catalysts in reduced, oxidized, and sulfided states and find that NO favors adsorption in twin form on the catalyst surface. Thus it seems reasonable to assign the bands at about 1780 and 1691 $cm^{-1}$ to $W^{4+}$ (I and II) $(NO)_2$ complex. This assignment is also justified by the parallelism in thermal stability of the two bands observed in desorption experiments. The band at about 1280 $cm^{-1}$ is most possibly due to adsorbed $N_2O_2^{2-}$ species (*25, 26*) and its formation indicates that, heating *in vacuo* at temperature higher than 423 K, the decomposition of $W^{4+}$ $(NO)_2$ complex takes place with subsequent oxidation of the surface. These phenomena were similarly observed by Millman and Hall (*24*) on reduced $Mo/Al_2O_3$ and by Zecchina *et al.* (*25*) on reduced $Cr/SiO_2$ catalysts.

From the desorption behavior, it is also inferred that the bands at 2117, 1801, and 1725 $cm^{-1}$ are due to some surface complex with both CO and NO liganded to $W^{4+}$ site. The most probable one is (CO) $W^{4+}$ (I) $(NO)_2$. Similar (CO) $Cr^{2+}$ $(NO)_2$ complex has been observed by Garrone *et al.* (*27*) on reduced $Cr/SiO_2$ catalysts. According to the reasons explained by Garrone *et al.* (*27*), it can be speculated that the NO in (CO) $W^{4+}$ (I) $(NO)_2$ should exhibit stretching frequency higher than that in $W^{4+}$ (I and II) $(NO)_2$ while the CO band should change in the opposite direction. These assumptions have been substantiated by our IR results (CO: 2117 $cm^{-1}$ vs 2176 $cm^{-1}$; NO: 1801 and 1725 $cm^{-1}$ vs 1780 and 1691 $cm^{-1}$).

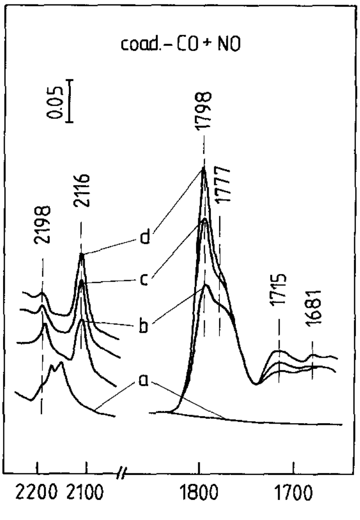


FIG. 4. IR spectra of CO + NO on $TA_{23.4}$ reduced at 973 K (a) ad-CO 80 min, CO + NO (b) 5 min, (c) 50 min, (d) 18 h.

The desorption mechanism for (CO) $W^{4+}$ (I) $(NO)_2$ complex, as represented in reaction (1) (see Scheme 1), is also inferred from the results in Fig. 3. The desorption of (CO) $W^{4+}$ $(NO)_2$ coadspecies is through a stepwise mechanism by losing CO at first stage. Thus the decrease in intensity of the bands at about 2117, 1801, and 1725 $cm^{-1}$ with a simultaneous increase in intensity of the bands at about 1780 and 1691 $cm^{-1}$ as clearly shown in Fig. 3 is easily understood.

More evidence was found to support that $W^{4+}$ (I) is responsible for the formation of (CO) $W^{4+}$ $(NO)_2$ species. Figure 4 shows the changes in the IR spectra with various exposure times of NO. Again the parallel growth in intensity of the bands at about 2117, 1801, and 1725 $cm^{-1}$ indicates that these bands are from the same surface complex. It should be noted that along with the growth of (CO) $W^{4+}$ (I) $(NO)_2$, the band at about 2198 $cm^{-1}$ decreases in intensity and its peak position shifts to the high frequency side. This can be best explained in the following way. After NO is introduced into the IR cell, the band at about 2198 $cm^{-1}$, which is due to $W^{5+}$ (CO) before NO adsorption, becomes an envelope (Fig. 4b) consisting of the band from $W^{5+}$ (CO) and $W^{4+}$ (I) (CO). With time, the envelope band becomes more that of $W^{5+}$ (CO) in character as more of $W^{4+}$ (I) (CO) complexes are converted to (CO) $W^{4+}$ (I) $(NO)_2$ complexes. After NO has been introduced into the IR cell for 18 h, all $W^{4+}$ (I) (CO) complexes are converted to (CO) $W^{4+}$ (I) $(NO)_2$ complexes and their contribution to the envelope is completely eliminated. The $W^{4+}$ (II) $(NO)_2$ complex may be formed through ligand replacement of $W^{4+}$ (II) (CO) which gives an IR band at 2154 $cm^{-1}$. It is generally accepted that NO interacts more strongly with transition metal ions than CO does. The replacement is, therefore, not surprising.

It may be questioned why $W^{4+}$ (I) can adsorb three probes to form (CO) $W^{4+}$ (I) $(NO)_2$ species, since for cations adopting an octahedral site of the oxide lattice, a maximum of two probes can be associated with each $W^{4+}$ cation in the surface. It is certainly true that the surface complex (CO) $W^{4+}$ $(NO)_2$ cannot be formed if only octahedral or distorted octahedral configuration is possible. But reduction is rather complicated for transition metal oxides and especially for well-dispersed oxides on a support in which the metal–oxygen bond lengths and bond angles may be quite different from bulk oxides (*28*). Moreover for (CO) $W^{4+}$ $(NO)_2$ surface complex, which contains oxygen ions as its ligands, W–CO and W–NO bonds are rather weak compared with W–O bonds, which are of electrostatic nature. And the bond strength and length of W–CO and W–NO can be varied depending on the local environment around the surface W-site. Thus it sounds reasonable to assume that surface $W^{4+}$-site in (CO) $W^{4+}$ $(NO)_2$ species has seven ligands (one CO, two NO, and four oxygen ions) after CO and NO coadsorption provided that the four oxygen ligands are in such position after reduction as to make $W^{4+}$-site accessible to both CO and NO molecules.

TABLE 2

Effects of Tungsten Loading and Reduction Temperature

| Catalyst | Reduction temperature (K) | | |
|---|---|---|---|
| | 773 | 873 | 973 |
| $TA_{11.4}$ | | | * |
| $TA_{17.0}$ | | * | * |
| $TA_{23.4}$ | * | * | * |

*Note.* * represents the occurrence of CO + NO coadsorption which is detectable by IR.

CO adsorption and CO + NO coadsorption were also performed on our $TA_{17.0}$ and $TA_{11.4}$ catalysts. The results are similar to those reported in Fig. 2 for the $TA_{23.4}$ catalyst except that higher reduction temperature is required to achieve any IR detectable CO adsorption or CO + NO coadsorption as tungsten-loading decreases. These results concerning the effects of reduction temperature and tungsten-loading are summarized in Table 2.

(*c*) *NO adsorption and NO + CO coadsorption.* NO adsorption on $TA_{23.4}$ reduced at 773 K gives two major bands at 1782 and 1691 $cm^{-1}$ and a very weak band at 1843 $cm^{-1}$ (Fig. 5). Evacuation at room temperature can remove the band at 1843 $cm^{-1}$ easily and has little effect on the other two bands. The bands at 1782 and 1691 $cm^{-1}$ are easily assigned to $W^{4+}$ $(NO)_2$ complex while the band at 1843 $cm^{-1}$ may be due to $W^{5+}$ (NO) complex. Our results are consistent with that obtained by Kazusaka and Howe (*6*) who have observed two IR bands at 1795 and 1685 $cm^{-1}$ (frequency accurate to ±5 $cm^{-1}$) for the $W^{4+}$ $(NO)_2$ complex on a W $(CO)_6$–$Al_2O_3$ catalyst activated at 473 K.

When CO is introduced into the IR cell, the IR bands at 2118, 1803, and 1727 $cm^{-1}$ grow in parallel at the expense of the bands at 1782 and 1691 $cm^{-1}$ (Fig. 5). This suggests that both $W^{4+}$ (I) and $W^{4+}$ (II) can adsorb NO to form $W^{4+}$ $(NO)_2$ complex, i.e., $W^{4+}$ (I) and $W^{4+}$ (II) cannot be distinguished by NO adsorption.

Comparing Fig. 5b, 5c with Fig. 2a (CO + NO 40 min, the ordinate scale of Fig. 2 is half of that of Fig. 5), it is concluded that the adsorption sequence has a strong effect on the formation of (CO) $W^{4+}$ (I) $(NO)_2$ complex. On the same surface, it takes longer to form (CO) $W^{4+}$ (I) $(NO)_2$ of approximately the same intensity in the case of NO + CO than in the case of CO + NO coadsorption (15 h vs 40 min). Let us consider the mechanisms of the formation of (CO) $W^{4+}$ (I) $(NO)_2$. There are two factors which govern the formation of (CO) $W^{4+}$ (I) $(NO)_2$. One is the steric hindrance and another is the coordination ability of the attacking ligand. As represented in reactions (2) and (3) (Scheme 1), it is obvious that the steric hindrance is smaller and the attacking molecule has higher coordination ability in reaction 2 than in reaction 3. The formation of (CO) $W^{4+}$ (I) $(NO)_2$, therefore, is easier for CO + NO coadsorption than it is for NO + CO coadsorption.

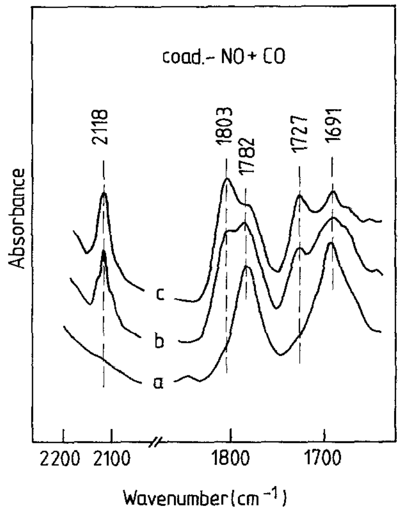
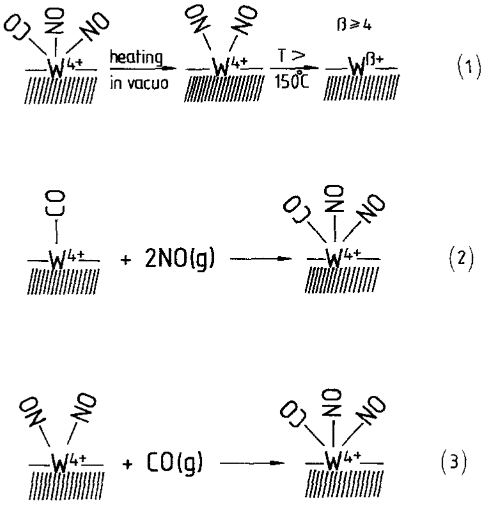


FIG. 5. IR spectra of NO + CO on $TA_{23.4}$ reduced at 773 K (a) ad-NO 60 min, NO + CO, (b) 2 h, (c) 15 h.



SCHEME 1

In the case of NO + CO coadsorption, the formation of (CO) $W^{4+}$ $(NO)_2$ is highly dependent on the reduction temperature. Figure 6 shows IR spectra of NO + CO coadsorption on $TA_{17.0}$ reduced at 973 K. After exposing the catalyst to NO, three IR bands at 1839, 1783, and 1690 $cm^{-1}$, which are readily assigned to $W^{5+}$ (NO) and $W^{4+}$ $(NO)_2$, are observed. When CO was introduced into the IR cell, the band at 1839 $cm^{-1}$ disappeared with the simultaneous appearance of a band at 2199 $cm^{-1}$. Clearly, the 2199 $cm^{-1}$ is due to $W^{5+}$ (CO). After CO has been added for 9 h, the amount of (CO) $W^{4+}$ $(NO)_2$ formed is relatively small compared with that of NO + CO on $TA_{23.4}$ reduced at 773 K (Fig. 5c). This effect is more pronounced in the case of $TA_{23.4}$ reduced at 973 K. After the band at 1839 $cm^{-1}$ has been pumped out at room temperature, CO and NO are introduced consecutively into the IR cell. No IR bands due to (CO) $W^{4+}$ $(NO)_2$ are observed even after CO and NO have contacted with the catalyst for 38 h (not shown for brevity). Based on the results reported in Figs. 5 and 6, it is obvious that reduction at a higher temperature makes the coordination sphere of the surface W-sites more crowded and less favorable for the formation of (CO) $W^{4+}$ $(NO)_2$. Besides its effects on the formation of the coadspecies,

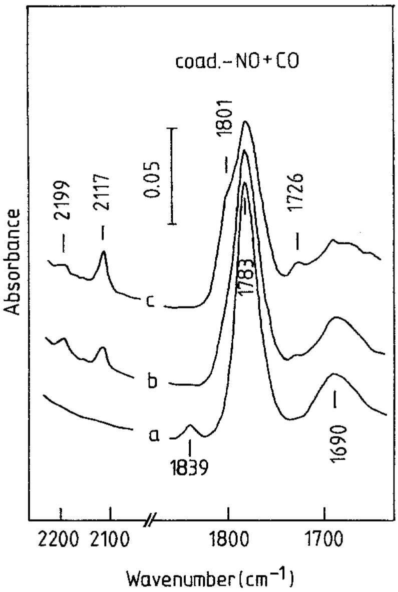


FIG. 6. IR spectra of NO + CO on TA$_{17.0}$ reduced at 973 K (a) ad-NO 14 h, NO + CO, (b) 6 h (c) 9 h.

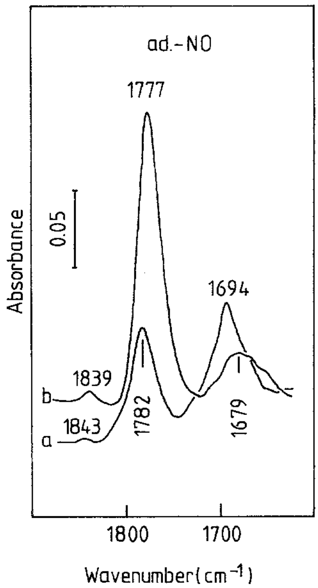


FIG. 7. IR spectra of NO on TA$_{23.4}$ reduced at (a) 773 K, (b) 973 K.

the reduction temperature also has some influence on the intensity ratio of the high frequency band and the low frequency band of W$^{4+}$ (NO)$_2$ complex. For W$^{4+}$ (NO)$_2$ complex, it is known (*29*) that the high frequency band arises from the symmetric stretching mode, whereas the low frequency band is due to asymmetric stretching mode and the relative intensity of these two bands is related to the angle of $2\theta$ between the two N–O bond directions by the relation of Is/Ias = $\cot^2\theta$. It can be expected that $2\theta$ will become smaller as the coordination sphere of the surface W-sites becomes more crowded. As shown in Fig. 7, $2\theta$ becomes evidently smaller as the reduction temperature is raised.

## TEMPERATURE-PROGRAMMED REDUCTION

Figure 8 shows the TPR patterns of W/Al$_2$O$_3$ catalysts with different tungsten concentration. The results are consistent with those obtained by Tomas *et al.* (*5*) and Scheffer *et al.* (*30*). Increasing the tungsten-loading, the onset reduction temperature decreases. These results are also in agreement with our IR results which have been given in Table 2. According to the XPS results obtained by Biloen and Pott (*31*), W/Al$_2$O$_3$ catalysts cannot be reduced at 823 K for 2 h. Our IR results, however, indicate that reduction does occur for the TA$_{23.4}$ catalyst treated in hydrogen at 773 K for 2 h. By checking Biloen and Pott's results closely, we find that the catalyst they used is 1.9 W

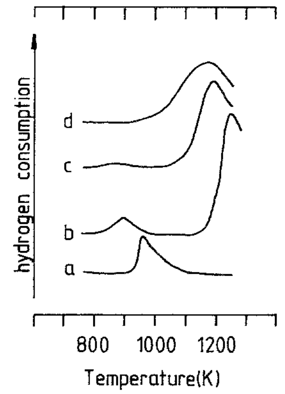


FIG. 8. TPR patterns of (a) $\gamma$-Al$_2$O$_3$, (b) TA$_{11.4}$, (c) TA$_{17.0}$, (d) TA$_{23.4}$.

atoms/nm$^2$ in concentration which is between $TA_{17.0}$ (2.6 W atoms/nm$^2$) and $TA_{11.4}$ (1.6 W atoms/nm$^2$). Thus it is not unexpected that Biloen and Pott's catalyst cannot be reduced at 823 K for 2 h in view of our $TA_{17.0}$ catalyst not being reduced under the same condition.

## CONCLUSIONS

(1) Three different kinds of surface W-sites are identified according to the IR results. These sites are possibly $W^{5+}$-sites, and two $W^{4+}$-sites of different coordination states.

(2) The coadsorption of CO and NO is more powerful in characterizing surface W-sites than either CO or NO single adsorption.

(3) A coadspecies in the form of $(CO) W^{4+} (NO)_2$ is evidenced in the IR spectra. Adsorption and desorption mechanisms for this coadspecies are discussed.

(4) The IR spectra are strongly dependent on tungsten-loading and reduction temperature.

(5) High temperature reduction makes the coordination sphere of surface W-sites more crowded and less efficient to form $(CO) W^{4+} (NO)_2$ surface complex.

## ACKNOWLEDGMENTS

The authors thank Xingtao Gao for LRS measurements. Thanks are also due to Can Li and Bing Zhou for many helpful discussions. The authors are very grateful to Hui Zhang for her cooperation throughout their work. The financial support for this work from the National Natural Science Foundation of China is gratefully acknowledged.

## REFERENCES

1. Katzer, J. R., and Sivasubramanian, R., *Catal. Rev.* **20,** 155 (1979).
2. Willis, D. E., *J. Catal.* **84,** 344 (1983).
3. Xin, Q., Guo, X., Prada Silvy, R., Grange, P., and Delmon, B., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, Canada, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 1, p. 66. The Chemical Institute of Canada, Ottawa, Canada, 1988.
4. Kung, M. C., and Kung, H. H., *Catal. Rev.* **27,** 425 (1985).
5. Thomas, R., Van Oers, E. M., de Beer, V. H. J., Medema, J., and Moulijn, J. A., *J. Catal.* **76,** 241 (1982).
6. Kazusaka, A., and Howe, R. F., *J. Catal.* **63,** 447 (1980).
7. Duchet, J. C., Lavaley, J. C., Housni, S., Ouafi, D., Bachelier, J., Lakhdar, M., Mennour, A., and Cornet, D., *Catal. Today* **4,** 71 (1988).
8. Thomas, R., Moulijn, J. A., and Kerkhof, F. P. J. M., *Recl. Trav. Chim. Pays-Bas* **96,** M134 (1977).
9. Thomas, R., Kerkhof, F. P. J. M., Moulijn, J. A., Medena, J., and de Beer, V. H. J., *J. Catal.* **61,** 559 (1980).
10. Salvati, L., Jr., Markovsky, L. E., Stencel, J. M., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **85,** 3700 (1981).
11. De Boer, J. H., Fahim, R. B., Linsen, B. G., Visseren, W. J., and De Vleesschauwer, W. F. N. M., *J. Catal.* **7,** 163 (1967).
12. Topsøe, N. Y., and Topsøe, H., *J. Catal.* **75,** 354 (1982).
13. Zecchina, A., Garrone, E., Ghiotti, G., and Coluccia, S., *J. Phys. Chem.* **79,** 972 (1975).
14. Massoth, F. E., *J. Catal.* **30,** 204 (1973).
15. Hall, W. K., and Lo Jacono, M., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 246. The Chemical Society, London, 1977.
16. Hall, W. K., and Massoth, F. E., *J. Catal.* **34,** 41 (1974).
17. Chung, K. S., and Massoth, F. E., *J. Catal.* **64,** 320 (1980).
18. Millman, W. S., Crespin, M., Cirillo, A. C., Jr., Abdo, S., and Hall, W. K., *J. Catal.* **60,** 404 (1979).
19. Seshadri, K. S., and Petrakis, L., *J. Catal.* **30,** 195 (1973).
20. Peri, J. B., *J. Phys. Chem.* **86,** 1615 (1982).
21. Lokhov, Y. A., and Davydov, A. A., *Kinet. Katal.* **21,** 1523 (1980).
22. Peri, J. B., *J. Phys. Chem.* **78,** 588 (1974).
23. Topsøe, N. Y., and Topsøe, H., *J. Catal.* **84,** 386 (1983).
24. Millman, W. S., and Hall, W. K., *J. Phys. Chem.* **83,** 427 (1979).
25. Zecchina, A., Garrone, E., Morterra, C., and Coluccia, S., *J. Phys. Chem.* **79,** 978 (1975).
26. Nakamoto, K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed., p. 132. Wiley, New York, 1978.
27. Garrone, E., Ghiotti, G., Coluccia, S., and Zecchina, A., *J. Phys. Chem.* **79,** 984 (1975).
28. Kung, H. H., *in* "Studies in Surface Science and Catalysis" (B. Delmon and J. T. Yates, Eds.), Vol. 45, pp. 91–93. Elsevier, Amsterdam, 1989.
29. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 3rd ed., p. 697. Wiley, New York, 1972.
30. Scheffer, B., Molhoek, P., and Moulijn, J. A., *Appl. Catal.* **46,** 11 (1989).
31. Biloen, P., and Pott, G. T., *J. Catal.* **30,** 169 (1973).