In Situ FT-IR Spectroscopic Studies of CO Adsorption on Fresh Mo₂C/Al₂O₃ Catalyst

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Received: November 28, 2002; In Final Form: April 27, 2003

The surface sites of supported molybdenum carbide catalyst derived from different synthesis stages have been studied by in situ FT-IR spectroscopy using CO as the probe molecule. Adsorbed CO on the reduced passivated Mo_2C/Al_2O_3 catalyst gives a main band at 2180 cm^{-1}, which can be assigned to linearly adsorbed CO on Mo^{4+} sites. The IR results show that the surface of reduced passivated sample is dominated by molybdenum oxycarbide. However, a characteristic IR band at 2054 cm^{-1} was observed for the adsorbed CO on MoO_3/Al_2O_3 carburized with CH_4/H_2 mixture at 1033 K (fresh Mo_2C/Al_2O_3), which can be assigned to linearly adsorbed CO on $Mo^{\delta+}$ ($0 < \delta < 2$) sites of Mo_2C/Al_2O_3. Unlike adsorbed CO on reduced passivated Mo_2C/Al_2O_3 catalyst, the IR spectra of adsorbed CO on fresh Mo_2C/Al_2O_3 shows similarity to that on some of the group VIII metals (such as Pt and Pd), suggesting that fresh carbide resembles noble metals. To study the stability of Mo_2C catalyst during H_2 treatment and find proper conditions to remove the deposited carbon species, H_2 treatment of fresh Mo_2C/Al_2O_3 catalyst at different temperatures was conducted. Partial amounts of carbon atoms in Mo_2C along with some surface-deposited carbon species can be removed by the H_2 treatment even at 450 K. Both the surface-deposited carbon species and carbon atoms in carbide can be extensively removed at temperatures above 873 K.

1. Introduction

Early transition metal carbides, produced by dissolving carbon atoms into the metal lattices, have received much attention because they are potential substitutes for noble metals as catalytic materials.[1−3] They have shown interesting catalytic properties in a number of hydrogen-involved reactions, such as hydrogenolysis of *n*-butane,[4] dehydrogenation of propane,[5] hydrogenation of CO_2[6] and benzene,[7] conversion of methane,[8] water-gas shift,[9] hydrodesulfurization (HDS),[10] and hydrodenitrogenation (HDN).[11,12] Molybdenum carbide has been the most frequently studied catalyst among the large class of transition metal carbide catalysts. Molybdenum carbides in either unsupported or supported forms show good acitivity and selectivity in many catalytic reactions and have attracted much attention over the past decades. One of their most interesting properties is that their combination with ZSM-5 effectively catalyzes the direct conversion of methane into benzene.[13−17] However, compared with the vast investigations on the catalytic reactivities, quite little work has been done on the fundamental understanding of the surface-active sites of molybdenum carbides.

A convenient way to characterize the surface-active sites of catalysts is IR spectroscopy using probe molecules. In this way, carbon monoxide was found particularly suitable because of its specific adsorption. Since the bulk molybdenum carbides usually have high scattering and strong light absorption in the IR region, it is difficult to get the information of the surface-active sites by IR spectroscopy until the preparation of a supported molybdenum carbide catalyst.[7,18] Another difficulty encountered when one wants to make IR studies of fresh Mo_2C catalyst is

that Mo_2C is not stable in air. Therefore, Mo_2C must be passivated before exposure to air to avoid the violent oxidation. So it is difficult to get information on the surface state of a real Mo_2C catalyst. Aegerter et al.[19] reported the IR study of CO adsorption on H_2-reduced passivated Mo_2C/Al_2O_3. Their results showed that the surface of the passivated sample was actually an oxycarbide even after a H_2 reduction at high temperatures. Yang et al.,[20,21] using in situ IR spectroscopy, observed big differences in surface properties between the reduced passivated Mo_2N/Al_2O_3 and fresh Mo_2N/Al_2O_3 catalysts. These findings strongly suggest that it is difficult to get true information for real nitrides using passivated nitrides even after reduction, instead of giving information for oxynitrides or oxygen-covered nitrides. So it might be the case that the surface of the passivated carbide does not reflect the real cases for fresh carbide catalyst because its surface is already partially oxidized.

In this work, we use in situ IR spectroscopy to characterize the surface nature of fresh Mo_2C/Al_2O_3, which was synthesized directly in the IR cell. CO was employed to probe the effect of different carburization temperatures on the surface sites of Mo_2C/Al_2O_3 catalyst. The results indicate that fresh carbide resembles the properties of some noble metals in terms of the adsorption behavior of CO. The changes of the surface sites of fresh Mo_2C/Al_2O_3 during H_2 treatment at different temperatures were also studies by in situ IR spectroscopy.

2. Experimental Section

2.1. Catalyst Preparation. A MoO_3/Al_2O_3 sample with 10 wt % Mo was prepared by the incipient impregnation method. γ-Al_2O_3 (Degussa, $S_{BET} = 108$ m^2 g^{-1}) was impregnated with an aqueous solution of ammonium heptamolybdate, followed by a drying at 397 K overnight and calcination at 773 K for 240 min. A Mo_2C/Al_2O_3 catalyst was prepared by temperature-programmed reaction (TPR) of MoO_3/Al_2O_3 with 20% CH_4/H_2

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mixture. The temperature was increased from room temperature (RT) to 573 K in 30 min and from 573 to 1033 K in 460 min, and then the final temperature was maintained for 60 min. Results from a DTA (differential thermal analysis) experiment indicate that Mo$_2$C/Al$_2$O$_3$ is formed at 1033 K. A passivated Mo$_2$C/Al$_2$O$_3$ sample was prepared by the treatment of the freshly carburized sample in a stream of 1% O$_2$/N$_2$ mixture at RT.

2.2. XRD and XPS Measurements. Crystalline phases of Al$_2$O$_3$ and bulk and alumina-supported carbide samples were detected by X-ray diffraction (XRD) using the packed powder method. Both bulk and alumina-supported molybdenum carbide catalysts were passivated in a 1% O$_2$/N$_2$ flow to avoid the violent oxidation before XRD measurements, which were performed with Cu Kα radiation (λ = 1.5418 Å) on a Rigaku Rotaflex Ru-200B diffractometer. An XPS experiment was carried out using a VG ESCALAB MK-2 spectrometer with an aluminum anode at 12.5 kV and 250 W.

2.3. FT-IR Studies. The MoO$_3$/Al$_2$O$_3$ sample was pressed into a self-supporting wafer with a weight of approximately 15 mg/cm^2. The wafer was placed in a quartz IR cell equipped with CaF$_2$ windows, in which in situ carburization could be performed, and then carburized in a flowing 20% CH$_4$/H$_2$ mixture using treatment conditions similar to those described in Catalyst Preparation (without passivation treatment). In separate experiments, the passivated Mo$_2$C/Al$_2$O$_3$ sample was reduced by H$_2$ in an IR cell at different temperatures. The sample carburized in the IR cell without passivation is called a fresh Mo$_2$C/Al$_2$O$_3$ catalyst, while the passivated sample reduced with H$_2$ is defined as the reduced passivated Mo$_2$C/Al$_2$O$_3$ catalyst.

IR experiments were carried out as follows: (1) Passivated Mo$_2$C/Al$_2$O$_3$ catalyst reduced by H$_2$ at 773 and 873 K was evacuated to 10^{-5} Torr at 773 K for 60 min, subsequently cooled to RT, and then exposed to about 10 Torr CO for IR study. (2) Fresh Mo$_2$C/Al$_2$O$_3$ catalyst carburized at different temperatures in IR cell was evacuated to high vacuum (10^{-5} Torr) at RT for CO adsorption (10 Torr). (3) Fresh Mo$_2$C/Al$_2$O$_3$ catalyst carburized at 1033 K for different times in an IR cell was evacuated to high vacuum (10^{-5} Torr) at RT for CO adsorption (10 Torr). (4) Fresh Mo$_2$C/Al$_2$O$_3$ catalyst carburized at 1033 K was treated by H$_2$ at different temperatures to remove deposited carbon species. After being cooled to RT, the sample was evacuated to high vacuum (10^{-5} Torr), and then 10 Torr CO was introduced. (5) Fresh Mo$_2$C/Al$_2$O$_3$ catalyst carburized at 1033 K was evacuated to high vacuum (10^{-5} Torr) at RT and exposed to 10 Torr CO. The system was not evacuated, and the sample was treated with trace O$_2$ to in situ mimic the process of passivation.

All IR spectra were collected at RT on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of 4 cm^{-1} and 64 scans in the region 4000–1000 cm^{-1}. Unless otherwise indicated, the spectra were obtained after the system was evacuated to 10^{-3} Torr to obtain the spectrum of chemisorbed CO.

2.4. Temperature-Programmed Reduction–Mass Spectroscopy (TPR-MS). Temperature-programmed reduction studies were performed to study the surface species formed during the process of H$_2$ treatment of the fresh Mo$_2$C/Al$_2$O$_3$ catalyst. The reactor used in this study was a U-shaped quartz tube. A 300 mg MoO$_3$/Al$_2$O$_3$ sample was placed into the reactor and carburized in 20% CH$_4$/H$_2$ mixture at 1033 K by the TPR method, and then the fresh Mo$_2$C/Al$_2$O$_3$ was treated in a stream of H$_2$ flowing (15 mL/min) from RT to 1033 K at a linear rate of 1 K/min. Gaseous products were continuously monitored by MS (Omnistar).
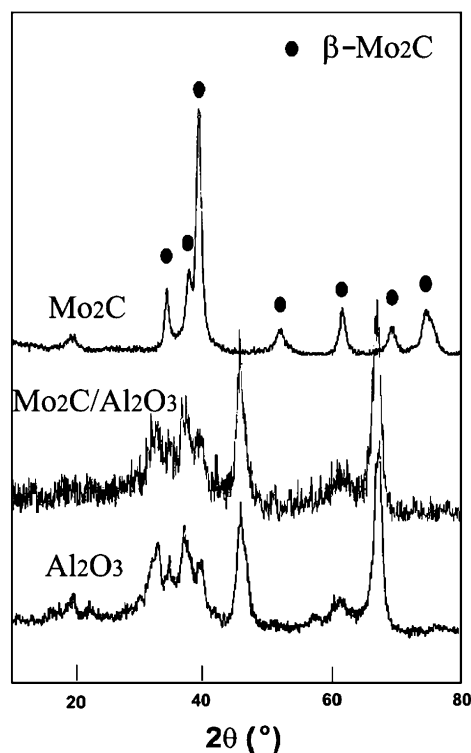
Figure 1. X-ray diffraction patterns of Al$_2$O$_3$, Al$_2$O$_3$/Mo$_2$C, and bulk Mo$_2$C.

TABLE 1. Binding Energies (eV) Measured by XPS of the Passivated and Reduced Passivated Mo$_2$C/Al$_2$O$_3$ Catalyst

|	Mo^{6+} 3d$_{5/2}$	Mo^{4+} 3d$_{5/2}$	Mo$^{\phi+}$ (0 < ϕ < 4) 3d$_{5/2}$
passivated Mo$_2$C/Al$_2$O$_3$	232.6 (73.2%)	230.7 (23.1%)	229.0 (3.8%)
reduced passivated Mo$_2$C/Al$_2$O$_3$	232.6 (56.7%)	230.7 (40.0%)	229.0 (3.3%)

3. Results

3.1. XRD and XPS of Mo$_2$C and Mo$_2$C/Al$_2$O$_3$. As shown in Figure 1, the diffraction pattern for a bulk Mo$_2$C catalyst prepared at 973 K shows peaks at 34.7, 38.0, 39.8, 62.1, and 75.5°, which are assigned to the {100}, {002}, {101}, {110}, and composition of an unresolved doublet of the {112} and {201} reflections of bulk β-Mo$_2$C, respectively. For a Mo loading of 10 wt %, the passivated Mo$_2$C/Al$_2$O$_3$ catalyst prepared at 1033 K shows broad XRD peaks which display the structure of γ-Al$_2$O$_3$. This result suggests that the Mo$_2$C particles be highly dispersed on the support for low Mo loading samples, so it is difficult to distinguish the Mo$_2$C phase from γ-Al$_2$O$_3$.

Table 1 lists a summary of XPS results of the passivated Mo$_2$C/Al$_2$O$_3$ sample and the passivated sample reduced by H$_2$ at 773 K. It can be found that Mo^{6+}, Mo^{4+}, and Mo$^{\phi+}$ (0 < ϕ < 4), with a binding energy of Mo 3d$_{5/2}$ at 232.6, 230.7, and 229.0 eV, respectively, are present for the passivated samples. The results revealed that the passivated procedure strongly modified the surface of Mo carbide, and accordingly, the passivated samples are mainly oxycarbides rather than carbides. Most surface Mo sites on reduced passivated sample are still in high valence state (Mo^{6+} and Mo^{4+}); namely, the sample is still in oxycarbide form, even it was treated with H$_2$ at 773 K.

3.2. IR Spectra of Adsorbed CO.

3.2.1. CO Adsorption on Reduced Passivated Mo$_2$C/Al$_2$O$_3$. The effect of different reduction temperatures on the spectra of CO adsorbed on H$_2$-reduced passivated Mo$_2$C/Al$_2$O$_3$ is shown in Figure 2. A main band at 2180 cm^{-1} and a weak one at 2090

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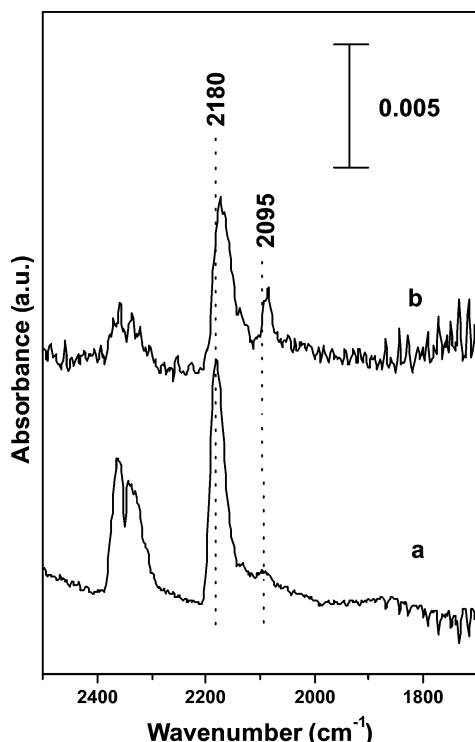
Figure 2. IR spectra of CO adsorbed at room temperature on passivated Mo_2C/Al_2O_3 reduced by H_2 at (a) 773 K and (b) 873 K.

cm^{-1} are detected when the sample is treated with H_2 at 773 K, attributable to linearly adsorbed CO on surface Mo^{4+} and $Mo^{\phi+}$ ($0 < \phi < 4$) sites, respectively.[19-21] When the reduction temperature is increased to 873 K, the bands at 2180 and 2090 cm^{-1} shift to 2170 and 2084 cm^{-1}, respectively. These results suggest that more $Mo^{\phi+}$ ($0 < \phi < 4$) sites for CO adsorption are generated owing to the deeper reduction, but most surface Mo sites on the reduced passivated Mo_2C/Al_2O_3 are still in high valence states.

3.2.2. CO Adsorption on Fresh Mo_2C/Al_2O_3. The IR spectra of CO adsorbed on fresh Mo_2C/Al_2O_3 catalyst carburized at different temperatures are illustrated in Figure 3. When the carburization temperature is 723 K, a broad band is detected with a main peak at 2163 cm^{-1}, as shown in Figure 3a. At 773 K, a band at 2018 cm^{-1} is observed (Figure 3b). Intensity of the band at 2018 cm^{-1} increases slightly at the carburization temperature of 873 K (Figure 3c) and increases remarkably at 973 K (Figure 3d). Meanwhile, a weak band at 2054 cm^{-1} is observed for the sample carburized at 973 K. Dramatic change of the spectra is observed when the sample is carburized at 1033 K (Figure 3e). The band at 2054 cm^{-1} increases significantly in intensity and becomes broader compared with the case of 973 K and a weak band at 2196 cm^{-1} appears (see the insert). The intensity of the band at 2054 cm^{-1} decreases greatly after a prolonged evacuation at room temperature, while the band at 2196 cm^{-1} remains stable. The above results suggest that the two bands are due to two different species formed from CO adsorption on the fresh Mo_2C/Al_2O_3. A blank experiment of CO adsorption on Al_2O_3 carburized at 1033 K does not show any IR band due to adsorbed CO. So it is unambiguously indicated that the two bands at 2054 and 2196 cm^{-1} are related to the adsorbed CO on the surface of Mo_2C component of the Mo_2C/Al_2O_3 catalyst.

Considering the effect of deposited carbon species on the surface sites, the fresh Mo_2C/Al_2O_3 catalyst was carburized at 1033 K for prolonged time. As presented in Figure 4, the 2054 cm^{-1} band shifts to 2071 cm^{-1} with decreased intensity and
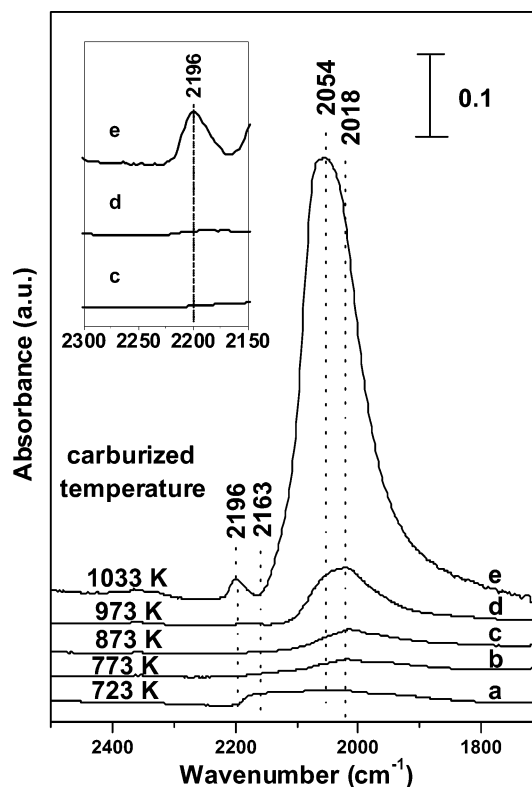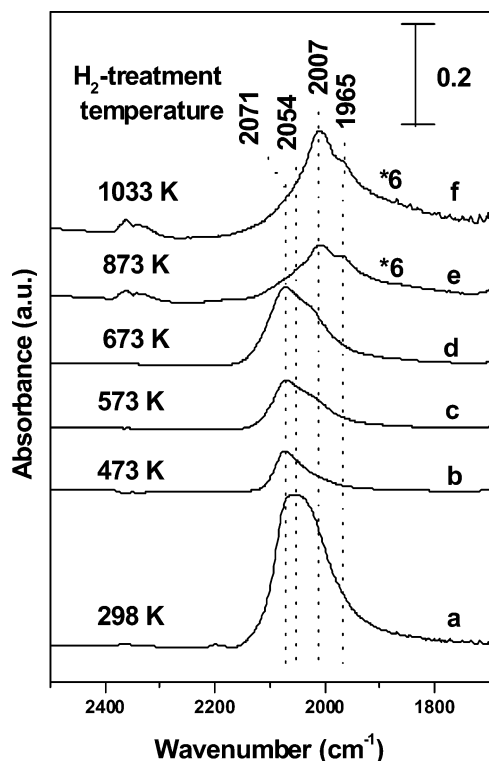

Figure 3. IR spectra of CO adsorbed at room temperature on MoO_3/Al_2O_3 carburized at (a) 723 K, (b) 773 K, (c) 873 K, (d) 973 K, and (e) 1033 K.
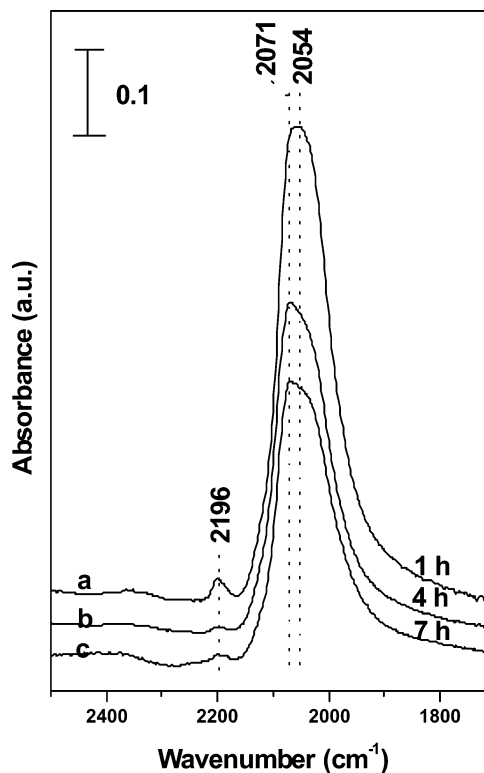
Figure 4. IR spectra of CO adsorbed at room temperature on fresh Mo_2C/Al_2O_3 carburized at 1033 K for (a) 60 min, (b) 240 min, and (c) 420 min.

becomes slightly asymmetric when the carburization time was prolonged for 240 min. The 2196 cm^{-1} band declines greatly in intensity. The shift of the band at 2054 cm^{-1} to 2071 cm^{-1} maybe due to the presence of more deposited carbon species

Figure 5. IR spectra of CO adsorbed at room temperature on fresh Mo$_2$C/Al$_2$O$_3$ pretreated by H$_2$ at (a) 298 K, (b) 473 K, (c) 573 K, (d) 673 K, (e) 873 K, and (f) 1033 K.

Figure 6. IR spectra results obtained after adsorption of increasing amounts of O$_2$ on fresh Mo$_2$C/Al$_2$O$_3$ preadsorbed with CO. (a)−(m) were acquired when the CO exposure was increasing. (n) was evacuation of (m) at RT.

on the surface of Mo$_2$C/Al$_2$O$_3$. This is based on the assumption that the deposited carbon species are more readily to deposit on surface Mo sites in a low valence state, which are very active in methane activation. The two bands at 2071 and 2196 cm^{-1} hardly change except for a small decrease in intensities at the carburization time of 420 min. These results indicate that the amount of the active sites, which the 2071 and 2196 cm^{-1} bands are attributed to, decreases after the carburization time was prolonged.

3.2.3. CO Adsorption on H$_2$-Treated Fresh Mo$_2$C/Al$_2$O$_3$ at Different Temperatures. H$_2$ treatment at high temperatures can remove deposited carbon species, and this is a usual method to remove the deposited coke from the surface of Mo$_2$C. IR spectra of CO adsorption on H$_2$-treated fresh Mo$_2$C/Al$_2$O$_3$ at various temperatures are illustrated in Figure 5. The ν_{CO} spectrum of the Mo$_2$C/Al$_2$O$_3$ sample treated by H$_2$ at 298 K does not change evidently compared with that of fresh Mo$_2$C/Al$_2$O$_3$. When the H$_2$-treatment temperature is increased to 473 K, the band at 2196 cm^{-1} disappears. But the band at 2054 cm^{-1} shifts to 2071 cm^{-1} and its intensity decreases. This maybe due to the dissociation of trace amount of CO[22] on the surface of the fresh Mo$_2$C/Al$_2$O$_3$ sample treated with H$_2$ at low temperature. Mo$_2$C might be slightly oxidized by the oxygen from CO dissociation. This is possibly the sequence that some surface carbons including the carbon atoms from molybdenum carbide are removed by the hydrogen treatment. The amount of active sites is decreased because of H$_2$ treatment, so the intensity of the 2071 cm^{-1} band is decreased. When the fresh Mo$_2$C/Al$_2$O$_3$ catalyst is treated by H$_2$ at 573 and 673 K, change of the band at 2071 cm^{-1} is almost the same as in the case when treated at 473 K except a little increase in intensity. A band at 2007 cm^{-1} grows gradually with increasing H$_2$-treatment temperatures up to 673 K. Great changes are observed for the IR spectra of adsorbed CO when the H$_2$-treatment temperature is higher than 873 K. The band at 2071 cm^{-1} is nearly eliminated, while the
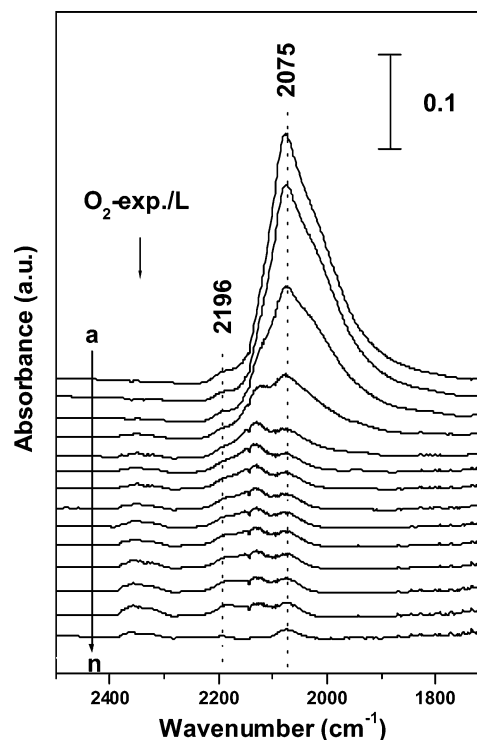
band at 2007 cm^{-1} becomes dominant. Meanwhile, a shoulder band at 1965 cm^{-1} is also observed. After the samples were treated by H$_2$ at 1033 K, the intensities of the two main IR bands at 2007 and 1965 cm^{-1} increased a little compared with those for the samples treated at 873 K.

3.2.4. Coadsorption of CO with O$_2$ on the Fresh Mo$_2$C/Al$_2$O$_3$. The studies on the surface of carbides usually focused on passivated or reduced passivated carbides.[19] On the basis of the above results, we know that the IR spectra of CO adsorption on the fresh Mo$_2$C/Al$_2$O$_3$ catalyst and the reduced passivated one are totally different. To mimic the process of passivation, the fresh Mo$_2$C/Al$_2$O$_3$ catalyst was exposed to a trace amount of O$_2$ in situ in the IR cell and the changes of the surface sites were detected by the IR spectra for CO adsorption.

Figure 6 gives the IR spectra of CO coadsorbed with O$_2$ on the fresh Mo$_2$C/Al$_2$O$_3$ sample at RT. The IR band for adsorbed CO on the fresh Mo$_2$C/Al$_2$O$_3$ sample is observed at 2075 cm^{-1} when the gas-phase CO is present. When O$_2$ is introduced into the system gradually, the intensity of the 2075 cm^{-1} band declines while that of the 2196 cm^{-1} band keeps stable. The intensity of the 2075 cm^{-1} band decreased dramatically with time. This manifests that the surface of the fresh Mo$_2$C/Al$_2$O$_3$ catalyst is quickly oxidized by O$_2$ and the two bands at 2075 and 2196 cm^{-1} are due to two different species. When the cell is evacuated to 10^{-3} Torr, two weak bands at 2075 and 2196 cm^{-1} maintain. This indicates that most of the surface of fresh Mo$_2$C can be easily oxidized to MoO$_3$ by O$_2$ while a certain type of Mo$_2$C species is stable enough to resist oxidation.

3.3. TPR-MS of Mo$_2$C/Al$_2$O$_3$. The surface species of fresh Mo$_2$C/Al$_2$O$_3$ catalyst during the process of H$_2$ treatment is examined, and the signal of CH$_4$ is detected by mass spectroscopy at the reactor outlet. Figure 7 shows the trend of CH$_4$ formation from H$_2$ treatment of fresh Mo$_2$C/Al$_2$O$_3$. CH$_4$ evolution is initially observed at 461 and 493 K. The maximal evolution of CH$_4$ is observed at 873 K.
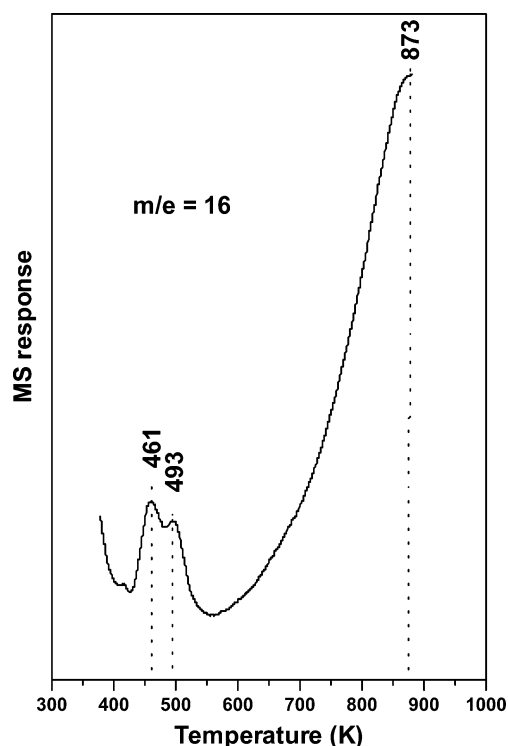
Figure 7. Temperature-programmed reaction results ($m/q = 16$) of fresh Mo_2C/Al_2O_3 treated by H_2. The TPR conditions are as follows: Mo_2C/Al_2O_3 loading, 0.3 g; flow rate, 15 mL/min; heating rate, 1 K/min.

4. Discussion

4.1. Surface Sites on Fresh Mo_2C/Al_2O_3 Catalyst Detected by CO Adsorption. CO adsorption on supported Mo-based catalysts has been well studied.[19−21,23−28] Aegerter et al.[19] reported that when passivated Mo_2C/Al_2O_3 was reduced by H_2 at 750 K for 2 h, a broad band at 2178 cm^{-1} and a weak shoulder band at 2060 cm^{-1} were observed when CO was adsorbed at 130 K. The band at 2178 cm^{-1} was assigned to CO adsorbed on Mo^{4+}, and the band at 2060 cm^{-1} to CO adsorbed on Mo^{2+}. They concluded that there was incorporation of oxygen into alumina-supported β-Mo_2C particles, even after reduction in flowing H_2 at 750 K. Wang et al. studied CO adsorption on a clean β-Mo_2C foil, which gives rise to a ν_{CO} band at 2069 cm^{-1}.[28] This band was assigned to adsorbed CO on Mo^{2+}, and the authors pointed out that its stretching frequency is close to the value of 2042 cm^{-1} for on-top-bonded CO on ruthenium. Using the technique of in situ IR spectroscopy combined with the adsorption of CO as probe molecule, Yang et al. found for the first time that the IR spectrum of adsorbed CO on the fresh Mo_2N/Al_2O_3 is totally different from that on the passivated Mo_2N/Al_2O_3 and reduced passivated Mo_2N/Al_2O_3.[20,21] A characteristic band at 2045 cm^{-1} was observed and attributed to linearly adsorbed CO on $Mo^{\delta+}$ ($0 < \delta < 2$) sites on the surface of fresh nitride. Unlike adsorbed CO on reduced passivated Mo_2N/Al_2O_3, the adsorbed CO on fresh Mo_2N/Al_2O_3 is very stable, behaving similarly to that on group VIII metals.

These studies could be good references for the assignment of the IR bands of adsorbed CO on molybdenum carbide. As can be seen from Table 2, linearly carbonyl species coordinated to $Mo^{\delta+}$ ($3 < \delta < 5$) sites exhibit ν_{MoC-O} frequencies higher than those of free CO molecule (2143 cm^{-1}). In contrast, those held by $Mo^{\delta+}$ ($0 < \delta < 3$) sites show ν_{MoC-O} frequencies lower than 2143 cm^{-1}. A band at 2070−2050 cm^{-1} can be assigned to adsorbed CO on Mo^{2+}.[19−21,23−28] Therefore, the IR bands of CO adsorbed on the Mo_2C/Al_2O_3 samples treated under various

TABLE 2. Frequencies and Assignments of Surface Species Formed by CO Adsorption on Molybdena-Based Catalysts Obtained under Various Pretreatment Conditions As Reported in the Literature

support	pretreatment conditns	IR bands, cm^{-1}	assgnt	ref
γ-Al_2O_3	H_2 reduced at 770 K	2204	$Mo^{5+}(CO)$	29
γ-Al_2O_3	H_2 reduced at 770 K	2194−2187	$Mo^{4+}(CO)$	29
	H_2 reduced at 973 K	2175, 2070	$Mo^{4+}(CO)$	30
SiO_2	H_2 reduced at 973 K	2177−2172	$Mo^{3+}(CO)$	23
γ-Al_2O_3	H_2 reduced at 973 K	2045, 2025	$Mo(CO)$	23

TABLE 3. Frequencies and Assignments of Surface Species Formed by CO Adsorption on Reduced Passivated Mo_2C/Al_2O_3 and on Fresh Mo_2C/Al_2O_3

treatment conditns	IR bands,^{a} cm^{-1}	assgnt
reduction at 773 K	2180 (w)	$Mo^{4+}(CO)$
	2090 (vw)	$Mo^{\phi+}(CO)$
reduction at 873 K	2170 (w)	$Mo^{4+}(CO)$
	2084 (vw)	$Mo^{\phi+}(CO)$
carbidation at 723 K	2163 (b)	$Mo^{4+}(CO)$
carbidation at 773 K	2018 (w)	$Mo^{\delta+}(CO)$
carbidation at 873 K	2018 (w)	$Mo^{\delta+}(CO)$
carbidation at 973 K	2054 (sh)	$Mo^{\delta+}(CO)$
	2018 (w)	$Mo^{\delta+}(CO)$
carbidation at 1033 K	2054 (s)	$Mo^{\delta+}(CO)$

^{a} s = strong, b = broad, sh = shoulder, w = weak, and vw = very weak. $0 < \delta < 2$, and $0 < \phi < 4$.

TABLE 4. Comparison of the Stretching Frequency of Linearly Adsorbed CO on Supported Noble Metals and Fresh Mo_2C/Al_2O_3

	Pt[31,32]	Pd[33,34]	Ru[35,36]	Rh[37,38]	Ir[39,40]	fresh Mo_2C/Al_2O_3
ν_{CO}, cm^{-1}	∼2070	2040−2080	2030−2045	2040−2070	2020−2045	2054

conditions can be easily assigned and are listed in Table 3. The band at 2054 cm^{-1} was assigned to adsorbed CO on the surface of fresh Mo_2C/Al_2O_3, which may be positively charged, i.e., $Mo^{\delta+}$ ($0 < \delta < 2$). The adsorption behavior of CO on the $Mo^{\delta+}$ ($0 < \delta < 2$) sites of fresh carbide is different from that on fully reduced Mo sites.[23] Adsorbed CO on fully reduced Mo sites can be removed by a prolonged outgassing at room temperature (RT).

It is noted that adsorbed CO on noble metals usually gives a characteristic IR band for linearly bonded CO around 2050 cm^{-1} (see Table 4[31−40]). The adsorption of CO on transition metals has been extensively studied. Dissociative adsorption readily occurs on early transition metals whereas molecular adsorption is observed for noble metals such as Ru and Pt.[41] CO adsorption on fully reduced Mo/Al_2O_3 is easily dissociated,[28] so only a weak band is observed. On the other hand, CO adsorbed on fresh Mo_2C/Al_2O_3 shows a strong molecular adsorption, just like noble metals. It is very interesting that the band position of CO adsorbed on $Mo^{\delta+}$ ($0 < \delta < 2$) sites is almost the same as that of CO adsorbed on some noble metals. This is an indication that the surface electronic property of Mo_2C/Al_2O_3 resembles that of group VIII metals. This is direct IR evidence demonstrating the similarity in surface electronic property between molybdenum carbide and noble metal.[1−3]

As mentioned earlier, the purpose of the mimic experiment (O_2 adsorption on a fresh Mo_2C/Al_2O_3 sample) is to obtain the change of intrinsic catalytic active surface sites during the passivation process. The characteristic of the IR spectra (Figure 6) gives results that the amount of Mo^{2+} decreased when passivated. A passivation treatment of carbide is actually a slow oxidation process, which leads to the incorporation of oxygen

Surface Sites of M$_2$C/Al$_2$O$_3$

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into the carbide. A protective and amorphous surface oxide slightly greater than one monolayer thick is produced.[42] As shown in Figure 2 and Table 1, MoO$_3$ and MoO$_2$ are dominating on the surface of a passivated Mo$_2$C/Al$_2$O$_3$ sample reduced by H$_2$ at various temperatures. The passivation procedure made a dramatic change of the carbide, i.e., from carbide to oxycarbide or oxygen-covered carbide. O$_2$ as a oxidant to passivate the fresh Mo$_2$C/Al$_2$O$_3$ is too acute to control the oxidation process. So another oxidant for passivation was desired. A detailed discussion will be provided elsewhere.[43]

It is also interesting that a weak but stable band at 2196 cm^{-1} is observed for fresh Mo$_2$C/Al$_2$O$_3$. CO adsorbed on Mo^{5+},[24,44] CO adsorbed on Al^{3+},[24] and CCO species[45,46] could be possible assignments for this band. However, this band cannot be attributed to CO adsorbed on Mo^{5+} or just Al^{3+} sites because adsorbed CO on these two sites can be easily removed by evacuation at room temperature. The C−O stretching frequencies of ketene are very sensitive to the substitution, and its value for the asymmetric stretch varies from 2085 to 2197 cm^{-1}.[45] Figure 5 demonstrates that the 2196 cm^{-1} band disappeared when the fresh catalyst was treated with hydrogen at low temperatures. The band at 2196 cm^{-1} might be assigned to a CCO species that is formed from the reaction of CO with surface-active carbon atoms created by the in situ carburization. The treatment with hydrogen at high temperatures can remove some of the surface-active carbon atoms; as a result, the band intensity of CCO species is eliminated considerably as shown in Figure 5. When the carburization time is prolonged (Figure 4), the quantity of deposited carbon should be increased. In fact, the band intensity of CCO species decreased. This indicates that CCO species are not formed by deposited carbon. The fact that the band intensity of CCO species is relatively much weaker than that of CO adsorbed on molybdenum sites might suggest that only a small portion of surface carbon atoms are active enough to react with CO, while most of the surface carbon atoms in the Mo$_2$C are inert to the CO adsorption.

4.2. Removal of Carbon Species Deposited on the Surface by H$_2$ Treatment. The carbon species deposited on the catalyst surface including amorphous or graphitic carbon, coke, and other aggregate forms are formed during carburization and are different from atomic carbon in the bulk or on the surface of carbides. Boudart et al. have done a series of experiments[47,48] about how to clean the surface of freshly prepared Mo$_2$C. They found that high ratio of H$_2$/CH$_4$ can restrain the formation of deposited polymeric carbon. H$_2$ treatment at high temperature also has the same effect. Although so many attempts were done to explore the possibilities to decrease or avoid coke deposition, the surface state of fresh Mo$_2$C/Al$_2$O$_3$ during H$_2$ treatment has not been well explored. Our results (Figures 5 and 7) provide an approach to remove the polymeric carbon on freshly prepared carbide and monitor the changes of the surface sites of fresh Mo$_2$C/Al$_2$O$_3$ during H$_2$ treatment at different temperatures.

The TPR data (Figure 7) show two CH$_4$ peaks at 461 and 493 K in the lower temperature range. These two peaks can be attributed to the elimination of some surface carbon atoms of carbide and some deposited carbon species. When temperature is increased, a strong band at 873 K is observed, possibly due to the elimination of bulk carbon atoms of carbide and some graphitic carbon species deposited on the surface of Mo$_2$C. Consistent with our TPR-MS assignment, when the fresh sample was treated at a temperature lower than 673 K, IR spectra of adsorbed CO give a main band at 2071 cm^{-1} with a weak shoulder at 2007 cm^{-1}. The fact that the intensity of 2071 cm^{-1} band decreased obviously maybe due to the elimination of some

surface carbon atoms of carbide. The amount of active sites of Mo$_2$C decreased. The 2007 cm^{-1} band can be attributed to CO adsorbed on fully reduced Mo^0 sites.[23,49] The formation of the unsaturated Mo^0 is ascribed to the removal of surface carbon atoms of carbide by H$_2$ reduction. The 2007 cm^{-1} band increases in intensity with the elevated reduction temperature, implying the elimination of more carbon atoms in the surface of Mo$_2$C/Al$_2$O$_3$ by H$_2$ treatment. When the treatment temperature is higher than 873 K, the 2007 cm^{-1} band becomes dominant and the band at 2071 cm^{-1} disappears, indicating that most of the carbon atoms in the surface of Mo$_2$C/Al$_2$O$_3$ are removed. These results are in good agreement with those in Figure 7.

The H$_2$-treatment temperature usually used in the literature is very high.[47,50−52] For example, Volpe et al.[47] found that methane was detected at the reactor exit when β-WC$_{1-X}$ and α-MoC$_{1-X}$ samples were treated by H$_2$ at 1000 K, the structure and crystallite size of the fcc phases were not altered, and there were no new phases appearing in the XRD patterns. The discrepancy between our finding and the results from literatures can be due to the fact that IR spectroscopy combined with CO probing gives predominant information from the surface of a catalyst while XRD provides information from the bulk. So we can infer that although H$_2$ treatment can remove the carbon species deposited on the surface of carbide catalysts, the carbon atoms in the surface of carbide will also be removed. So the catalytic activities of thus-treated carbide catalysts cannot reflect the case of true carbides. Lee et al.[48] also found that, after an isothermal H$_2$ treatment of Mo$_2$C with a surface free of contamination by noncarbidic carbon at 875 K, a continuous decrease in S$_g$ and CO chemisorption was observed, but XRD patterns corresponded only to Mo$_2$C. Their results showed that the surface structure was changed while the bulk structure was maintained when fresh prepared carbide was treated by H$_2$ at 875 K. So we can infer that when treatment temperature is higher than 450 K, both surface carbon atoms of Mo$_2$C and some deposited carbon species are eliminated. A H$_2$-treatment temperature higher than 873 K can eliminate the surface polymeric carbon of carbide catalysts, and the carbon in the bulk carbide maybe also removed. So the catalytic activities of thus-treated carbide catalysts cannot reflect the case of true carbides. On the basis of the assignments, the whole processes including carburization, passivation, and H$_2$ reduction were schematically depicted in Figure 8.

5. Conclusions

CO adsorption on fresh Mo$_2$C/Al$_2$O$_3$ and reduced passivated Mo$_2$C/Al$_2$O$_3$ were studied by IR spectroscopy. For the fresh Mo$_2$C/Al$_2$O$_3$ catalyst, Mo$^{\delta+}$ (0 < δ < 2) is mainly on the surface as probed by adsorbed CO giving an IR band at 2054 cm^{-1}, assigned to linearly adsorbed CO on Mo sites. Unlike adsorbed CO on reduced passivated Mo$_2$C/Al$_2$O$_3$, the adsorption of CO on fresh Mo$_2$C/Al$_2$O$_3$ catalyst is very strong and stable. The characteristics of CO adsorption on fresh Mo$_2$C/Al$_2$O$_3$ catalyst indicate that fresh carbide resembles the properties of noble metals in terms of the IR band position and adsorption behavior of CO. TPR and IR results on the fresh catalyst treated by H$_2$ at different temperatures indicate that temperatures above 450 K can decrease the amount of the carbon species deposited on the surface of carbide and also partially remove the carbon atoms from molybdenum carbide. Flushing the fresh sample with H$_2$ at a high temperature (>873 K) can extensively remove both surface carbon atoms of carbide and deposited carbon species and dramatically alter the surface structure of molybdenum carbide.
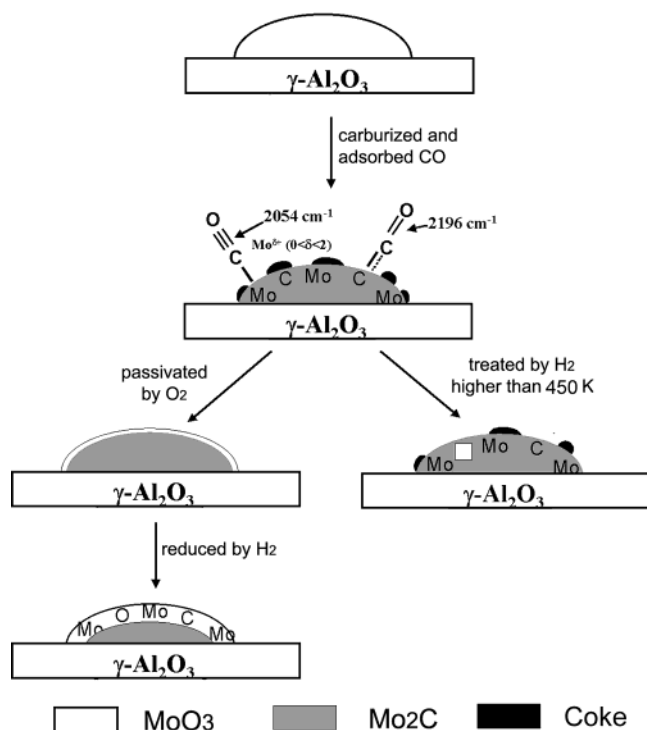
Figure 8. Schematic description of the carburization of MoO_3/Al_2O_3 and H_2 reduction of passivated Mo_2C/Al_2O_3.

References and Notes

(1) Oyama, S. T. *Catal. Today* **1992**, *15*, 179.

(2) Chen, J. G. *Chem. Rev.* **1996**, *96*, 1477.

(3) Oyama, S. T., Ed. *The Chemistry of Transition Metal Carbides and Nitrides*; Blackie Academic & Professional, Glasgow, U.K., 1996.

(4) Lee, J. S.; Locatelli, S.; Oyama, S. T.; Boudart, M. *J. Catal.* **1990**, *125*, 157.

(5) Solymosi, F.; Németh, R.; Óvári, L.; Egri, L. *J. Catal.* **2000**, *195*, 316.

(6) Nagai, M.; Oshikawa, K.; Kurakami, T.; Miyao, T.; Omi, S. *J. Catal.* **1998**, *180*, 14.

(7) Lee, J. S.; Yeom, M. H.; Park, K. Y.; Nam, I. S.; Chung, J. S.; Kim, Y. G.; Moon, S. H. *J. Catal.* **1991**, *128*, 126.

(8) York, A. P. E.; Claridge, J. B.; Brungs, A. J.; Tsang, S. C.; Green, M. L. H. *Chem. Commun.* **1997**, 39.

(9) Patt, J.; Moon, D. J.; Phillips, C.; Thompson, L. *Catal. Lett.* **2000**, *65*, 193.

(10) Costa, P. D.; Potvin, C.; Manoli, J. M.; Lemberton, J. L.; Pérot, G.; Djéga-Mariadassou, G. *J. Mol. Catal. A: Chem.* **2002**, *184*, 323.

(11) Miyao, T.; Oshikawa, K.; Omi, S.; Nagai, M. In *Hydrotreatment and hydrocracking of oil fractions*; Froment, G. F., Delmon, B., Grange, P., Eds.; Chapman & Hall: Tokyo, 1997; p 255.

(12) Sayag, C.; Suppan, S.; Trawczy'nski, J.; Djéga-Mariadassou, G. *Fuel Process. Technol.* **2002**, *77–78*, 261.

(13) Wang, L.; Tao, L.; Xie, M.; Xu, G.; Huang, J.; Xu, Y. *Catal. Lett.* **1993**, *21*, 35. Xu, Y.; Liu, S.; Wang, L.; Xie, M.; Guo, X. *Catal. Lett.* **1995**, *30*, 135.

(14) Solymosi, F.; Erdöhelyi, A.; Szöke, A. *Catal. Lett.* **1995**, *32*, 43. Solymosi, F.; Szöke, A.; Cserényi, J. *Catal. Lett.* **1996**, *39*, 157. Solymosi, F.; Cserényi, J.; Szöke, A.; Bánsági, T.; Oszkó, A. *J. Catal.* **1997**, *165*, 150. Solymosi, F.; Németh, R.; Óvári, L.; Egri, L. *J. Catal.* **2000**, *195*, 316.

(15) Wang, D.; Lunsford, J. H.; Rosynek, M. P. *J. Catal.* **1997**, *169*, 347.

(16) Liu, S.; Dong, Q.; Ohnishi, R.; Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1445.

(17) Borry, R. W., III; Lu, E. C.; Young-ho, K.; Iglesia, E. *Stud. Surf. Sci. Catal.* **1998**, *119*, 403.

(18) Miyao, T.; Shishikura, I.; Matsuoka, M.; Nagai, M.; Oyama, S. T. *Appl. Catal., A* **1997**, *165*, 419.

(19) Aegerter, P. A.; Quigley, W. W. C.; Simpson, G. J.; Ziegler, D. D.; Logan, J. W.; McCrea, K. R.; Glazier, S.; Bussell, M. E. *J. Catal.* **1996**, *164*, 109.

(20) Yang, S.; Li, C.; Xu, J.; Xin, Q. *Chem. Commun.* **1997**, 1247.

(21) Yang, S.; Li, C.; Xu J.; Xin, Q. *J. Phys. Chem.* **1998**, *36*, 6986.

(22) Bugyi, L.; Solymosi, F. *J. Phys. Chem. B* **2001**, *105*, 4337.

(23) Peri, J. B. *J. Phys. Chem.* **1982**, *86*, 1615.

(24) Zaki, M. I.; Vielhaber, B.; Knözinger, H. *J. Phys. Chem.* **1986**, *90*, 3176.

(25) Lee, J. S.; Lee, K. H.; Lee, J. Y. *J. Phys. Chem.* **1992**, *96*, 362.

(26) Müller, B.; Van Langeveld, A. D.; Moulijn, J. A.; Knözinger, H. *J. Phys. Chem.* **1993**, *97*, 9028.

(27) Diaz, A. L.; Bussell, M. E. *J. Phys. Chem.* **1993**, *97*, 470.

(28) Wang, J.; Castonguay, M.; Deng, J.; McBreen, P. H. *Surf. Sci.* **1997**, *374*, 197.

(29) Delgado, E.; Fuentes, G. A.; Hermann, C.; Kunzmann, G.; Knözinger, H. *Bull. Soc. Chim. Belg.* **1984**, *83*, 735.

(30) Peri, J. B. In *Catalysis-Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: West Berlin, 1984; Vol. 5, pp 171–220.

(31) Bourane, A.; Dulaurent, O.; Chandes, K.; Bianchi, D. *Appl. Catal., A* **2001**, *214*, 193.

(32) Ferri, D.; Burgi, T.; Baiker, A. *J. Phys. Chem. B* **2001**, *105*, 3187.

(33) Almusaiteer, K.; Chuang, S. C. C. *J. Catal.* **1999**, *184*, 189.

(34) Ferri, D.; Burgi, T.; Baiker, A. *J. Catal.* **2002**, *210*, 160.

(35) Martins, R. L.; Baldanza, M. A. S.; Schmal, M. *J. Phys. Chem. B* **2001**, *105*, 10303.

(36) Shen, J. Y.; Sayari, A.; Kaliaguine, S. *Res. Chem. Intermed.* **1993**, *19*, 407.

(37) Paul, D. K.; Mckee, M. L.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *J. Phys. Chem.* **1989**, *93*, 4598.

(38) Almusaiteer, K. A.; Chuang, S. S. C. *J. Phys. Chem. B* **2000**, *104*, 2265.

(39) Bourane, A.; Nawdali, M.; Bianchi, D. *J. Phys. Chem. B* **2002**, *106*, 2665.

(40) Zhou M.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 7773.

(41) Hoffman, R. *Rev. Mod. Phys.* **1988**, *60*, 601.

(42) Markel, E. J.; Van Zee, J. W. *J. Catal.* **1990**, *126*, 643.

(43) Manuscript in preparation.

(44) Gao, X.; Xin, Q. *J. Catal.* **1994**, *146*, 306.

(45) Lin-Vien, D.; Cothup, N. B.; Fatetey, W. G.; Graselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic: San Diego, CA, 1991.

(46) Wagner, B. D.; Arnold, B. R.; Brown, G. S.; Lusztyk, J. *J. Am. Chem. Soc.* **1998**, *120*, 1827.

(47) Volpe, L.; Boudart, M. *J. Solid State Chem.* **1985**, *59*, 348.

(48) Lee, J. S.; Oyama, S. T.; Boudart, M. *J. Catal.* **1987**, *106*, 125.

(49) Decanio, E. C.; Storm, D. A. *J. Catal.* **1991**, *130*, 653.

(50) Ribeiro, F. H.; Dalla Betta, R. A.; Boudart, M.; Baumgartner, J.; Iglesia, E. *J. Catal.* **1991**, *130*, 86.

(51) Miyao, T.; Shishikura, I.; Matsuoka, M.; Nagai, M.; Oyama, S. T. *Appl. Catal., A* **1997**, *165*, 419.

(52) Santos, J. B. O.; Valenca, G. P.; Rodrigues, J. A. J. *J. Catal.* **2002**, *210*, 1.