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Study of residual oxygen species over molybdenum carbide prepared during *in situ* DRIFTS experiments

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In situ diffuse reflectance infrared Fourier transform spectroscopy was applied to monitor the temperature-programmed carburization of molybdenum trioxide. This technique indicated the existence of surface residual oxygen species on Mo_2C synthesized even up to 973 K, indicating incomplete carburization. The presence of residual oxygen species on the carbide was deduced from the IR band at $790\,cm^{-1}$. It was observed that the Mo_2C sample, prepared with a final temperature of 1023 K, presented a higher density of sites titrated by carbon monoxide and a higher activity in benzene hydrogenation than the samples prepared at 923 or 973 K. This higher density of sites and activity were interpreted in terms of improved degrees of carburization at the surface of the carbide. The temperature-programmed desorption of benzene over those three Mo_2C samples showed that the higher the activity in benzene hydrogenation, the lower the maximum desorption temperature: the tendency also observed going from Mo to Ru. This desorption temperature evolution could be explained in terms of an increased degree of carburization, which conferred to Mo_2C a reactivity toward benzene closer to that of Ru.

KEY WORDS: molybdenum carbide; surface residual oxygen species; *in situ* DRIFTS; density of sites; benzene hydrogenation and TPD.

1. Introduction

Molybdenum carbide (Mo_2C) presents a high activity in hydrogenation or hydrogenolysis of hydrocarbons contrarily to molybdenum itself and the activity of Mo_2C in these reactions is often similar to that of noble metals [1–7]. This striking activity enhancement from molybdenum to molybdenum carbide can be explained in terms of an electronic band structure modification at the Fermi level [2,8]. Carbon insertion into the Mo lattice causes a contraction of the *d* band width at the Fermi level [9], giving rise to a higher *d* band filling [10]. Consequently, the *d* band filling of Mo_2C is quite similar to that of noble metal. Considering the empirical "Principle of Sabatier" [11,12], Mo_2C will show a higher catalytic activity than pure Mo, since the latter, much more deficient in electrons than Mo_2C, will form too strongly adsorbed species, which block the active sites of the catalyst.

It is now well known that oxygen alters very significantly the "intrinsic" catalytic properties of molybdenum carbide. For instance, the hydrogenation and hydrogenolysis functions of Mo_2C are completely suppressed after oxygen chemisorption, whereas it begins to show a new catalytic function, like *n*-alkane isomerization [7,13–17]. Pure molybdenum carbide chemisorbs associatively CO as well as noble metals [18–20], but CO chemisorption capacity is progressively lowered by oxygen insertion into Mo_2C [7,21]. Therefore, any contamination of Mo_2C by oxygen should be avoided to produce Mo_2C, having excellent catalytic activity in hydrogenation and hydrogenolysis.

Indeed, our previous study [22] has shown that the site time yield (STY) of Mo_2C, in benzene hydrogenation at room temperature, increases strikingly with the degree of carburization, and gets closer to that of Ru catalyst. This work [22] underlined, therefore, the importance of a complete carburization of the oxide-type precursor, even at the expense of the specific surface area of the final material, by using a severe carburization condition (*e.g.*, higher temperatures) in order to maximize the activity of Mo_2C in hydrogenation reactions. In fact, considering the evolution of the global carbidic carbon content (measured by elemental analysis) and that of the global residual oxygen content (determined by the water formed during the temperature-programmed reduction of fresh samples), the evolution of the degree of carburization was evidenced in the previous study [22], without nevertheless giving any direct information on the degree of carburization at the surface of the solid where catalysis actually takes place. The determination of the density of sites titrated by CO has been proposed as a good method for indirectly evaluating the degree of carburization at the surface.

The present paper concerns our attempt to further clarify the correlation between the *degree of carburization* and *hydrogenating activity* of Mo_2C, giving thus more

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insight into the origin of activity enhancement of Mo_2C, compared with those of Mo and Ru. Two additional techniques were employed in this study and discussion on the obtained results will be made, in what follows, in close relation with the previous work [22]. First, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was utilized to verify if any residual oxygen species persist on the Mo_2C surface prepared in the temperature range frequently used in Mo_2C synthesis. This approach came from the idea that only surface Mo–oxygen species of Mo_2C can lead to Mo–oxygen stretching bands active in IR, since IR spectra of Mo_2C and Mo–oxygen species in the bulk are nearly impossible to obtain due to the metallic character and opacity of Mo_2C. On the other hand, the temperature-programmed desorption of benzene was performed on Mo_2C samples, prepared with different final temperatures of carburization, thus with different degrees of carburization. Different bond strengths, between Mo_2C and benzene, deduced from the different desorption temperatures on the carbide samples, will be interpreted in connection with the evolution of the hydrogenating activity of different catalysts.

2. Experimental

2.1. *In situ DRIFTS study of the temperature-programmed carburization of molybdenum trioxide*

The DRIFTS experiments were conducted on a Bruker IFS66V spectrometer equipped with a mercury–cadmium–telluride (MCT) detector, and a DRIFTS accessory (Collector, Spectratech). The latter includes a high-temperature environmental chamber where temperature-programmed carburization can be performed. Molybdenum trioxide (99.998%, Johnson Matthey), precursor of Mo_2C, was simply dispersed into synthetic single-crystalline diamond powder (IR-transparent and diffusing matrix) with an average particle size of 6 μm [23]. About 60 mg of 14 wt% MoO_3/diamond was placed in the environmental chamber and exposed to a gas flow (30 μmol s^{-1}), composed of CH_4, H_2 and Ar. The ratio of methane to hydrogen was fixed at 10 vol%, in order to approach the carburization conditions normally employed at the laboratory scale [18,22]. This CH_4/H_2 mixture was then diluted to 50 vol% in Ar, permitting the sample to be heated to high temperatures. Without Ar dilution, high thermal conductivity of H_2 did not allow us to heat the sample above 900 K, due to a high rate of heat conduction from the sample to the chamber wall. The temperature of the sample was increased from 303 to 673 K with a heating rate of 220 K h^{-1} and then more slowly (60 K h^{-1}) to 973 K.

During the carburization, single-beam spectra were collected at a resolution of 4 cm^{-1} by averaging 512 scans. The final spectra were calculated by using the single-beam spectra of the sample and the spectra of the non-absorbing reference (diamond matrix), registered under the same conditions as for carburization. The calculated DRIFT spectra were subsequently converted to the Kubelka–Munk format.

For the sake of comparison, the temperature-programmed reduction of MoO_3 was also monitored by DRIFTS, using the same procedure as described above for the carburization. In addition, a DRIFT spectrum of MoO_2 powder (Aldrich) was obtained, after *in situ* pretreatment of the sample at 423 K under flowing Ar.

2.2. *Separate preparation of molybdenum carbide samples in a laboratory-scale reactor*

Molybdenum carbide was prepared by temperature-programmed carburization of molybdenum trioxide (99.998%, Johnson Matthey). For each preparation, the MoO_3 precursor was loaded on a coarse quartz fritted disk, in a quartz reactor that could be isolated by stopcocks after synthesis, and then transferred to chemisorption or benzene adsorption/desorption units, without any contact of the sample with air. Methane (99.90%, Air Liquide) and hydrogen (99.995%, Air Liquide) were used as reactant gases. Prior to entry into the reactor, the gaseous mixture (10 vol% CH_4/H_2) was purified by flowing successively through a molecular sieve trap, an oxygen trap (Oxy-Purge N, Alltech) and an indicating oxygen trap (Indicating Oxy-Purge, Alltech). Carbide synthesis was conducted at atmospheric pressure with a molar hourly space velocity of 68 h^{-1}. Temperature-programming was performed by a temperature regulator/controller (Setaram TGC 85). A heating rate of 53 K h^{-1} and final temperatures of 923, 973 or 1023 K were used. The reactor was maintained at a given final temperature for 1 h before being quenched to room temperature (RT) under flowing H_2.

2.3. *Characterization*

A Siemens D500 automatic diffractometer with a Cu K_α monochromatized radiation source was used for the X-ray diffraction (XRD) powder patterns of various solids. The identification of the different solid phases was made using the Joint Committee on Powder Diffraction Standards (JCPDS) library.

The specific surface areas of the samples were obtained from nitrogen desorption after adsorption of N_2 at different partial pressures (10, 20 and 30 kPa) at 77 K by means of the BET method. Measurements were performed on a Quantachrom-Quantasorb Jr. in dynamic conditions. Measurements were done after pretreatment of the sample in flowing N_2 (41 μmol s^{-1}) (99.995%, Air Liquide) at 673 K for 1 h.

A pulsed chemisorption technique was used to measure the amount of irreversibly chemisorbed CO or

O_2 on Mo_2C samples. Pulses of a known amount (17 μmol) of CO (99.997%, Air Liquide) or O_2 (99.5%, Air Liquide) were injected every 5 min on the sample (0.34 g) at RT, in flowing He (30 μmol s^{-1}) (99.995%, Air Liquide) purified by an oxygen trap (Oxysorb, Messer Griesheim). The injection proceeded until the surface was saturated by probe molecules. After each injection, the quantity of probe molecules not chemisorbed was measured at the outlet of the reactor using a conventional device equipped with a thermal conductivity detector (TCD).

Benzene adsorption was carried out at RT and atmospheric pressure by exposing the catalyst to a stream of benzene/helium mixture for 35 min. A gaseous mixture of benzene in helium was obtained by flowing He (74 μmol s^{-1}) purified as for the synthesis, in a benzene (99.8%, Merck) saturator at RT, then in a condenser maintained at 286 K. Thus the initial partial pressures of benzene and hydrogen were 6.9 and 94.4 kPa, respectively. Then the benzene/helium gas mixture was replaced by pure He (74 μmol s^{-1}) in order to purge the reactor. Flowing helium was maintained until no benzene was detected by an on-line gas chromatograph (HP 5890 Series II) equipped with a flame ionization detector and a 50-m-long and 0.2-mm-diameter (i.d.) capillary column (HP PONA, 0.5 μm film thickness). For thermal desorption of benzene, the flow rate of He was lowered to 22 μmol s^{-1} and then the catalyst bed was heated from RT to 873 K with a heating rate of 300 K h^{-1}. The composition of the gas mixture at the outlet of the reactor was analyzed by the above-mentioned chromatograph.

The same apparatus was used for evaluating the hydrogenating activities of different catalysts in benzene hydrogenation at RT and atmospheric pressure under dynamic differential conditions [22]. The activities were expressed in terms of STY, which was defined as the number of benzene molecules transformed per second per site titrated by CO chemisorption (average turnover rate).

3. Results and discussion

3.1. In situ DRIFTS monitoring of temperature-programmed carburization of molybdenum trioxide

Figure 1 presents the DRIFT spectra obtained during the temperature-programmed carburization of powdered MoO_3 diluted in a diamond matrix. In order to facilitate the interpretation of the spectra, a DRIFT spectrum was also acquired for a commercial MoO_2 (figure 2), known as an intermediate of MoO_3 carburization to Mo_2C [22,24,25]. Moreover, the temperature-programmed reduction of MoO_3 by H_2 instead of a CH_4/H_2 mixture was also monitored by DRIFTS (figure 3). The IR spectral region 1020–650 cm^{-1}, examined in this work, is characteristic of Mo–O vibration modes [26]. In the following, we will give a brief interpretation of these spectra. The main emphasis will be on the evolution of spectra in an effort to qualitatively evaluate the "completeness" of the carburization, rather than on the

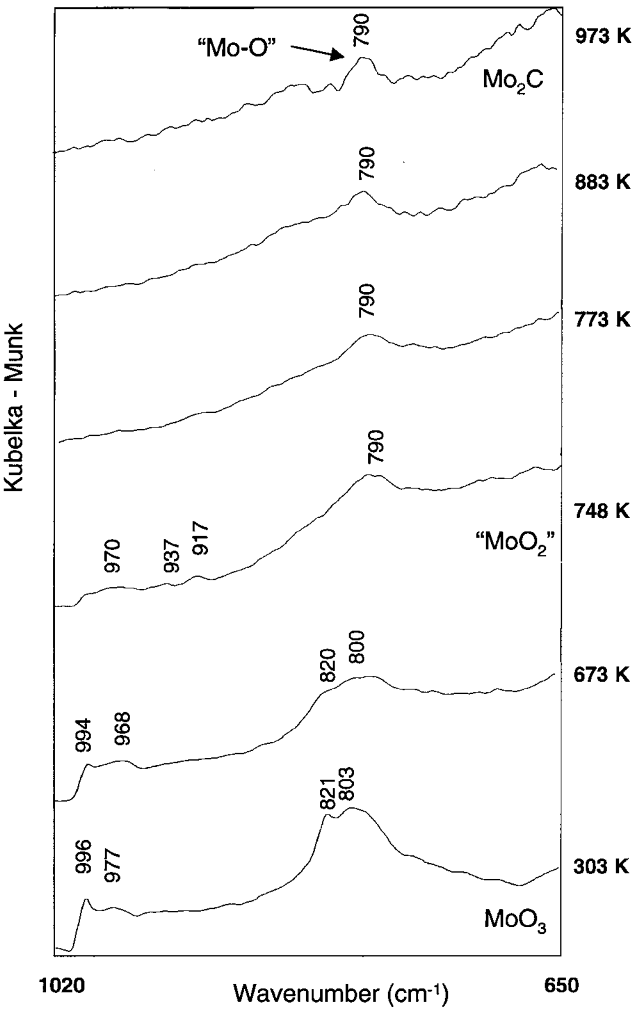

Figure 1. DRIFT spectra obtained during the carburization of MoO_3 dispersed in a diamond matrix (14 wt%), in flowing 10 vol% CH_4/H_2, diluted to 50 vol% in Ar.

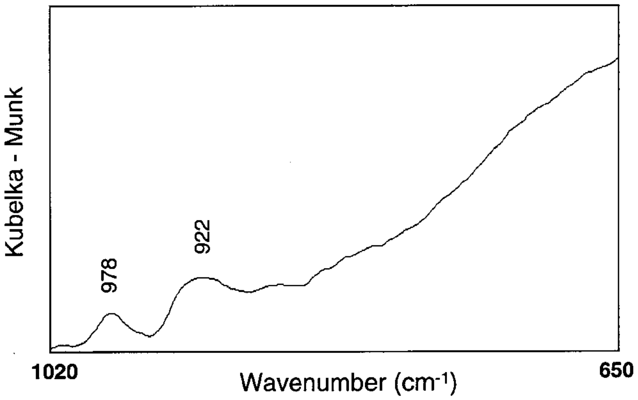

Figure 2. DRIFT spectrum of MoO_2 dispersed in a diamond matrix (14 wt%) in flowing Ar.

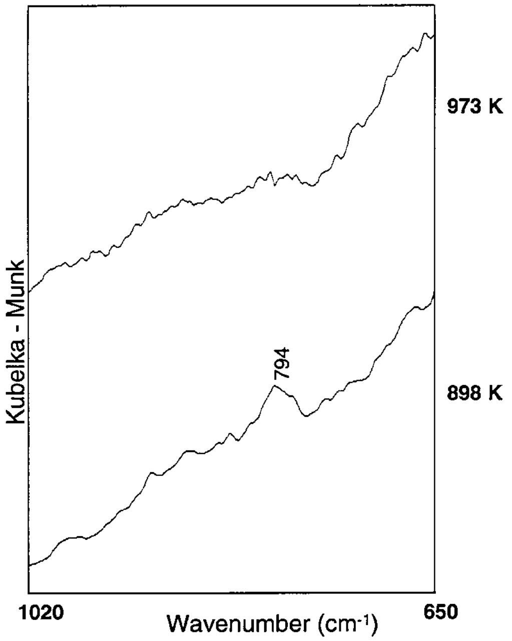

Figure 3. DRIFT spectra registered at high temperatures during the reduction of MoO_3 dispersed in a diamond matrix (14 wt%), in flowing pure H_2, diluted to 50 vol% in Ar.

attribution of the bands, which is beyond the scope of this work. In fact, apart from MoO_3 [27–29] or MoO_4 tetrahedral units [28], very few data are available in the literature for sub-oxides like MoO_2 or other Mo–oxygen species present on Mo_2C.

The spectrum registered at 303 K (figure 1) corresponds to the MoO_3 precursor showing characteristic bands at 996, 977, 821 and 803 cm^{-1} [27,29]. Up to 748 K, the intensity of bands at 996 and 821 cm^{-1}, attributed respectively to Mo=O and Mo–O–Mo stretching vibrations of MoO_3 [29], decreases progressively, characterizing the reduction of MoO_3. At 748 K, broad absorption bands around 970, 937, 917 and 790 cm^{-1} can be observed. Some of these bands (970, 937, 917 cm^{-1}) are close to the characteristic bands of MoO_2 shown in figure 2. In the spectrum obtained at 748 K (figure 1), however, an additional broad band at 790 cm^{-1} is observed, which is absent from the spectrum of MoO_2 (figure 2). It indicates that even though the bulk of the sample could be MoO_2 at this temperature [22,24,25], other Mo–O species can exist at the surface due to a different extent of reduction of the surface relative to the bulk. Indeed, at 773 K only a broad band at 790 cm^{-1} exists, while absorption bands at 970, 937 and 917 cm^{-1} have completely disappeared. At 883 K this band around 790 cm^{-1} is still present and broader. By increasing the temperature of carburization up to 973 K, this broadening disappears, but the small band around 790 cm^{-1} persists. Until now, we cannot attribute this band to a *specific* Mo–O vibration. However, it is important to note that this band informs us of the existence of residual oxygen species on the surface of Mo_2C formed at 973 K. It is unlikely that this band at 790 cm^{-1} was due to any H-containing carbonaceous species formed under high-temperature conditions, since no significant specific IR band was observed in the other IR regions (not shown) than that presented in figure 1. In addition, this band at 790 cm^{-1} is also observed at high temperature (898 K) during the temperature-programmed reduction of MoO_3 (figure 3), performed under flowing H_2. In figure 3, the band around 790 cm^{-1} disappeared at 973 K, indicating a complete reduction of the sample to metallic Mo. XRD analysis of the final product of carburization, recovered from the spectrometer, confirmed the formation of hexagonal Mo_2C in the DRIFTS environmental chamber. Nevertheless some very small peaks of MoO_2 were also observed, but this MoO_2 residue can be assumed to be in the center of the solid Mo_2C particles. Indeed, there is no indication of the presence of crystalline MoO_2 on the Mo_2C surface, as shown by the DRIFT spectrum obtained at 973 K (figure 1), compared with the spectrum of MoO_2 (figure 2). To further confirm the absence of Mo oxide on the surface, a Mo_2C sample, prepared in a conventional reactor and passivated, was reduced by flowing H_2 in a DRIFTS chamber. This passivated sample showed only the XRD pattern of Mo_2C. The sample treated at 873 K showed a spectrum very similar to that of 973 K in figure 1. The difficulty of completely removing surface oxygen species, by H_2 reduction, from a passivated Mo_2C was previously observed [21].

3.2. Chemisorptive properties and hydrogenating activity over molybdenum carbide samples prepared at different final temperatures of carburization

As shown above, residual oxygen is still present on the Mo_2C surface prepared at 973 K and it supports the results previously obtained [22], which also have evidenced the existence of residual oxygen, even at 973 K, by analyzing the bulk of the catalyst. Unfortunately, the temperature of reaction could not be increased above 973 K, due to technical limits of the DRIFTS environmental chamber. However, a carburization at higher temperatures should further decrease the content of residual oxygen, leading to a more complete carburization. A more complete carburization results in the increase of the density of sites titrated by CO, as well as the enhancement of the hydrogenating activity in benzene hydrogenation [22].

Three samples of Mo_2C were prepared in a conventional reactor under the same conditions except for the final temperature (923, 973 and 1023 K). Table 1 reports specific surface areas and chemisorptive properties of the samples. First of all, a progressive decrease in the surface areas with temperature can be noted. Concerning oxygen chemisorption, a rather constant oxygen site density (nO_2) was obtained (0.83×10^{15} cm^{-2} and 0.87×10^{15} cm^{-2}). This means that no polymeric carbon contamination occurred during the carburization until 1023 K [22].

Table 1

Specific surface areas (S_g) and chemisorptive properties of Mo_2C samples carburized at different final temperatures (T_f). All three samples were synthesized from MoO_3, under the same conditions except for the final temperature in flowing 10 vol% CH_4/H_2

Catalyst code	T_f (K)	S_g ($m^2 g^{-1}$)	CO uptake ($\mu mol\ g^{-1}$)	nCO [a] ($\times 10^{15}$ cm^{-2})	O_2 uptake ($\mu mol\ g^{-1}$)	nO_2 [b] ($\times 10^{15}$ cm^{-2})	nCO/nO_2
Mo_2C-I	923	56	264	0.28	– [c]	– [c]	– [c]
Mo_2C-II	973	48	344	0.43	664	0.83	0.52
Mo_2C-III	1023	35	334	0.57	508	0.87	0.66

[a] Density of sites titrated by CO.

[b] Density of sites titrated by O_2.

[c] Not determined.

On the contrary, the density of sites evaluated from carbon monoxide chemisorption (nCO) was enhanced significantly by increasing the final temperature of carburization, confirming our previous results [22]. According to the latter, the increased degree of carburization also brings about the enhancement of the hydrogenating activity of Mo_2C. The STY values of the Mo_2C samples in benzene hydrogenation are presented in table 2, with those of Mo and 5 wt% Ru/Al_2O_3 for comparison. A spectacular increase in activity can be noticed with carburization of metallic Mo. With increasing final temperature of carburization, the activity is further improved and gets closer to that of Ru catalyst, well-known for its excellent hydrogenating activity. Considering, as explained in the introduction, that a more complete carburization will lead to a molybdenum carbide with an enhanced noble metal-like catalytic activity, the results of the TPD of benzene shown in figure 4 are revealing. Comparison of the three Mo_2C samples, presenting different STY in benzene hydrogenation, clearly shows a shift in the maximum temperature of benzene desorption: the higher the hydrogenating activity, the lower the temperature of the TPD peak of benzene (figure 4(a)). Let us compare these desorption temperatures with those obtained over Mo or Ru/Al_2O_3 (figure 4(b)). Molybdenum gave two desorption peaks at 377 and 473 K, while Ru/Al_2O_3 had only one peak at 384 K. Referring to the "Principle of Sabatier", the poor activity of Mo in benzene hydrogenation, in contrast to Ru, could be explained in terms of a too-strong interaction between Mo and benzene (see peak at 473 K). In the case of Mo_2C, the sample prepared at 1023 K, having the lowest desorption temperature, is the most active in benzene hydrogenation among the three Mo_2C samples studied.

Table 2

Benzene hydrogenation activities (STY) of different catalysts at RT

Catalyst	STY (s^{-1}) [a]	Remark
Mo [b]	0.0002	This work
Mo_2C I	0.006	Ref. [22]
Mo_2C II	0.024	Ref. [22]
Mo_2C III	0.081	Ref. [22]
5% Ru/Al_2O_3	0.350	Ref. [22]

[a] Based on CO uptakes at RT, with the stoichiometry of Mo : CO = 2 : 1 for metallic Mo and that of 1 : 1 for Mo_2C samples and Ru/Al_2O_3.

[b] Prepared by reduction of molybdic acid (Fluka) in flowing H_2 (flow rate = 5 l h^{-1}, precursor loading = 0.5 g, heating rate = 53 K h^{-1}, final temperature = 903 K).

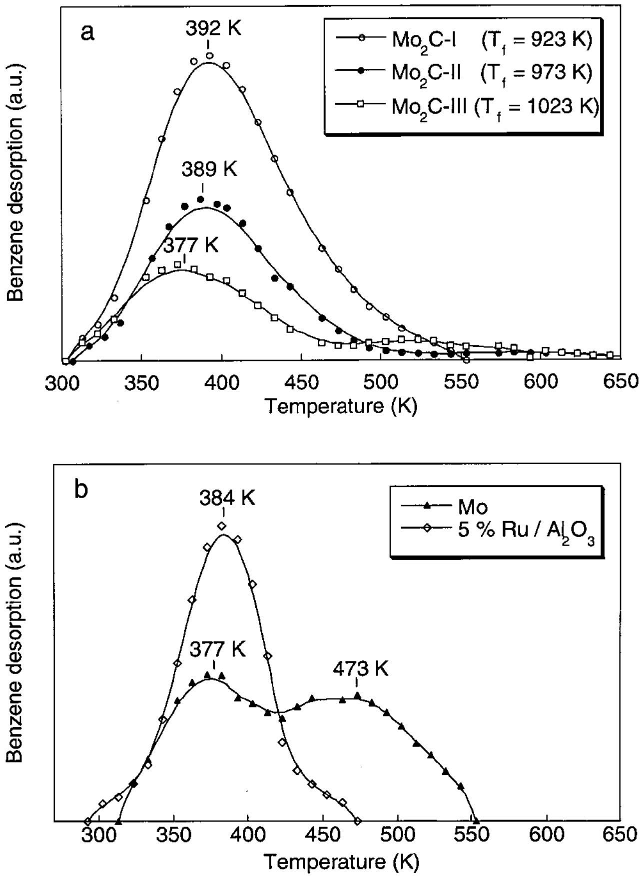

Figure 4. Temperature-programmed desorption of benzene in flowing He on (a) Mo_2C samples carburized at different final temperatures and (b) Mo and Ru/Al_2O_3 (He flow rate = 1.8 l h^{-1}, heating rate = 300 K h^{-1}). The areas of desorption were normalized to the number of sites titrated by CO chemisorption.

4. Conclusions

Molybdenum carbide (Mo_2C) was prepared by temperature-programmed carburization of MoO_3 in flowing CH_4/H_2 mixture in a DRIFTS environmental chamber. During the carburization, the various stages of the transformation of the sample could be monitored *in situ* by DRIFTS. This technique permitted the reduction of MoO_3 to MoO_2, then the reduction of MoO_2 leading to the carbide, to be followed. Nevertheless, a broad IR band around 790 cm^{-1} in the domain of Mo–O vibration modes was still detected on Mo_2C prepared at 973 K, indicating the existence of surface residual oxygen species on the prepared Mo_2C. This result corroborates our previous conclusion on the difficulty of completely removing residual surface oxygen species [22]. Among three Mo_2C samples prepared in a conventional reactor under the same conditions but at different final temperatures of carburization (923, 973 and 1023 K), the sample prepared at 1023 K showed the highest density of sites titrated by CO, and the highest activity (STY) in benzene hydrogenation due to a deeper deoxygenation and subsequent higher carburization. The benzene TPD showed that a higher final temperature of carburization also lowers the desorption temperature of benzene from Mo_2C, giving to the carbide a desorption behavior similar to that of Ru/Al_2O_3 rather than that of Mo. This means that the carburization lowers the adsorption strength of benzene over Mo, conferring to it a hydrogenating activity comparable with that of Ru catalyst.

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