

Adsorption and Reaction of CO₂ on Mo₂C Catalyst

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Received: February 7, 2002; In Final Form: June 10, 2002

The reaction between CO₂ and ZSM-5- and SiO₂-supported Mo₂C catalysts, found to be active in the aromatization of methane, has been studied in a flow and static system by measuring changes in the gas composition. The reaction was also followed with X-ray photoelectron spectroscopy. The decomposition of CO₂ occurred above 823 K to give CO and O atoms. Using ¹³CO₂ it was possible to establish that a fraction of O atoms oxidized the carbon of Mo₂C into CO, the other part reacted with Mo to give MoO_x species. The ratio of ¹³CO/¹²CO varied between 5 and 6.0. XPS study confirmed the oxidation of Mo resulting in the formation of Mo ions of various oxidation states. Although the dominant oxidation state is Mo⁶⁺ at every temperature, Mo⁴⁺ and Mo⁵⁺ were present in the sample even after the reaction at 1073 K. The reaction proceeded at a faster rate on Mo₂C/ZSM-5 than on Mo₂C/SiO₂.

1. Introduction

In searching new and effective catalysts, Mo₂C is obviously unique in many respects. One of its most interesting properties is that its combination with ZSM-5 or with SiO₂ effectively catalyzes the direct conversion of methane into benzene.^{1–4} This was observed after the discovery of a Chinese group that MoO₃/ZSM-5 is active for that reaction.⁵ Subsequently it was found, however, that MoO₃ is reduced during the reaction and a large amount of carbon is deposited on the catalyst surface.⁶ This led to the recognition that Mo₂C is formed in the reaction, which is the key compound in the mild activation of methane.^{1–4} An interesting feature of this reaction is that a small amount of CO₂ prevents the deactivation of the Mo₂C/ZSM-5 catalyst.^{7,8} Supported Mo₂C is also a good catalyst for the aromatization of ethane,⁹ ethylene,¹⁰ propane,¹¹ and in the oxidative dehydrogenation of these compounds using CO₂ as an oxidant.^{12,13} Mo₂C is also active for the hydrogenation of CO₂ into hydrocarbons and for the CH₄ + CO₂ reaction to give synthesis gas, H₂ and CO.^{14,15}

To understand the role of CO₂ in the above processes, we examined the interaction of CO₂ with Mo₂C prepared on Mo-(100) surface with several tools of surface science in UHV.^{16,17} CO₂ adsorbed mostly weakly and reversibly on Mo₂C/Mo(100) surface at low temperature, 100–200 K. Deposition of potassium adatoms, however, dramatically enhanced the reactivity of Mo₂C toward CO₂. In the continuation of this program in the present work we examine the interaction and reaction of CO₂ with Mo₂C deposited on ZSM-5 and SiO₂ of high surface area in the temperature range of the above catalytic reactions.

2. Experimental Section

2.1. Materials. Supported Mo₂C catalysts were prepared by the application of the method of Lee et al. developed for the

preparation of unsupported Mo₂C.¹⁸ Briefly, about 0.5 g of 2 wt % MoO₃/support was heated in 1:4 methane–H₂ mixture flowing at 250 mL (STP)/min (20 K/min) in a quartz cell with two stopcocks. Preparation temperature was increased rapidly to 773 with 20 K/min and at 3 K/min from 773 to 1023 K, and maintained at 1023 K for 3 h. Following the suggestion of Lee et al., the sample was deactivated at 300 K with 1% O₂ + 99% Ar, or used in situ for catalytic studies.¹⁸ The adsorbed O formed has been reduced during the reductive pretreatment of the samples before the measurements. The calcination temperature of MoO₃/support before carburization was 863 K.

Mo₂C was also prepared by the reaction of MoO₃ with ethane. This process takes place at lower temperatures than with methane and presumably produces Mo₂C of higher dispersity.^{15,19} In this case the supported MoO₃ samples were heated under 10% v/v C₂H₆/H₂, from room temperature to 900 K at a heating rate of 0.8 K min^{–1}.

The samples have been characterized by XPS. The binding energies for Mo(3d_{5/2}) and Mo(3d_{3/2}) were 227.75–228.25 eV and 230.7–231.05 eV. For C(1s) we obtain a value of 283.8 eV. These values are consistent with those obtained in previous studies.^{3,4} The properties of Mo₂C samples have been described in several reviews.^{20–24}

2.2. Methods. The reaction of Mo₂C samples with CO₂ has been followed by different methods. In temperature-programmed reaction (TPR), 0.5 g of supported Mo₂C was placed in a catalytic reactor, and was heated in an Ar + CO₂ gas mixture containing 10–25% CO₂. The amount of CO produced in the reaction was determined by a Hewlett-Packard 5890 gas chromatograph and a Porapak QS column. The flow rate of the gas was ca. 12 mL/min, and the heating rate was 4 K/min. The same reactor and method were used for the study of the reaction under isotherm conditions. In this case, the amount of CO₂ was also followed. Prior to the reactions catalyst pellets were pretreated in H₂ flow at 873 K for 1 h to remove the excess carbon of Mo₂C. Thermogravimetric measurements were made by a Netzsch STA 409 PC Luxx thermobalance, which allowed us to perform measurements in a vacuum, at atmospheric

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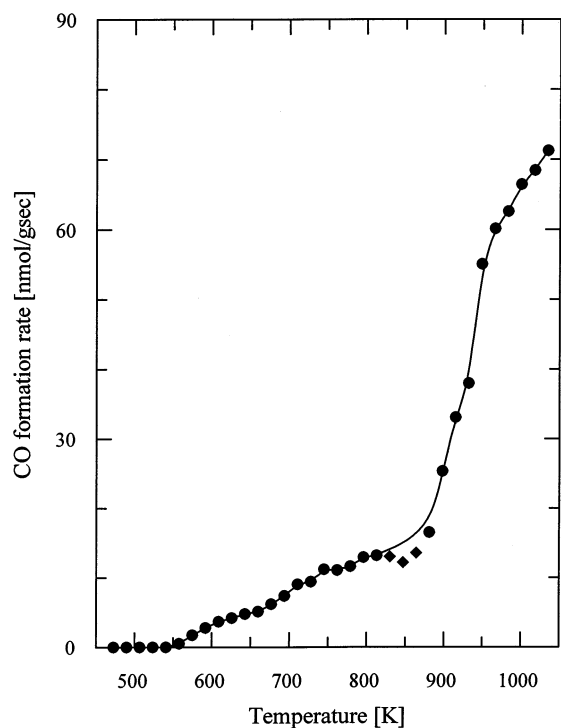


Figure 1. Temperature-programmed reaction of 1.4% Mo₂C/ZSM-5 sample with Ar + CO₂ (10%) gas mixture.

pressure, and in a gas flow. The sensitivity of the balance is 2.0 μg . Some experiments have been performed in a closed circulation system. In this case the reaction was followed by analyzing the composition of gas phase with an MS 10 mass spectrometer.

X-ray photoelectron spectroscopic (XPS) studies were made in a Kratos XSAM 800 instrument at a base pressure of 5×10^{-9} Torr using Al K α primary radiation. To compensate for possible charging effect, binding energies (BE) were normalized with respect to the position of the Si(2p) peak in SiO₂ (BE =

103.4 eV) for supported samples and to the Fermi level for the Mo₂C. During spectrum acquisition the X-ray gun was operated at 225 W power (15 kV, 15 mA). The energy step between the channels was 50 meV. From a single channel, counts were collected for 300 ms. The pass energy was set to 20 eV (ZSM-5 support) or 40 eV (SiO₂ support). Usually 10 scans of the Mo-(3d) region were added to record a spectrum. Fitting and deconvolution of the spectra were made using the VISION software (Kratos). The pretreatment of the samples and the reaction were performed in the preparation chamber attached to the UHV system. All the Mo₂C samples prepared separately have been pretreated in the preparation chamber in pure H₂ at 873 K to remove the excess carbon of Mo₂C. Then the solid sample was exposed to a flow of Ar + CO₂ gas mixture containing 25% CO₂. From time to time the system was evacuated and the Mo₂C was transferred to the analyzing chamber.

3. Results and Discussion

3.1. TPR Measurements. The reaction of Mo₂C samples with CO₂ was first followed by TPR. Figure 1 shows that the product of the reaction, CO, was detected first at ~ 600 K. A more extended decomposition of CO₂, however, occurred above 850 K.

3.2. Measurements under Isotherm Conditions. Based on TPR curves the reaction was studied under isotherm conditions in the temperature range 923–1073 K. Analysis of the gas phase indicated that the reaction involves the consumption of CO₂ and the formation of CO. A characteristic pair of curves taken at 973 K for Mo₂C/ZSM is shown in Figure 2A. The rate of the reaction declines in time on stream, but it does not cease even after 100 min. With the increase of temperature the initial reaction of CO₂ is greatly increased. The ratio of CO formed and CO₂ consumed is slightly below 1 and—apart from some scattering of the data—it remains constant throughout the measurements. This value is practically independent of the temperature at 923–1023 K (Figure 2B). This would suggest

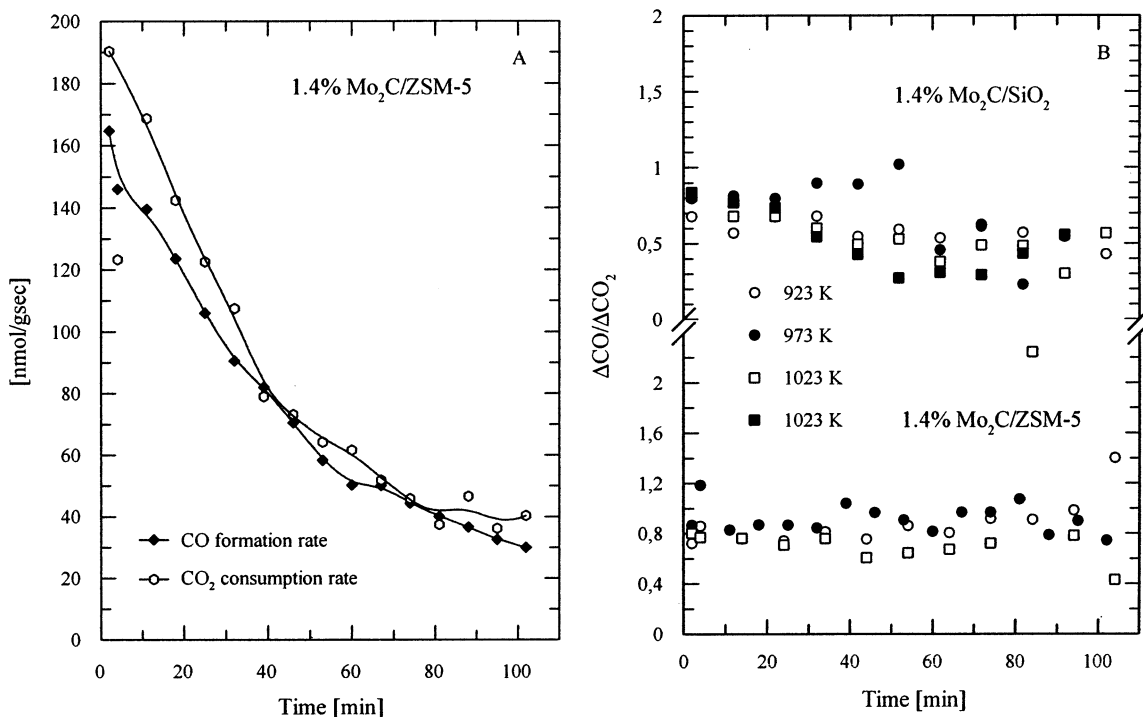


Figure 2. (A) Reaction of 1.4% Mo₂C/ZSM-5 with Ar + CO₂ (10%) gas mixture at 973 K. (B) Ratios of CO formed and CO₂ consumed ($\Delta\text{CO}/\Delta\text{CO}_2$) at different temperatures for Mo₂C/ZSM-5 and Mo₂C/SiO₂.

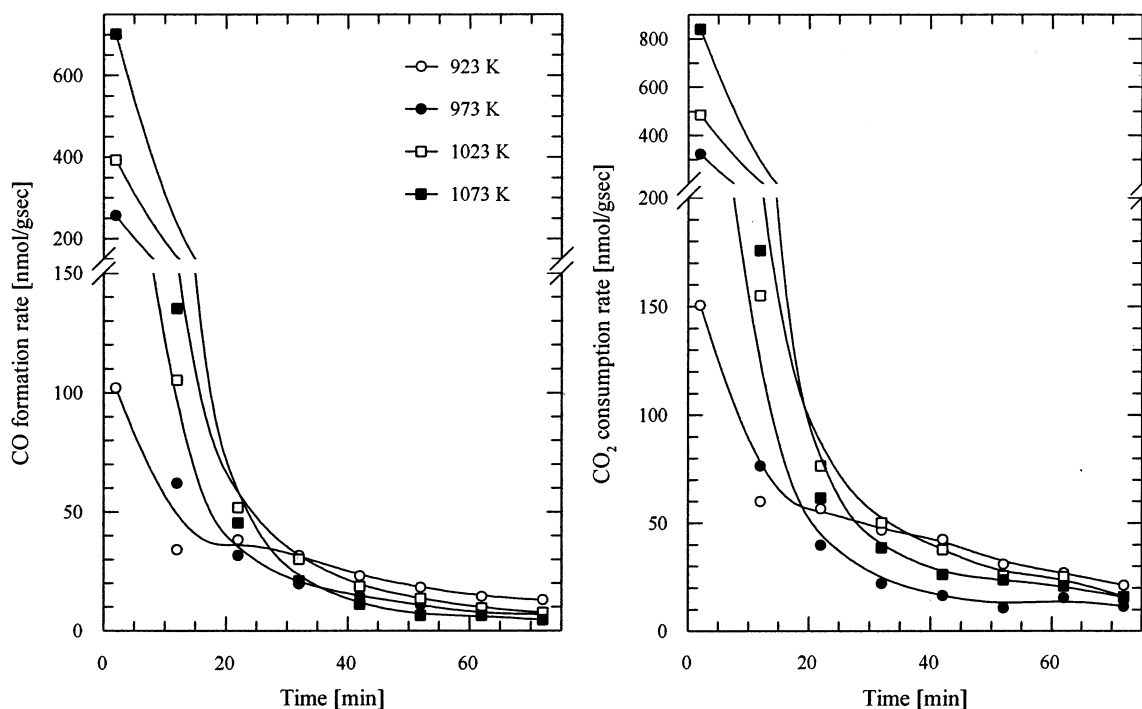


Figure 3. Reaction of 1.4% Mo₂C/SiO₂ with Ar + CO₂ (10%) gas mixture at different temperatures.

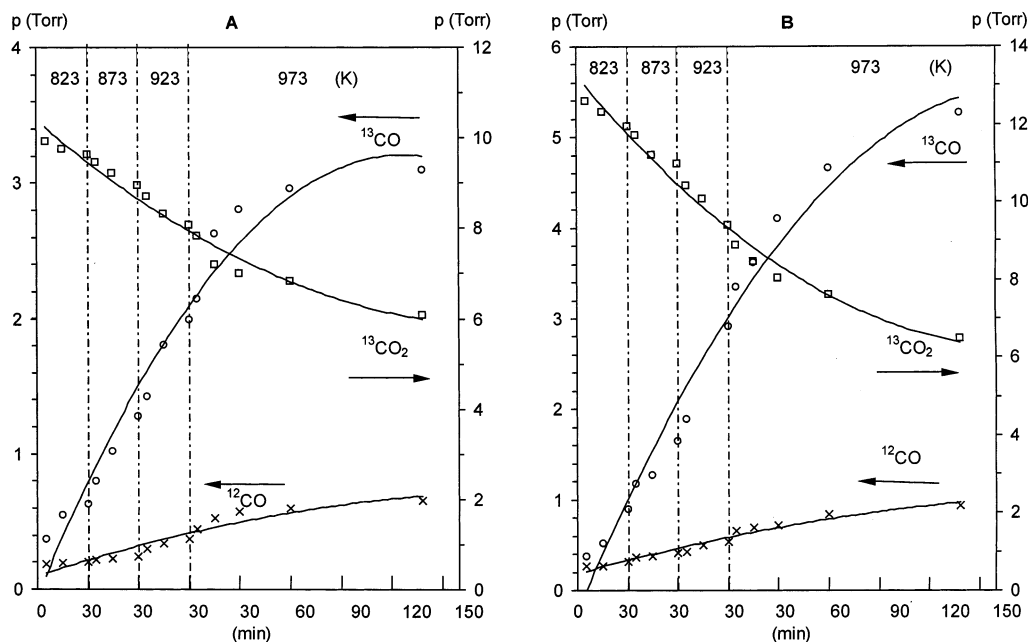
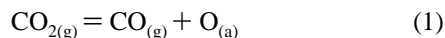
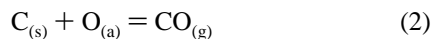


Figure 4. Formation of ¹³CO and ¹²CO in the reaction of ¹³CO₂ with 1.4% Mo₂C/ZSM-5 (A) and 1.4% Mo₂C/SiO₂ (B) at 823–973 K in a closed circulation system. 10 Torr of ¹³CO₂ was introduced in the reactor. The reaction time was 30 min at 823–893 K.

that CO comes from the decomposition of CO₂:



and the contribution of the reaction of carbon in Mo₂C with the O atoms formed in the CO₂ dissociation



is limited. We may assume that the oxygen of CO₂ is attached to Mo₂C resulting first in Mo oxy carbide and then Mo oxides.

Qualitatively similar features were experienced for Mo₂C/SiO₂. The reaction, however, was faster compared to Mo₂C/ZSM-5 as indicated by the rate of formation of CO and that of

the consumption of CO₂. The fast initial stage was followed by a rather slow phase. Some reaction curves are shown in Figure 3. The $\Delta\text{CO}/\Delta\text{CO}_2$ values showed larger scattering and from the initial value, 0.8, definitely decreased with the progress of the reaction. This is illustrated in Figure 2B.

3.3. Use of Labeled CO₂. To obtain a deeper insight into the reaction between CO₂ and Mo₂C, some measurements have been performed with ¹³CO₂. In this case the reaction was studied in a closed circulation system and changes in the composition of gas phase were monitored by mass spectrometry. Results obtained for 1.4% Mo₂C/ZSM-5 are shown in Figure 4A. The evolution of ¹³CO started already at 823 K and slowly increased with the rise of the temperature. Faster reaction occurred above

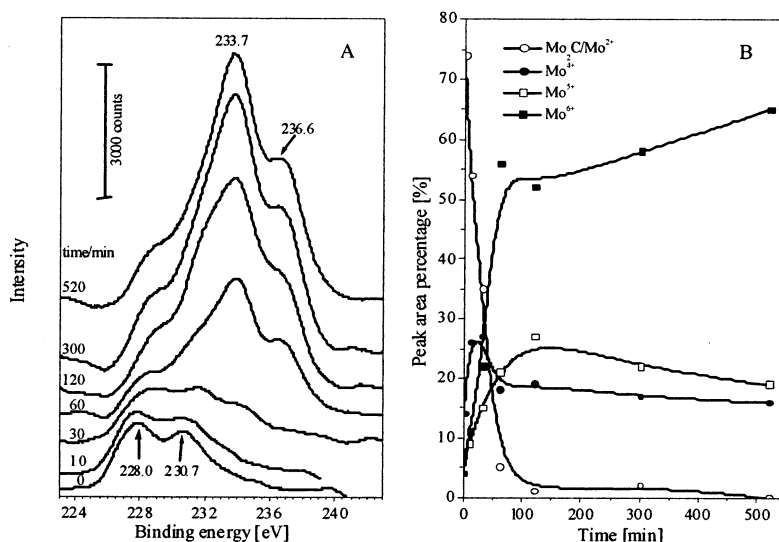


Figure 5. (A) Changes in XP spectra of $\text{Mo}_2\text{C}/\text{SiO}_2$ and (B) in the relative areas of different Mo ions in the flow of Ar + CO_2 (25%) gas mixture at 873 K.

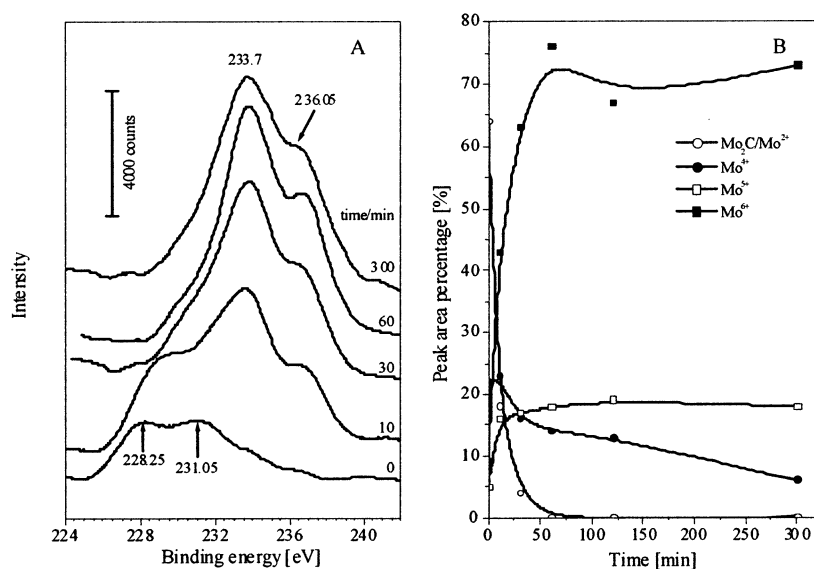
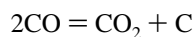


Figure 6. (A) Changes in XP spectra of 1.4% $\text{Mo}_2\text{C}/\text{SiO}_2$ and (B) in the relative areas of different Mo ions in the flow of Ar + CO_2 (25%) gas mixture at 1073 K.

873 K. The formation of ^{12}CO was also observed at and above 923 K. The ratio of $^{13}\text{CO}/^{12}\text{CO}$ was 4.5 at 923 K and remained practically constant up to 973 K (Figure 4A). The ratio of CO produced and CO_2 consumed has been calculated in this case, too. We obtained a value of ~ 0.9 , which was practically independent of the temperature. Similar measurements were performed with $\text{Mo}_2\text{C}/\text{SiO}_2$. The reaction was somewhat faster than in the previous case (Figure 4B). The $\Delta\text{CO}/\Delta\text{CO}_2$ ratio was the same as for the $\text{Mo}_2\text{C}/\text{ZSM-5}$, but the $^{13}\text{CO}/^{12}\text{CO}$ ratio was slightly higher, 5.0–6.0.

All these results confirm the assumption drawn from the analysis of previous data, namely, that the main reaction of CO_2 on supported Mo_2C is its decomposition to CO and O (eq 1). The formation of ^{12}CO , however, supports the assumption that a smaller fraction of O atoms formed in the dissociation process oxidizes the carbon in Mo_2C to CO, and its larger fraction is incorporated into Mo_2C . As the CO formed was somewhat less than the CO_2 consumed, it was assumed that a fraction of CO disproportionated



on the Mo_2C surface. Control measurements confirmed the occurrence of this process: at 973 K about 10% of CO (10 mbar) has been disproportionated in 2 h.

The reactivity of Mo_2C was clearly higher when it was prepared with $\text{C}_2\text{H}_6/\text{H}_2$ mixture. This is very likely due to the higher dispersity. It was observed in both cases that when the supported Mo_2C samples have not been pretreated with H_2 to remove the excess carbon, the reaction between Mo_2C samples and CO_2 was slower by a factor of 2 or 3.

3.4. Thermogravimetric Measurements. The reaction has been also followed by thermogravimetric measurements. In this case the Mo_2C content has been increased to 7.0%. Treating the $\text{Mo}_2\text{C}/\text{ZSM-5}$ with H_2 at 873 K caused a weight loss of 0.6%. (The weight of the sample was 162.9 mg). Assuming that H_2 reacted only with the excess carbon produced during the preparation of Mo_2C , this shows that the sample contained $0.97 \mu\text{g}$ of C, corresponding to 5.95% of Mo_2C content of the $\text{Mo}_2\text{C}/\text{ZSM-5}$. This value is 9.23% for Mo_2C on SiO_2 .

In the presence of CO_2 -Ar flow, we observed an initial fast increase in the weight of the $\text{Mo}_2\text{C}/\text{ZSM-5}$ sample, which became almost constant after 30–40 min. The total weight

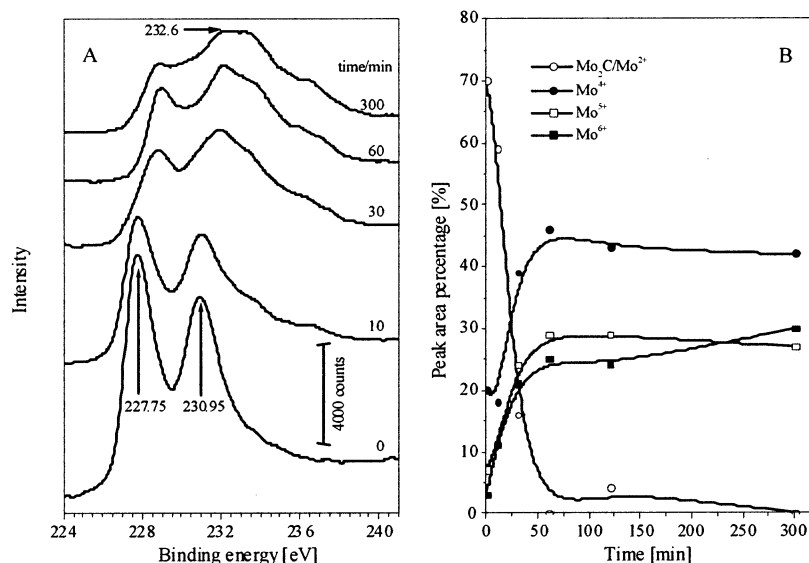


Figure 7. (A) Changes in XP spectra of 1.4% Mo₂C/ZSM-5 and (B) in the relative areas of different Mo ions in the flow of Ar + CO₂ (25%) gas mixture at 873 K.

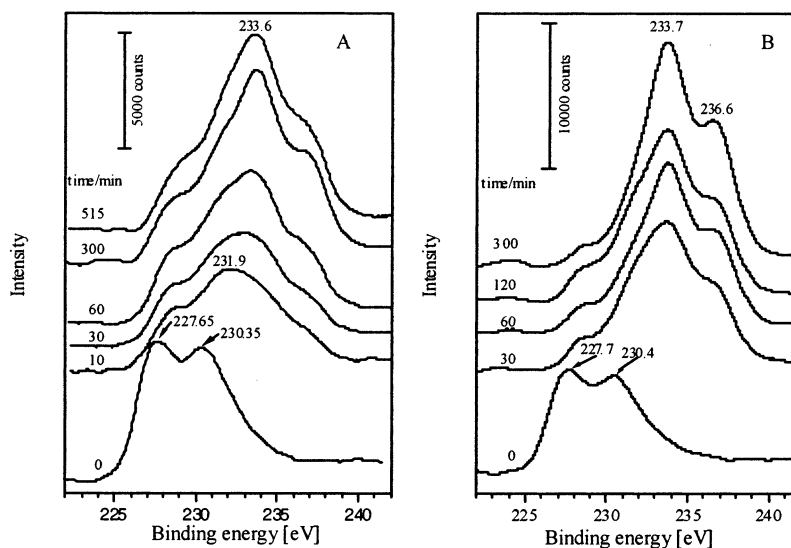


Figure 8. Changes in XP spectra of 1.4% Mo₂C/ZSM-5 in the flow of Ar + CO₂ (25%) gas mixture at (A) 973 K; (B) 1073 K.

increase in 60 min is 1.66 mg. This value was 2.17 mg for Mo₂C/SiO₂. Taking into account the amount of Mo₂C in both samples, the rough calculation gave the following composition: Mo₂O_{1.3}C/ZSM-5 and Mo₂O_{2.0}C/SiO₂. If we consider the amount of ¹²CO formed in the reaction of C and O (eq 2), then we obtain: Mo₂O_xC/ZSM-5 (0 < x ≤ 2) and Mo₂O_xC/SiO₂ (0 < x ≤ 3).

3.5. XPS Study. Mo₂C/SiO₂. Figure 5 shows the XP spectra of Mo₂C/SiO₂ reacted with CO₂ for different time at 873 K. The initial binding energies of the Mo(3d) doublet located at 228.0 and 230.7 eV are characteristic of Mo₂C. The shape of the spectrum began to alter even after 10 min of treatment, but the changes became obvious only after 30 min. As the reaction progressed, the peak characteristic of Mo(3d_{5/2}) in Mo₂C turned into a shoulder of the complex spectrum with maximum 233.7 eV, while another shoulder developed at around 236.6 eV on the high binding energy side of the spectrum. This latter became separated after a longer reaction time. This peak stems from the Mo⁶⁺(3d_{5/2}) orbital. Another feature of the series of spectra is the monotonic increase of the Mo(3d) signal intensity as a function of reaction time. After 520 min of reaction it is about three times higher than it was before CO₂ treatment. Such

variations between consecutive spectrum acquisitions cannot be explained with the alteration of the mutual geometrical positions of the sample and the X-ray gun. Monotony is also against this argument. The probable reason of the change is the increase of dispersity of Mo with reaction time, which leads to the enhancement of the component at or near the surface responsible for the XP signal. The uncertainty resulting from geometrical variations can partly be eliminated with plotting the ratios of the peak areas. In this representation the C/Mo ratio decreases to about one-fourth of its starting value.

Next, the Mo(3d) spectra have been deconvoluted into Mo₂C + Mo²⁺, Mo⁴⁺, Mo⁵⁺, and Mo⁶⁺ components. The starting parameters were the positions of the individual components—letting the software count with a few tenths of eV uncertainty—the energy difference of the Mo(3d_{5/2})–Mo(3d_{3/2}) doublet (3.15 eV), and the intensity ratio of the two peaks (3:2). The restriction on the fwhms was that they should be equal for all components. Gaussian-Lorentzian functions were used in the process. The result of the fit of a given state provided the input parameters of the fit for the following state in the series.

The positions of Mo(3d) in Mo₂C and Mo²⁺ could not be distinguished, so they were considered as a single state. Data

obtained in this way reveal that during the preparation MoO₃ has not been converted completely into Mo₂C (Figure 5B). The approximate surface composition of the starting sample after hydrogen treatment is ~75% Mo₂C + Mo²⁺, ~14% Mo⁴⁺, ~7% Mo⁵⁺, and 4% Mo⁶⁺. These values suggest that the carburization of MoO₃ samples was not complete. Another explanation is that the software used for the deconvolution of the XPS curves is not perfect. This latter may influence the data as a post-carburization of the samples in the preparation chamber of the XPS system exerted only slight influence. Following the CO₂ treatment the share of Mo₂C + Mo²⁺ state steeply decreases, that of the Mo⁶⁺ state rapidly increased. After the initial violent changes, from about 100 minutes of reaction, the modification of the surface composition gets slower. After the maximum reaction time studied (520 min), the Mo₂C + Mo²⁺ state practically disappeared. The composition of the sample: ~65% Mo⁶⁺ and 16–19% Mo⁴⁺ and Mo⁵⁺.

Similar features were observed at higher temperature, when a significant increase in the intensity of Mo(3d) was also experienced. At 1073 K, the initial value enhanced by a factor of 3.5 already in 10 min, then it became constant. The reaction between CO₂ and Mo₂C occurred rapidly as demonstrated by the spectral changes displayed in Figure 6A. Even after 10 min of reaction the dominant peak in the XPS was at 233.7 eV. The Mo(3d_{5/2}) peak of the Mo₂C state at ~228.0 eV was hardly detectable after 30 min of reaction. The final composition of the sample was attained almost at 60 min (Figure 6B). This was (~0% Mo₂C + Mo²⁺), ~13% Mo⁴⁺, ~17% Mo⁵⁺, and ~70% Mo⁶⁺.

Mo₂C/ZSM-5. A new feature of the XP spectra obtained on zeolite-supported catalysts was the high Mo(3d) signal intensity of the starting material, which remained practically unaltered during the high-temperature reaction. This suggests a high dispersion of Mo₂C on ZSM-5. Taking into account this feature, we set the pass energy to a lower value, 20 eV, thus increasing the resolution.

The binding energies of Mo(3d_{5/2}) of this sample are located at 227.75 and 230.95 eV (Figure 7A). Based on the results of the deconvolution of the spectra, the starting composition was as follows: Mo₂C + Mo²⁺ ~ 70%; Mo⁴⁺ ~ 20%, Mo⁵⁺ ~ 7%, Mo⁶⁺ ~ 3%. On the effect of CO₂ at 873 K spectral changes occurred at 30 min, it was however, not so dramatic as in the case of Mo₂C/SiO₂ (Figure 5). As shown in Figure 7B the share of the Mo₂C + Mo²⁺ state rapidly decreased to 5%. The shares of the other components first increased in this period of time, then remained almost constant. Unlike the experiments carried out on SiO₂-supported samples, the ratio of Mo⁴⁺ with respect to the sum of all states was the highest, 43%. This value was practically the same, 27–30%, for Mo⁵⁺ and Mo⁶⁺. Accordingly, the extent of oxidation of Mo₂C by CO₂ on ZSM-5 at 873 K is less than that on SiO₂ support.

Much faster spectral changes were observed at higher temperatures 973–1073 K (Figure 8). In contrast to the data obtained at 873 K, Mo⁶⁺ was the dominant species even after short reaction time, 60–30 min. The share of Mo⁵⁺ and Mo⁴⁺ was near the same both at 973 and 1073 K.

The results obtained disclosed several features of the interaction and reaction of CO₂ with the Mo₂C. The fact that CO₂

reacts readily with the carbon in Mo₂C may help to understand its role in preventing the deactivation of the catalysts in the aromatization of methane.^{1–8,25,26} The Mo–O species formed at higher CO₂ pressure and temperature can be considered as an active center in the reactions of hydrocarbons to produce synthesis gas or unsaturated compounds.^{12–15}

4. Conclusion

The interaction of CO₂ with Mo₂C deposited on SiO₂ or ZSM-5 was observed above 823 K. It consisted of the following processes: decomposition of CO₂, oxidation of C in the Mo₂C to CO, disproportionation of CO, and the reaction between Mo and O atoms to give MoO_x. The reaction between CO₂ and Mo₂C was initially fast, followed by a slow process. XPS study revealed the transient formation of Mo⁴⁺ and Mo⁵⁺. In the temperature range of 973–1073 K the main Mo species is Mo⁶⁺. The complete oxidation to MoO₃ was not achieved even at 1073 K after several hours. The reaction occurred at a faster rate on Mo₂C/SiO₂ than on Mo₂C/ZSM-5.

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