Effects of potassium on the chemisorption of CO_2 and CO on the Mo_2C/Mo(100) surface

F. Solymosi and L. Bugyi

*Institute of Solid State and Radiochemistry, University of Szeged, Reaction Kinetics Research Group of the Hungarian Academy of Sciences**,
PO Box 168, H-6701 Szeged, Hungary

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The interaction of CO_2 with K-promoted Mo_2C/Mo(100) has been studied with high-resolution electron energy loss spectroscopy, work function measurements and temperature-programmed desorption. Pre-adsorbed potassium dramatically affects the adsorption behavior of CO_2 on the Mo_2C/Mo(100) surface. It increases the rate of adsorption, the binding energy of CO_2 and it induces the dissociation of CO_2 through the formation of negatively charged CO_2. Potassium adatoms also promote the dissociation of adsorbed CO over Mo_2C.

Keywords: Mo_2C catalyts, potassium promoter, activation of CO_2, promoted dissociation of CO_2, CO adsorption on Mo_2C, carbonate formation

1. Introduction

There has been an increasing interest in the catalytic behavior of the Mo_2C catalyst. It has been reported that its catalytic efficiency approached or even exceeded that of several Pt metals, thus initiating an extensive research in this area [1–5]. Among others Mo_2C is an active catalyst in the hydrogenation of CO and CO_2 [6–8]. Recently, it has been observed that Mo_2C deposited on ZSM-5 is an effective catalyst in the direct conversion of methane into benzene with 70–80% selectivity at 10% conversion [9–12], and also in the oxidative dehydrogenation of ethane using CO_2 as an oxidant [13].

As potassium is a very good promoter for several reactions involving CO, CO_2 and hydrocarbons [14,15], a work was undertaken to examine its influence on the catalytic performance of Mo_2C. Whereas the effects of alkali metals on the chemisorption of CO and CO_2 over transition metals have been extensively studied in the last decades [14–17], no reports were found in the literature on their influence on the adsorptive properties of Mo_2C. Furthermore, we found no information as regards the adsorption of potassium on this surface. The primary aim of the present study is to investigate the main characteristics of effects of potassium on the adsorption behavior of CO_2 and CO on the Mo_2C/Mo(100) surface.

2. Experimental

A standard UHV system containing facilities for AES, HREELS, TPD and work function ($\Delta\phi$) measurements was used for the experiments. The Mo_2C layer over Mo(100) was prepared by a slight modification of the method of Schöberl [18]. The Mo(100) surface was exposed to 200 L of ethylene at 900 K. Details can be found in our previous paper dealing with the reactions of CH_2 and C_2H_5 species on a Mo_2C/Mo(111) surface [19]. The resulting surface as checked by AES and XPS showed the characteristic features of carbide. As we had no facility for LEED measurements in our system the structure of the Mo_2C layer was not determined. However, Mo_2C prepared on Mo(100) by the above method has been characterized by LEED, and a c(2×2) structure was observed [20,21]. Potassium was deposited onto the Mo_2C layer by heating a commercial SAES Getter source situated 3 cm from the sample.

3. Results and discussion

3.1. Adsorption of potassium

The deposition of potassium on a clean Mo_2C/Mo(100) surface at 300 K lowered its work function by 3.3 eV at monolayer coverage. The adsorption of potassium was accompanied by the appearance of a new loss feature in the HREEL spectrum at 230 cm^{-1}. At low K coverage, potassium desorbs at very high temperature, $T_p = 950$ K. With the increase of the potassium concentration, this peak temperature shifted to lower temperature, at monolayer to 450 K, and above monolayer to 354 K (figure 1(A)). The onset of desorption from the second adlayer was accepted as a completion of the first adlayer (1 ML). The adsorbed CO_2 was found to stabilize the pre-adsorbed potassium on the surface, and in the saturated adlayer desorption of potassium occurred simultaneously with that of CO_2 with a $T_p =$ 680–696 K. This is also illustrated in figure 1(A).

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* These laboratories are part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

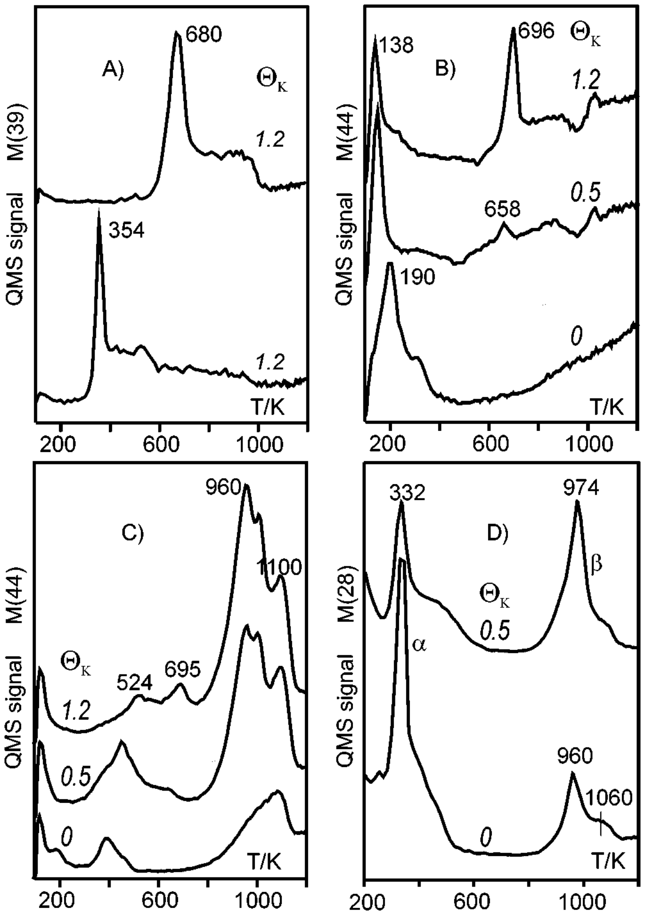

Figure 1. Desorption of K (A), CO_2 (B) and CO (C) from the Mo_2C/MoC(100) surface. In the case of (A) the lower curve represents the desorption from the K-dosed surface, whereas the upper curve that from the K + CO_2 co-adsorbed layer. For (B) and (C), CO_2 (2.0 L) was adsorbed on clean and K-covered surfaces. For (D) the Mo_2C was exposed to 4.0 L of CO. The adsorption temperature for CO_2 and CO was 90 and 150 K, respectively. The numbers of the curves indicate the coverage of potassium in monolayer.

3.2. Adsorption of CO_2

As concerns the adsorption of CO_2 the behavior of K-free Mo_2C resembles that of Pt metals; the adsorption is weak and non-dissociative. In the HREEL spectrum we detected vibration losses at 2345–2355, 1260–1340 and 660 cm^{-1}, which are characteristic for the unperturbed CO_2 molecule (table 1). These spectral features were eliminated by heating up the adsorbed layer to above 150 K. In the TPD spectrum we observed one peak for CO_2 desorption with $T_p = 190$ K The weak adsorption of CO_2 suggests that CO_2 bonds at the surface via a lone pair of an O, with the molecular bond vertically as proposed for Pt and Cu surfaces [17].

A completely different picture was obtained in the presence of co-adsorbed potassium, which exerted a dramatic influence on the adsorption of CO_2. The weakly adsorbed CO_2 desorbed at lower temperature, $T_p = 138$ K. A new adsorption state developed at 658 K at $\Theta_K = 0.5$ ML, which shifted to 696 K at monolayer K coverage (figure 1(B)). At the same time, the desorption of CO was also observed with $T_p = 524$ and 695 K and in several high-temperature peaks (figure 1(C)). We assume that the formation of CO above 800 K is the result of the oxidation of Mo_2C by atomic oxygen produced by the dissociation of CO_2. The formation of CO strongly suggests that potassium activates the adsorbed CO_2 molecule, very likely through an electron donation from the surface, and yields partially negatively charged CO_2 which easily dissociates:

$$CO^{-}_{2(a)} \rightleftharpoons CO_{(a)} + O^{-}_{(a)}$$

This interpretation is strengthened by work function measurements. The adsorption of CO_2 on potassium-dosed Mo_2C led to a work function increase of 1.0 eV at nearly a monolayer of potassium. This indicates a substantial charge transfer from the potassium-dosed sample to an empty CO_2 π^* orbital and a corresponding large dipole moment of the chemisorbed CO_2. This leads to a strengthening of the substrate–C bond and to a weakening of the C–O bond of the adsorbed CO_2, which may result in its dissociation. It is very likely that the extended electronic interaction involves changes in the structure of the adsorbed CO_2, i.e., the formation of a metal–carbon bond in the form of a monodentate or bidentate structure.

The effect of potassium was also exhibited in the HREEL spectrum. This is displayed in figure 2(A). Following the adsorption of CO_2 on Mo_2C containing a monolayer of potassium at 90 K, new vibrational features appeared at 1665, 1475, 1260 and 750 cm^{-1}. The latter peak was very weak. Taking into account the previous results and interpretation on CO_2 adsorption of K-promoted metals [16,17,22,23], the vibrations at 1665, 1260 and 750 cm^{-1} are attributed to the formation of negatively charged CO_2. Vibration losses observed and their assignments are given in table 1.

When the temperature of CO_2 adsorption was varied, we found that the vibration losses at 2370 and 660 cm^{-1} attributed to unperturbed CO_2 were no longer detectable at 150 K. At 200–210 K the 1675 and 1260 cm^{-1} loss features attenuated, and at the same time, the loss peak at 1475 cm^{-1} was markedly enhanced. Its maximum intensity was attained at 300 K. Above this temperature its intensity gradually decayed and the loss peak completely disappeared above 650 K. The position of this loss and its thermal stability resemble that for carbonate species, which may be formed in the disproportionation of a K^+–CO_2^- surface complex,

$$2CO^{-}_{2(a)} \rightleftharpoons CO^{2-}_{3(a)} + CO_{(a)}$$

as was suggested first for the CO_2 + K/Pd(100) system [24,25]. Accordingly, the high-temperature release of CO_2 shown in the TPD spectra is the result of the decomposition of surface carbonate species. The formation of a stable surface compound is also suggested by the stabilization of potassium in the co-adsorbed layer and the coincidence desorption of both CO_2 and K (figure 1(A)). Similar features were reported in the first study dealing with the activation

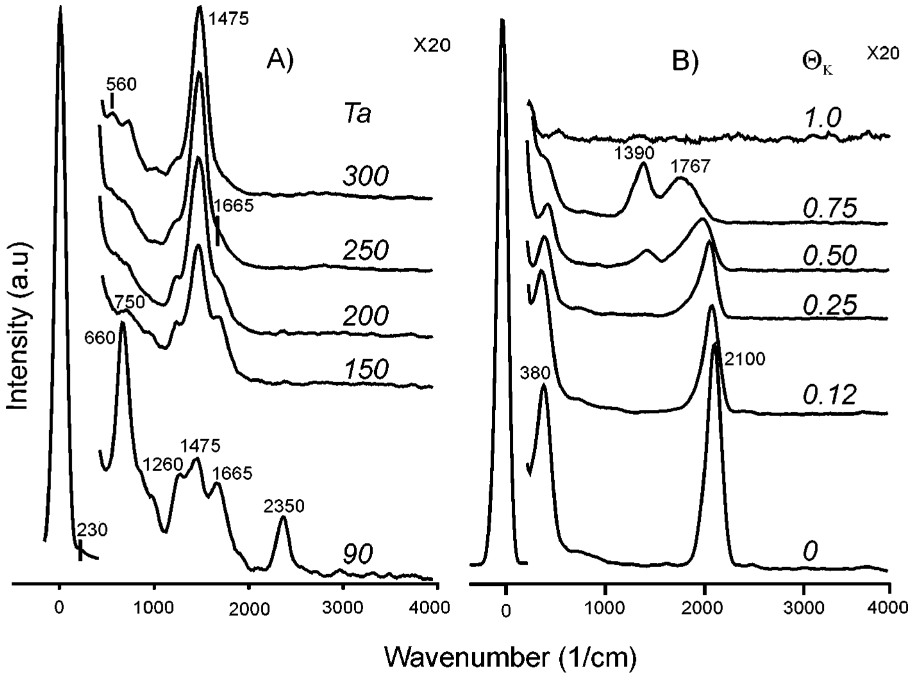

Figure 2. (A) Effects of adsorption temperature of CO_2 on the HREELS spectra of $Mo_2C/Mo(100)$ at 1.0 monolayer of potassium coverage. (B) Effects of K coverage on the HREEL spectra of adsorbed CO on $Mo_2C/Mo(100)$ at 150 K.

Table 1

Characteristic vibrations of adsorbed CO_2 and CO_2^-, following the adsorption of CO_2 on various surfaces at 90–100 K.

Sample	$\delta(CO_2)$	$\delta(CO_2^-)$	$\nu_s(CO_2^-)$	ν_s(OCO) monodentate CO_3	$\nu_a(CO_2^-)$	$\nu_a(CO_2)$	Ref.
$Mo_2C/Mo(100)$	640–660	–	1260–1340	–	–	2345–2355	present work
$K/Mo_2C/Mo(100)$ $\Theta_K = 1$ ML	660	750	1260	1475	1665	2350	present work
K/Rh(111) $\Theta_K = 0.36$ ML	640	840	1340	1440	1630	2350	[23]

of CO_2 by potassium over Pd(100) and Rh(111) surfaces [24–26], and were confirmed by subsequent works on several metals reviewed [16,17].

3.3. Adsorption of CO

There are different observations concerning the nature of CO adsorption on the C-modified Mo surfaces [27–29]. Whereas an early study suggested that the deposition of a monolayer of elemental carbon on the Mo(100) surface completely suppressed the dissociation of CO [27], recent work has disclosed that CO dissociates on β-Mo_2C at low coverage [28,29]. A weak recombinative thermal desorption feature appeared at 1200 K. Thermal desorption spectra for CO from potassium-dosed $Mo_2C/Mo(100)$ have been studied as functions of Θ_K and CO exposure. From K-free Mo_2C a fraction of CO desorbed in a peak (denoted by α) at 332 K. In addition, a small desorption peak appeared at 960 K (denoted by β) which is probably the result of the associative desorption of CO. With the increase of the K coverage, the area of the α peak decreased, whereas that of the β peak somewhat increased (figure 1(D)). At 0.8–1.0 ML of potassium coverage, the α peak was no longer detectable. If we accept the assumption that the high-temperature CO peak is the result of the recombination of C and O formed in the CO dissociation, then we can conclude that the dissociation process is enhanced by potassium adatoms. Note that the uptake of CO considerably decreased at higher K coverages, as also shown by the reduced intensity of CO vibration loss in the HREEL spectra.

CO adsorption on clean $Mo_2C/Mo(100)$ at 100–150 K gives a strong loss at 2100 cm^{-1} (figure 2(B)). In the presence of potassium adatoms, this peak is shifted to 1988 cm^{-1} at 0.5 ML and to 1767 cm^{-1}at 0.75 ML of potassium coverage. In both cases additional low-frequency peaks appeared at 1410 and 1390 cm^{-1}, respectively. At higher potassium content, no spectral features were detected at 4–8 L of CO exposure.

The adsorption of CO at 0.40 ML of potassium coverage caused a work function increase of 1.5 eV. These features can be ascribed to the enhanced back-donation of metal electrons into the lowest unoccupied molecular orbital ($2\pi^*$) of CO. This is responsible for the shift in the position of CO loss to lower energies.

4. Conclusion

(i) Potassium adatoms dramatically affect the adsorption and reactivity of CO_2 on Mo_2C/Mo(100). It leads to the dissociation of CO_2 through the formation of a negatively charged CO_2 species. At higher K content, a mutual stabilization of K and CO_2 occurs, which is attributed to a direct interaction between the two adsorbed species and to the formation of carbonate-like surface compound. (ii) Potassium adlayer also promotes the dissociation of adsorbed CO over Mo_2C.

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References

[1] R.L. Levy and M. Boudart, Science 181 (1973) 547.
[2] F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J. Baumgartner and E. Iglesia, J. Catal. 130 (1991) 86.
[3] S.T. Oyama, Catal. Today 15 (1992) 179.
[4] L. Leclercq, in: *Surface Properties and Catalysis by Nonmetals*, eds. J.P. Bonelle, B. Delmon and E.G. Derouane (Reidel, Dordrecht, 1993).
[5] G. Djega-Mariadassou, in: *Catalytic Activation and Functionalism of Light Alkane*, eds. E.G. Derouane, J. Haber, F. Lemos, F.R. Ribeiro and M. Guisnet (Kluwer Academic, Amsterdam, 1998).
[6] M. Saito and R.B. Anderson, J. Catal. 63 (1980) 438.
[7] G.S. Ranhotra, G.W. Haddix, A.T. Bell and J.A. Reimer, J. Catal. 108 (1987) 24.
[8] G.S. Ranhotra, A.T. Bell and J.A. Reimer, J. Catal. 108 (1987) 40.
[9] F. Solymosi, A. Erdőhelyi and A. Szöke, Catal. Lett. 32 (1995) 43.
[10] D. Wang, J.H. Lunsford and M.P. Rosynek, Topics Catal. 3 (1996) 299.
[11] F. Solymosi, J. Cserényi, A. Szöke, T. Bánsági and A. Oszkó, J. Catal. 165 (1997) 150.
[12] D. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.
[13] F. Solymosi and R. Németh, Catal. Lett. 62 (1999) 197.
[14] H.P. Bonzel, Surf. Sci. Rep. 8 (1988) 43.
[15] M.P. Kiskinova, Stud. Surf. Sci. Catal. 71 (1992).
[16] H.J. Freund and M.W. Roberts, Surf. Sci. Rep. 25 (1996) 225.
[17] F. Solymosi, J. Mol. Catal. 65 (1991) 137.
[18] T. Schöberl, Surf. Sci. 327 (1995) 285.
[19] F. Solymosi, L. Bugyi, A. Oszkó and I. Horváth, J. Catal. 185 (1999) 160.
[20] C. Guillot, R. Riwan and J. Lecante, Surf. Sci. 59 (1976) 581.
[21] J.G. Chen, Chem. Rev. 96 (1996) 1477.
[22] Z.M. Liu, F. Solymosi and J.M. White, Surf. Sci. 245 (1991) 280.
[23] F. Solymosi and G. Klivényi, Surf. Sci. 315 (1994) 255.
[24] A. Berkó and F. Solymosi, Surf. Sci. 201 (1986) L489.
[25] F. Solymosi and A. Berkó, J. Catal. 101 (1986) 458.
[26] F. Solymosi and L. Bugyi, J. Chem. Soc. Faraday Trans. I 83 (1987) 2015
[27] E.I. Ko and R.J. Madix, Surf. Sci. 109 (1981) 221.
[28] B. Früberger and J.G. Chen, Surf. Sci. 342 (1995) 38.
[29] J. Wang, M. Castonguay, J. Deng and P.H. McBreen, Surf. Sci. 374 (1997) 197.