Reactivity of $Mo_2C/Mo(1\,0\,0)$ toward oxygen: LEIS, AES, and XPS study

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Abstract

Ion scattering spectroscopy (LEIS) was used in conjunction with X-ray photoelectron (XPS) and Auger electron spectroscopies (AES) for the study of the structure and the reactivity of surface Mo_2C prepared on $Mo(1\,0\,0)$. At 1265 K the carbide phase transformed into an oxide layer in the presence of O_2. The oxidation starts in the outermost layer but at higher oxygen exposition subsurface O is also formed. LEIS results suggest the existence of different adsorption centers for O in the topmost layer. Carbon could be completely removed both from the first layer and from deeper regions as was shown by LEIS and AES. The carbidisation of the oxide phase with high temperature decomposition of ethylene was also investigated. After several carbidisation cycles approximately clean Mo layer could be achieved as an intermediate state. At higher ethylene exposures carbide accumulates simultaneously in the different layers of the surface region.
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1. Introduction

Metal carbides are formed when carbon atoms, produced by decomposition of hydrocarbons or other C-containing molecules, are incorporated into the metal interstitial sites. Because of their refractory and conducting nature, the main practical application of metal carbides is in material science [1,2]. In addition, these materials exhibit unique catalytic properties. Among these carbides, Mo_2C deposited on ZSM-5 turned out to be the active component in the aromatisation reaction of methane [3–6] and several other hydrocarbons [7–

9]. The knowledge of surface composition and structure is fundamental in the evaluation of the mechanism of surface reactions. In the present paper we examine the structure and reactivity of Mo_2C layer prepared over $Mo(1\,0\,0)$ by the high temperature decomposition of ethylene. Since low-energy ion scattering is extremely surface sensitive, a LEIS combined with other surface science tools, could give useful informations about the surface events in the topmost layer.

2. Experimental

The experiments were performed in a UHV system (base pressure 5×10^{-10} mbar), equipped

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with facilities for LEIS, AES and XPS. LEIS spectra were obtained using the same hemispherical energy analyzer as for XPS and AES but with the signs of the voltage biases inverted in order to detect He ions. AES was performed with 2.5 keV electron energy and 5 V modulation. An Al K$_\alpha$ X-ray anode was used for XPS with 100 eV pass energy.

Primary energy in LEIS measurements was 800 eV. The mean scattering angle was 95° with an incident angle of 50° with respect to surface normal. Due to the ±15° acceptance angle of the analyser direct recoil peaks were also present in the spectra at low kinetic energies. Areas of peaks due to He ions scattered in single collisions were used to calculate C/Mo and O/Mo LEIS peak ratios, while in the case of AES, peak to peak heights of Mo MNN (221 eV), C KLL (271 eV) and O KLL (503 eV) were monitored. Areas of the C1s peak and of the Mo3d doublet were used to calculate C/Mo from XP spectra.

The Mo(1 0 0) was cleaned by heating in oxygen. This was followed by argon-ion bombardment and annealing at 1400 K. Mo$_2$C over Mo(1 0 0) surface was prepared by the method of Schöberl [10]. Cycles of C$_2$H$_4$ exposions (∼40 L) at 900 K followed by flashes to 1265 K were repeated until the C content of the surface region reached a maximum monitored by XPS, AES and LEIS. The C/Mo AES peak ratio was 0.67 at maximum. Several monolayers of C are accumulated in the surface region in this way [10]. Both the position of the C1s XPS peak (283.2 eV) and the characteristic three-lobe structure of the KLL C AES peak proved the formation of carbidic C. Carbon atoms of the outermost layer probably reside in four-fold hollow sites [11–13].

3. Results and discussion

3.1. Oxidation of the carburised Mo(1 0 0) surface

The carbide layer was oxidised in the following manner: first the surface was saturated with O$_2$ at 300 K then it was annealed to 1265 K in the presence of oxygen (2×10^{-8} mbar). After a few of such cycles the sample was flashed to 1265 K in

vacuum and LEIS as well as AES spectra were recorded during cooling down of the crystal. This approach decreased the gas uptake from the background. Normalised LEIS and AES peak ratios as a function of the number of oxidation cycles are shown in Fig. 1. A decrease in LEIS C/Mo ratio set in after a few cycles due to C loss in the outermost layer caused by its combination with O and desorption as CO. At the same time an increase in O/Mo ratio is observed indicating the accumulation of O on the surface. Similar changes in the C/Mo and O/Mo ratios are also observed in the AES spectra, but they appeared at a later phase (after 30 oxidation cycles). This suggests that C consumption and O accumulation initially take place in the topmost layer. (Note that the AES O/Mo ratio of the fully carburised sample is not zero, because AES spectra are recorded after LEIS spectra and this time delay allows adsorption of CO from background.) Migration of C from the second or deeper layers to the empty sites of the first layer probably also occurs causing its reaction with O. Subsequent oxidation results in an abrupt decrease of AES C/Mo in conjunction with O/Mo increase. The slopes of AES C/Mo and O/Mo curves are larger than those of the corresponding LEIS curves between 50 and 70 cycles which shows that the oxidation of the second and probably deeper layers sets in. This feature suggests that a
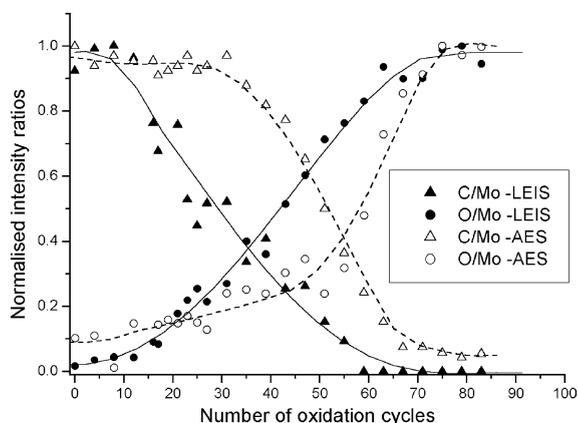

Fig. 1. Normalised C/Mo and O/Mo intensity ratios measured by different methods as a function of the number of oxidation cycles (see text).

subsurface oxygen is probably formed as indicated by the difference between the LEIS and AES O/Mo curves and also because O can be removed only by thorough carburisation with C_2H_4 (see below).

Flashing the sample to 1265 K in vacuum several times reduced AES O/Mo ratio and increased C/Mo, in accordance with the assumption of C migration to the surface. Almost all the carbon could be removed by ∼80 oxidation cycles.

The oxidation method described here can be used to prepare and control oxygen-modified carbide surfaces with oxygen only in the topmost layer or with subsurface O, too, which allows the study of the effect of oxygen in the catalytic reactions of Mo_2C. Lower temperature (e.g. 300 K) O_2 adsorption is not always the right choice to study the effect of O in the first layer, as it can result in inert surfaces, as in the case of oxygen modified C/W(1 1 1) due to different population of surface sites by C and O [14].

The Mo LEIS signal decreased by ∼8% during transformation from carbide to oxide, which suggests a slightly higher occupation of surface Mo sites in the oxidised state. The O LEIS signal of the fully oxidised sample was 33% higher than after room temperature saturation of the carbide with O_2. The maximal O/Mo AES ratio was 0.53 which is 25% higher than after saturation of the carburised surface with O_2 at 300 K.

3.2. Carburisation of the oxidised Mo(1 0 0) surface

The fully oxidised Mo_2C layer on the Mo(1 0 0) surface can be converted into the carbide phase with cycles of C_2H_4 adsorption at 900 K and with flashes to 1265 K in vacuum. The transformation was monitored by LEIS and AES and partly by XPS. Spectra were collected in the order LEIS, AES and XPS.

Areas of Mo, C and O peaks of LEIS spectra as a function of C_2H_4 exposition are displayed in Fig. 2. Spectra were recorded after flashes to 1265 K. The oxygen coverage decreases steeply at small expositions in conjunction with a dramatic increase in Mo peak area. The oxygen signal is reduced to 30% of its initial value at 100 L of C_2H_4 exposition. At the same time the Mo peak area is doubled and still no carbon appeared in the out-
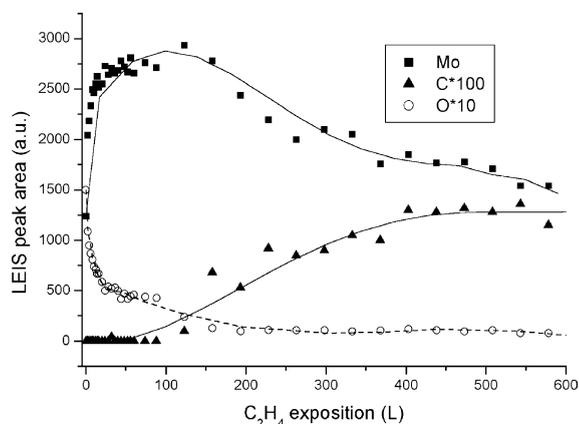

Fig. 2. LEIS peak areas obtained after 1265 K flashes as a function of C_2H_4 exposition (at 900 K). All spectra were recorded during cooling down of the sample.

ermost layer. This means that a relatively clean Mo surface can be achieved as an intermediate state of the conversion of oxide to carbide. Such a metal-like state was not observed in the oxidation process.

The low kinetic energy range of the LEIS spectra of the fully oxidised sample and those recorded after small ethylene exposures are displayed in Fig. 3. The peak at 466 eV belongs to He ions scattered on O atoms, while the smaller peak at 42 eV belongs to atoms sputtered off the surface and ionised by He ions. No peak was observed in that energy region of the spectrum of the fully carburised sample which suggests that neither C atoms nor Mo atoms contribute to its intensity. It is assigned to O atoms ionised and recoiled from the surface in single scattering events. Just after the first C_2H_4 dose (2 L), a dramatic decrease in its intensity was found while the intensity of the O peak at 466 eV decreased only by 30%. To explain this phenomenon we assume that O atoms bonded to different metal sites with divergent stability exist on the fully oxidised surface, and the first C_2H_4 dose removes mainly the less stable O atoms (which have greater recoil probability). These adsorption centers are probably more exposed to the ion beam (possibly two-fold hollow sites or on top sites), which could be another reason of a larger recoil probability. Further studies are nee-
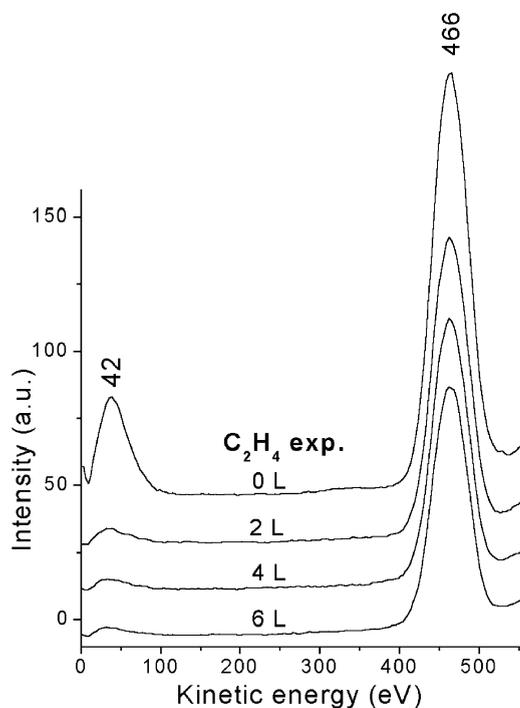
Fig. 3. LEIS spectra of the fully oxidised surface and after increasing C_2H_4 exposures at 900 K. All spectra were recorded after 1265 K annealing, during cooling down of the sample.
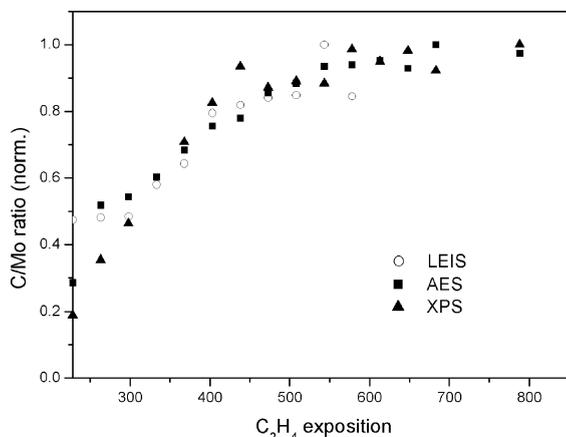

Fig. 4. Normalised C/Mo peak ratios obtained after 1265 K flashes, during cooling down of the sample, as a function of C_2H_4 exposition.

ded, however, to determine the exact bonding geometry of the different oxygen species on the surface. The existence of different O adsorption centers (two-fold, quasi three-fold and on top) was verified on Mo(1 1 0) by HREELS [15].

Applying ethylene exposures larger than 100 L, the appearance of the C LEIS peak and the decrease of the Mo peak were observed. The C peak reached a saturation value at 500–600 L when only trace amount of O remained on the outermost layer. To gain insight into the accumulation of carbon in the different layers of the surface region normalised C/Mo peak ratios obtained by LEIS, AES and XPS are displayed in Fig. 4. Apparently the three curves are very similar indicating that C accumulates simultaneously in the surface region under our circumstances.

C/Mo AES peak ratios recorded just after C_2H_4 expositions were regularly higher by 50% than after 1265 K flashes. The difference in C/Mo XPS ratios was ~25%. Both the shape of C1s XPS peak

and the structure of KLL C AES peak indicated the presence of some graphitic C. LEIS is not applicable in this case to monitor the difference in the amount of surface C before and after 1265 K flashes, because its sensitivity toward graphitic C is less by two orders of magnitude than toward carbidic C. The reason is quasi-resonant neutralisation taking place when He ions are scattered on graphite [16].

4. Conclusions

1. The carbide phase can be transformed into an oxide layer by O_2. The oxidation starts in the outermost layer, but further oxidation leads to the formation of subsurface O. Carbon could be completely removed both from the first layer and from deeper regions as was shown by LEIS and AES. LEIS suggests the existence of different oxygen adsorption sites on the topmost layer.
2. During the transformation of the oxide phase into carbide with high temperature decomposition of ethylene, the production of a rather clean Mo layer could be achieved as an intermediate state. At higher ethylene exposures carbide accumulates simultaneously in the different layers of the surface region.

Acknowledgements

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