Oxidation and adsorption properties of Mo_2C/Mo(100) studied by photon, electron and ion spectroscopic methods

Ph.D. Thesis

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2007

Preceding works and aims of this study

Efficiency and selectivity of catalysts always plays an important role in the research. Industry has a stronger claim toward the technology with which products could be produce cleaner, in greater extent and with environmentally friendly way. Today's World is out to decrease and optimize the power-handling capability input and to develop new or alternative fuels. Especially those countries pay great attention to this kind of investigations where the sources for hydrocarbon fuels are uncertain or diminished. It seems to be obvious that instead of the use of hydrocarbons, the alternative resources for example wind, sun, water and geothermal energy are more effective and suitable. These are adopted in many cases like prominent solution in local purposes. Another way is to develop new resources like hydrogen or fuel cell in the case of cars furthermore solar cells which could be financed in a big volume up to now only in the space-research. Beyond that there are a lot of requirements which show the way to the science (or chemistry) how could we expand the catalysts and the processes for the new, environmentally friendly and effective energy resources. Inside the chemistry there has been recently made a great progress in the study of this research area. Surface science technics are able to facilitate this effort thereby that scientists can map the elementary reactions on the catalysts.

Our group has carried out a series of extensive catalytic studies concerning the conversion of several alkanes into aromatics. It was found that CH_4 and other hydrocarbons can be transformed into aromatics with high selectivity on zeolite-supported Mo_2C catalysts. However the carbide phase produced on Mo single crystal has similar catalytic behaviour to those of platinum metals, so they may substitute for expensive noble metals in some cases in the industry. These results inspired us to investigate the structural and oxidation properties of Mo_2C in the well characterized carbidized Mo(100) system. After that we wanted to analyze the adsorption properties of two molecules, which play dominant role in the above mentioned aims, on the Mo_2C/Mo(100) surface.

The aim of the present work was the characterization of the carburized Mo(100) surface with regards to the stochiometry and the C concentration profile and also to get a more detailed picture of its interaction with oxygen at both low and high temperatures. Special attention was paid to the migration of C and O perpendicular to the surface. The

different surface sensitivity of LEIS, AES, and angle-resolved X-ray photoelectron spectroscopy (ARXPS) allowed us to obtain a certain depth profile of the sample. Detailed XPS measurements helped us determine changes in the oxidation states of Mo and C.

After that we decided to monitoring the reaction of the widely used alcohol (ethanol) on the elaborate characterized Mo_2C/Mo(100) surface. The motivation of this work couldn't be a question because the research, to change the fossil fuels and to work out more environmentally friendly methods, are play domminant role in the leader labs of the world.

Furthermore we wanted to analyze the catalytic activity of the Mo_2C/Mo(100) surface towards alkyl groups. Since in our group studied previously the behaviour of propyl group on this surface in this work we report the influence of potassium additive on the reaction pathway of propyl, C_3H_7, species.

Although our work is clearly basic research, the knowledge and qualitative characterisation of the elementary steps of the reactions on the catalyst surfaces could be normative to planning and design the catalytic processes so it is the first step toward the consummation of the social and environmental requirements.

Experimental methods

The experiments were performed in three separate stainless steel ultra high vacuum (UHV) chambers with a routine base pressure of $5x10^{-10}$ mbar produced by turbomolecular and rotational pumps. The adsorbed gases could be dosed through a capillar from the pre-vacuum chamber. The diameter of the Mo(100) crystal used in this work was 10 mm which we could analyze in the temperature range between 90-1500 K. The temperature of the substrate followed with cromel-alumel thermocouple. The sample (with the sample holder) could be rotated and tilted for angle resolved measurements.

The Mo(100) surface was carburized by repeating C_2H_4 adsorption (50 L) at 900 K and annealing in a vacuum to 1265 K, similar to the method of Schöberl, until the carbon content reached saturation, monitored by LEIS, AES, and XPS. The characteristic three-lobe structure of the C KLL AES peak indicates the formation of carbidic (rather than graphitic or amorphous) carbon.

The chamber, in which we investigated the oxidation and carbidization reactions of Mo(100) crystal, was equipped with facilities for low energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES) and Mass spectroscopy (MS) methods. The adsorption reaction on the Mo_2C/Mo(100) surface were followed in another well-equipped UHV chamber with high resolution electron energy loss spectroscopy (HREELS, LK3000) furthermore the temperature programmed desorption (TPD) measurements performed with Balzers QMS200 mass spectrometer. The adsorption of alkyl halogenids were investigated by Kratos XSAM 800 apparatus.

New scientific results

1. We investigated the structure and the reactivity of the Mo_2C layer produced on a Mo(100) surface, including the reactivity towards oxygen at different temperatures (300-1000 K).
    1.1. Detailed crystallographic studies on carbide overlayers absent as well as the knowledge of the C concentration profile are lacking at present in the literature of Mo_2C. Our results showed that a Mo_2C overlayer with a homogeneous C distribution down to the information depth of XPS, estimated to be 5.7 nm, was produced on Mo(100) by repeated C_2H_4 adsorption at 900 K and annealing in vacuum to 1265 K.
    1.2. The well established phase can be transformed into an oxide layer by O_2, which adsorbs dissociatively on the carbide layer at room temperature. One part of the chemisorbed oxygen is bound to both the C and Mo sites, as indicated by LEIS. Another fraction of oxygen atoms probably resides in the hollow sites not occupied by C.
    1.3. It was shown that the oxidation starts in the outermost layer where, as a result of the reaction between the oxygen and surface carbon, CO formation was observed from T_{ads}=500 K. The removal of surface C resulted in an increase in the saturation O coverage, but all adsorbed oxygen atoms are located on the topmost layer up to T_{ads} =600 K and even at 800 K at small O_2 exposures. At higher exposures at 800 K, the migration of O to subsurface sites sets in, forming this way a kind of oxycarbide, characterized by oxidized Mo states.
    1.4. Carbon could be completely removed both from the first layer and from the deeper regions as was shown by LEIS and AES. The removal of carbon atoms from subsurface sites by oxygen starts at T_{ads}=900 K. A strong gradient in the C concentration was observed at this temperature, which is attenuated at 1000 K, probably due to the larger diffusion rate of C.

2. The reaction pathways of the dissociation of ethanol were investigated on the well-characterized Mo_2C catalyst under our circumtances.
    2.1. Ethanol readily adsorbs on clean Mo_2C/Mo(100) surface, with high sticking probability, which is almost constant up to monolayer coverage and adsorbs dissociatively on Mo_2C/Mo(100) even at 100 K to yield adsorbed hydrogen and ethoxy.
    2.2. A number of desorbing products are observed in the TPD spectra that are produced in the surface reactions like ethane, acetaldehyde, carbon-monoxide, methane and hydrogen. The major part of the remaining ethoxy underwent complete dissociation to surface carbon and hydrogen. The spectral feature at 1153–1173 cm^{-1} is the only one, which is characteristic merely of C_2H_5 species and we believe that the appearance of this loss feature is indicative of the formation of C_2H_5 species, and for the occurrence of the ethanolic C-O bond rupture.

3. We followed also the influence of potassium (as a surface additive) on the catalytical properties of Mo_2C/Mo(100) surface towards alkyl groups.
    3.1. We observed that the weakly adsorbed C_3H_7I on Mo_2C/Mo(100) surface was slightly strengthened by the presence of potassium, which manifested itself in a new molecular desorption state with T_p = 188 K.
    3.2. Depending on the coverage, preadsorbed potassium induced the cleavage of C–I bond even at 100 K to produce C_3H_7 and I. The extent of the dissociation of coadsorbed layers can be enhanced by UV light irradiation at 100 K.
    3.3. Propyl groups stabilized by potassium yielded propene and propane. The desorptions of both compounds are reaction limited processes. The coupling reaction of propyl groups resulting in the formation of hexene and hexane was also promoted by potassium.
    3.4. The adsorbed potassium and iodine arising from the dissociation of C_3H_7I desorbed with the same desorption peak (T_p = 648–688 K), verifying their mutual stabilization through the formation of a surface KI ionic compound. The formation of KI was also supported by the appearance of a loss feature at ~375 és 650 cm^{-1} in the HREEL spectra attributed to a phonon mode of KI (Fuchs-Kliewer modes). These modes were also

detected for coadsorbed layer irradiated at 100 K, which requires the surface diffusion of K, I and C_3H_7 groups.

List of publications

Publications to the Ph. D. thesis: *Impact Factors:*

1. L. Óvári, J. Kiss, **A. P. Farkas**, F. Solymosi :
   Reactivity of Mo_2C/Mo(100) toward oxygen: LEIS, AES, and XPS study
   Surf. Sci. **566-568** (2004) 1082-1086
   IF: **2,168**
2. L. Óvári, J. Kiss, **A. P. Farkas**, F. Solymosi:
   Surface and subsurface oxidation of Mo_2C/Mo(100): Low-energy ion-scattering, auger electron, angle-resolved X-ray photoelectron, and massspectroscopy studies
   J. Phys. Chem. B **109** (2005) 4638-4645
   IF: **4,033**
3. **A.P. Farkas**, Á. Koós, L. Bugyi and F. Solymosi
   Effects of potassium on the reaction pathway of C_3H_7 species over Mo_2C/Mo (100)
   Surf. Sci. **600** (2006) 2355-2363
   IF: **1,78**
4. **A.P. Farkas** and F. Solymosi
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   Surf. Sci. **601** (2007) 193-200
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5. **A. P. Farkas**, L. Bugyi, Á. Koós, F. Solymosi
   Effects of potassium on the reaction pathways of CH_2 fragment over Mo_2C/Mo(100)
   Surf. Sci. Accepted for publication.
   IF: **1,78**

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6. L. Óvári, J. Kiss, **A.P. Farkas**, F. Solymosi
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   IF: ***2,378***

   Full impact factors: **15,203**

Performances

1. L. Óvári, J. Kiss, **A.P. Farkas**, F. Solymosi
   Reactivity of Mo_2C/Mo(100) toward oxygen: LEIS, AES, and XPS study
   22nd European Conference on Surface Science, Prága (Csehország) – 2003. Szeptember 7-12.
2. L. Óvári, J. Kiss, **A. P. Farkas**
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   Kémiai Előadói Napok (KEN), Szeged, 2003. Október 28.
3. L. Óvári, J. Kiss, **A. P. Farkas**, F. Solymosi
   Reactivity of Mo_2C/Mo(100) toward oxygen: LEIS, AES, and XPS study
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4. L. Óvári, J. Kiss, **A. P. Farkas,** and F. Solymosi
   The adsorption of oxygen on a carbidized Mo(100) surface: an XPS, AES, LEIS and MS study
   16th International Vacuum Congress, Velence (Olaszország), 2004.06.28-07.02.
5. L. Óvári, J. Kiss, **A. P. Farkas,** and F. Solymosi
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   10th Joint Vacuum Conference, Portoroz (Szlovénia) 2004.09.28-10.02.
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8. **A. P. Farkas**, L. Deák, Á. Koós és F. Solymosi
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   Előadás és Ph. D. eredmények bemutatása
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