STUDY OF SURFACE REACTIONS WITH X-RAY PHOTOELECTRON SPECTROSCOPY

Doctoral (Ph.D.) theses

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Preliminary and objectives

Technical progression in the last few decades brought about the development of a wealth of surface analytical methods, which gradually became available to researchers involved in surface science. In the beginning most of these techniques were applied to study nearly perfect surfaces under excessively clean conditions. In the possession of the knowledge and experience obtained this way, attention was drawn to problems with more practical aspects. One of the powerful techniques suitable for studying such problems is X-ray photoelectron spectroscopy (XPS).

In many cases the information provided by XPS is not available to other methods. Also, the information obtained may be used to corroborate data acquired by other methods.

The objective of this dissertation is to demonstrate the applicability of XPS in the study of solid surfaces used as catalysts, and also in the characterization of surface active sites. The discussion of measurements carried out on the adsorbed layer on surfaces was intended to display the use of XPS in the study of reactions occurring on these surfaces. These studiess may help us understand the elementary steps of catalytic reactions.

Experimental

Measurements were carried out with a Kratos XSAM 800 X-ray photoelectron spectrometer under ultrahigh vacuum (UHV) conditions. The ultimate pressure attainable by turbomolecular, iongetter and titanium sublimation pums was 2×10^{-10} mbar after the bakeout of the analyzing chamber.

Cooling of the metal single crystal was achieved by cooling with liquid nitrogen the tantalum wires spotwelded to the edge of the crystal. The samples were heated by electric current flowing through tantalum and tungsten wires fixed to the side of and below the crystals.

Catalytic reactions and heat-treatments of wafers pressed from supported and unsupported powder catalysts were performed in the flowing system of the reaction chamber directly attached to the analyzing chamber via a gate valve.

Novel results

1. *Characterization of surfaces used as catalysts*

1.1.　　　　On the spectra of MoO_3 and unsupported alkali metal molybdates the $Mo(3d_{5/2})$ binding energy was found the highest (233.0 eV) in MoO_3. The binding energy continuously decreased from Li_2MoO_4 (232.7 eV) to Rb_2MoO_4 and Cs_2MoO_4 (231.8 eV). The decrease of the binding energies can be explained by the increase of bonding lengths, which in turn is the consequence of the growing alkali metal cation size. There were only minor changes in the $Mo(3d_{5/2})$ binding energies on the spectra of SiO_2 supported MoO_3 and alkali metal molybdates. A possible reason is that the influence of cation on the anion is negligible on the support. The binding energies of the $Mo(3d)$ doublets were nearly the same in K_2MoO_4/SiO_2 catalysts prepared in different ways.

1.2.　　　　On the spectra of WO_3 the $W(4f_{7/2})$ binding energy was nearly 1 eV higher (35.95 eV) than that measured on K_2WO_4 (35.0 eV). The $W(4f_{7/2})$ binding energies measured in K_2WO_4 on various supports as well as on WO_3/SiO_2 (35.7-36.05 eV) were closer to that found in WO_3 than to the value detected in K_2WO_4. From this it follows that the support has only minor effect on the binding energy of electrons in tungsten atoms. Taking as unit the $W(4f)$ peak area on the XP spectrum of the K_2WO_4/SiO_2 catalyst, we determined the number of tungsten atoms in the different samples. The number of W atoms decreased in the $K+WO_3/SiO_2 > K_2WO_4/TiO_2 > WO_3/SiO_2 > K_2WO_4/Al_2O_3 > K_2WO_4/SiO_2 > K_2WO_4/MgO$ order. The $K(2p)/W(4f)$ peak area ratios were also calculated for the potassium containing catalysts. The K/W ratio varied between 1.4-3 with the exception of $K+WO_3/SiO_2$; in this latter case its calculated value was cca. 25. From the $W(4f_{7/2})$ binding energy measured on this catalyst we concluded that doping with potassium does not lead to K_2WO_4 formation.

1.3.　　　　The XP spectra of oxidized (473 K, 30 min) Rh/TiO_2 revealed that a part of surface Rh is in the +3 oxidation state. The rest of the metal atoms is less oxidized. The ratio of the number of atoms in the two states is about 3:1. Following the reductions at increasing temperatures (473, 573 and 673 K, 1 hour) the binding energies of the $Rh(3d_{5/2})$ orbitals and full widths at half maximum (FWHM) of the peak decreased, but they did not reach the values characteristic of metallic Rh even after the reduction at the highest temperature. There are practically no changes in the $Ti(2p)$ binding energies and FWHMs of the TiO_2 support. The decrease of the $Rh(3d)$

peak areas with the increasing reduction temperature is the consequence of the decrease in dispersity.

1.4.   We studied the substitution of Al^{3+} ions for Fe^{3+} ions in Keggin ion salts with XP spectrometry. We demonstrated that in the sample containing only iron, Fe^{3+} ions are present possibly in $FeO(OH)$ form. On the Fe(2p) spectra of the samples containing both iron and aluminium, a new shoulder – originating from Fe^{3+} ions – was detected on the high binding energy side of the photoelectron peak. The intensity of the shoulder increased with increasing iron content. Based on literature data we came to the conclusion that the appearance of the shoulder can be explained by the incorporation of Fe^{3+} ions into the octahedral positions of the Keggin ion salt.

1.5.   We recorded the XP spectra of unsupported and ZSM-5 supported Mo-based catalysts. We established that supported molybdenum-oxide catalysts are reduced during the induction period that precedes the conversion of methane under non-oxidative conditions. Comparing the Mo(3d) and C(1s) spectra to those obtained on Mo_2C-containing catalysts prepared in different ways, we concluded that part of the MoO_3 was transformed into Mo_2C.

2. *Characterization of catalyst surface changes due to adsorption and catalytic reactions*

2.1.   In the interaction of SiO_2 and ZSM-5 supported Mo_2C catalysts with carbon dioxide we established that CO_2 reacts with Mo_2C and as a consequence the latter gets partially oxidized. The complete oxidation into MoO_3 was not achieved even after several hours of interaction at the highest temperature (1073 K) applied. On both supports the share of the Mo^{6+} oxidation state was the greatest in the 973-1073 K temperature range. The reaction rate was higher on the SiO_2 supported catalysts than on the zeolite supported ones. The Mo(3d) peak areas of the XP spectra obtained on the SiO_2 supported samples gradually increased with the increase of reaction time. The reason of this is very likely the increase of Mo dispersity.

2.2.   After the introduction of 12.5 % C_3H_8 + 25 % CO_2/Ar gas mixture onto the Mo_2C/SiO_2 catalyst at 873 K, the Mo(3d) spectra only slightly changed. We explained the slow rate of changes by the fast reaction of propane and Mo-O groups formed in the CO_2+Mo_2C reaction.

3

2.3.   The appearance of the XP peak characteristic of iodine atom ($I_{(a)}$) after the adsorption and heating of hydrocarbon halogenide layers on $Mo_2C/Mo(111)$ or $Mo_2C/Mo(100)$ surfaces was attributed to the dissociation of the molecule.

2.3.1   Methyl iodide adsorbed molecularly on the $Mo_2C/Mo(111)$ surface at 90-100 K; the dissociation of the molecule set on around 140 K. The presence of the molecularly bonded state, characterized by 620.1 eV binding energy, up to 300-350 K may be related to the fact that a fraction of adsorbed CH_3I is bonded strongly to the surface.

2.3.2   Methylene iodide adsorbed molecularly on $Mo_2C/Mo(111)$ independently of the exposure. The dissociation of the molecule began at 190 K, after the desorption of the condensed layer. The dissociation was complete at around 250 K.

2.3.3   Ethyl iodide adsorbed molecularly on the $Mo_2C/Mo(111)$ surface at 90 K. The dissociation of C_2H_5I – characterized by the development of a peak at 618.9 eV – became obvious from 190 K. The 620.0 eV peak due to molecularly adsorbed C_2H_5I, could not be detected above 275 K.

2.3.4   Photoelectron spectra taken after the adsorption of propyl iodide on $Mo_2C/Mo(100)$ surface at 100 K refer to molecular adsorption of the compound. Between 160-260 K the intensity of the peak originating from molecularly adsorbed C_3H_7I decreased. At the same time the peak broadened and its binding energy shifted to lower values. Above 260 K a single peak at 618.6 eV could be detected; this peak is due to $I_{(a)}$ species formed in the dissociation of C_3H_7I.

2.3.5   According to measured binding energies, allyl iodide adsorbs partially dissociatively at low exposures on $Mo_2C/Mo(100)$ surface at 100 K. The shift of the binding energies at higher surface concentrations is due to the formation of a molecularly adsorbed layer.

2.3.6   Independently of the exposure phenyl iodide adsorbed molecularly on $Mo_2C/Mo(100)$ at 100 K. The dissociation temperature of the molecule depended on the coverage. Exposing the surface to 2 L phenyl iodide the XP peak assigned to the dissociation of the molecule appeared at 120 K, while at 4 L exposure it developed only at 150 K.

2.4   Exposing the K + $Mo_2C/Mo(100)$ surface to CO_2 at 100 K led to the increase of the work function at all K coverages. Heating the co-adsorbed layer to 300 K also increased the work function. This increase was attributed to the disproportionation of negatively charged CO_2 and to the species formed in the decomposition of carbonate groups. Adsorbed potassium significantly modified the adsorption and reactivity of

CO_2: it bonded weakly and reversibly on clean $Mo_2C/Mo(100)$ surface. At low potassium coverage ($\Theta_K = 0,1$ ML) we could distinguish two kinds of adsorbed CO_2 states: $CO_{2(a)}^-$ and linearly adsorbed CO_2. At higher coverage ($\Theta_K = 1$ ML) the formation of carbonate species after CO_2 exposure started already at 115 K.

2.5   Methyl and ethyl iodide adsorbed molecularly both on clean and oxygen pre-covered Rh(111) at 100 K regardless of the exposure. Coadsorbed oxygen had only a minor effect on the uptake. The surface oxygen layer significantly enhanced the thermal stability of methyl and ethyl iodide: the dissociation of the molecules took place at temperatures 50-100 K higher than observed on clean Rh(111) surface. We think the reason of this phenomenon is the blocking of surface active sites by oxygen atoms.

Practical aspects

The results obtained are belong primarily to the scope of fundamental research. However, the knowledge of the elementary composition of catalytic surfaces, and that of the changes of these surfaces due to catalytic reactions may help us develop more active and selective catalysts. The exploration of the reactions of molecules adsorbed on metal single crystal surfaces at low temperature, and that of the behaviour of reaction intermediates may contribute to the understanding of how catalysts work.

List of publications

Publications related to the dissertation

1. F. Solymosi, L. Bugyi, **A. Oszkó**: Generation of C_2H_5 Species: Thermal and Photoinduced Dissociation of C_2H_5I on Rh(111)
   Langmuir **12**, (1996) 4145-4152

2. L. Bugyi, **A. Oszkó**, F. Solymosi: Oxidation of Adsorbed CH_3 and C_2H_5 Species on Rh(111) [Effects of coadsorbed species on the chemistry of CH_3I on Rh(111)]
   Journal of Catalysis **159**, (1996) 305-312

3. F. Solymosi, J. Cserényi, A. Szőke, T. Bánsági, **A. Oszkó** : Aromatization of Methane over Supported and Unsupported Mo-Based Catalysts
   Journal of Catalysis **165**, 150-161, (1997)

4. F. Solymosi, L. Bugyi, **A. Oszkó**: Formation and Reactions of CH_3 Species over Mo_2C/Mo(111) Surface
   Catalysis Letters **57** (1999) 103-107

5. **A. Oszkó**, J. Kiss, I. Kiricsi: XPS Investigations on the Feasibility of Isomorphous Substitution of Octahedral Al^{3+} for Fe^{3+} in Keggin Ion Salts
   Phys. Chem. Chem. Phys. **1** (1999) 2565-2568

6. F. Solymosi, L. Bugyi, **A. Oszkó**, I. Horváth: Generation and Reactions of CH_2 and C_2H_5 Species on Mo_2C/Mo(111) Surface
   Journal of Catalysis **185** (1999) 160-169

7. L. Bugyi, **A. Oszkó**, F. Solymosi: Spectroscopic Study on the Formation of CO_2^- on K-promoted Mo_2C/Mo(100) Surface
   Surface Science **461** (2000) 177-190

8.   A. Erdőhelyi, K. Fodor, R. Németh, A. Hancz, **A. Oszkó**: Partial Oxidation of Methane on Silica Supported Different Alkali Metal Molybdates
Journal of Catalysis **199** (2001) 328-337

9.   A. Erdőhelyi, R. Németh, A. Hancz, **A. Oszkó**: Partial Oxidation of Methane on Potassium Promoted WO_3/SiO_2 and on $K_2WO_4/SiO2$
Applied Catalysis A: General **211** (2001) 109-121

10.   F. Solymosi, R.Németh, **A. Oszkó**: The Oxydative Dehydrogenation of Propane with CO_2 over Supported Mo_2C Catalyst
Studies in Surface Science and Catalysis **136** (2001) 339-344

11.   É. Novák, K. Fodor, T. Szailer, **A. Oszkó**, A. Erdőhelyi: CO_2 Hydrogenation on Rh/TiO_2 Previously Reduced at Different Temperatures
Topics in Catalysis **20** (2002) 107-117

12.   F. Solymosi, **A. Oszkó**, T. Bánsági, P. Tolmacsov: Adsorption and Reaction of CO_2 on Mo_2C Catalyst
Journal of Physical Chemistry, in press

Other publications

1. Z. Homonnay, A. Vértes, Á. Cziráki, **A**. **Oszkó**, Gy. Menczel, L. Murgás:
    Mössbauer Study of $Al_6(Fe, Mn)$ Formation in Al-rich Al-Fe-Mn Alloys
    J. Radioanal. Nucl. Chem. Articles **139** (1990) 127-134

2. F. Solymosi, J. Raskó, E. Papp, **A. Oszkó**, T. Bánsági: Catalytic Decomposition and
    Oxidation of CH_3Cl on Cr_2O3-doped SnO_2
    Applied Catalysis A: General **131** (1995) 55-72

3. G. Galbács, J. Sneider, **A. Oszkó**, F. Vanhaecke, L. Moens: X-ray Photoelectron
    Spectroscopic and Atomic Force Microscopic Studies of Pyrolytically Coated
    Graphite and Highly Oriented Pyrolytic Graphite Used for Electrothermal
    Vapourization"
    Journal of Analytical Atomic Spectroscopy **12** (1997) 951-955

4. P. Fejes, J. B. Nagy, J. Halász, **A. Oszkó**: Heat-treatment of Isomorphously
    Substituted ZSM-5 and its Structural Consequences
    An X-ray Diffraction, ^{29}Si MAS-NMR, XPS and FT-IR Spectroscopy Study
    Applied Catalysis A: General **175** (1998) 89-104

5. Fejes Pál, Kiricsi Imre, Kukovecz Ákos, Kovács Kristóf, Lázár Károly, Marsi
    István, **Oszkó Albert** és Bánvölgyi György: Vas beépítése szodalitok szerkezetébe
    és átalakításuk más, vasat tartalmazó zeolitféleségekké
    Magyar Kémiai Folyóirat **107** (2001) 107-115

6. Z. Kónya, J. Kiss, **A. Oszkó**, A. Siska, I. Kiricsi: XPS Characterization of Catalysts
    during Production of Multiwalled Carbon Nanotubes
    Phys.Chem. Chem. Phys. **3** (2001) 155-158

7. P. Fejes, I. Kiricsi, K. Kovács, K. Lázár, I. Marsi, **A. Oszkó**, A. Rockenbauer, Z.
    Schay: Incorporation of Iron in Sodalite Structures and their Transformation into
    Other Iron Containing Zeolites Synthesis of Fe-NaA (LTA)
    Applied Catalysis A: General **223** (2002) 147-160

Presentatations and posters

1. G. Galbács, F. Vanhaecke, J. Sneider and **A. Oszkó**: Study of Topographical and Compositional Changes on Pyrolythic Graphite Sample Holder Surfaces Used in ETV-ICP Spectroscopy
European Winter Conference on Plasma Spectrochemistry , Gent, January 1997

2. F. Solymosi, L. Bugyi, **A. Oszkó**: Methane Conversion into Benzene: Reaction of CH_2, CH_3 and C_2H_5 Species on $Mo_2C/Mo(111)$ Surface
16th Meeting of the North American Catalysis Society, Boston (Massachusetts), USA May 30 - June 4, 1999

3. A. Erdőhelyi, R. Németh, A. Hancz, **A. Oszkó**: Partial Oxidation of Methane on K Promoted WO_3/SiO_2 and on K_2WO_4/SiO_2 Catalysts
12th International Congress on Catalysis
Granada, Spain, July 9-14, 2000

4. **A. Oszkó**, R. Németh, J. Raskó, A. Erdőhelyi: Spectroscopcic Characterization of Alkali Metal Molybdates
XIVth International Symposium on the Reactivity of Solids
Budapest, Hungary, August 27-31, 2000

5. E. Nigro, F. Testa, R. Aiello, P. Lentz, A. Fonseca, **A. Oszkó**, P. Fejes, A. Kukovecz, I. Kiricsi, J. B. Nagy: Synthesis and Characterization of Co-containing Zeolites of MFI Structure
13th International Zeolite Conference
Montpellier, France, 2001

6. F. Solymosi, R. Németh, **A. Oszkó**: The Oxidative Dehydrogenation of Propane with CO_2 over Supported Mo_2C Catalyst
6th Natural Gas Conversion Conference
Girdwood, Alaska, June 2001