Investigation of elemental reactions on rhodium supported by oxide and inverse catalytic systems

Ph.D. thesis

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1 Introduction and aims

Thin oxide films have received considerable attention in recent years, because of their unique and unprecedented properties. In heterogeneous catalysis, the study of two-dimensional reducible oxides is typically carried out on model systems, i.e., ultra-thin films formed on single crystals under high or ultra-high vacuum conditions. The purpose of the research in this field is to identify interesting aspects of simple systems that can be studied by surface science methods and understood through theoretical descriptions.

The research conducted by the MTA-SZTE Research Group on Reaction Kinetics and Surface Chemistry focuses primarily on the possibilities of producing simple and complex nanostructures and characterizing the nanostructures and their interfaces. I did my PhD work in this research group and aimed to improve the properties of platinum metals and other metal catalysts by using atomic thickness layers. Among the platinum metals, I preferred Rh because of its outstanding catalytic activity in reactions that are important for pure energy production. Since it is a rather expensive metal, its substitution with cheaper alternatives such as active oxide layers is of utmost importance. I chose atomic layer thick titanium oxides and molybdenum oxides, which have excellent promoter effect and can easily be prepared under UHV conditions. The catalytic activity of the catalysts was tested by CO adsorption experiments.

Further adsorption experiments were carried out on the surface of reduced TiO_2 (110) supported Rh nanoparticles, which aimed to gain a deeper understanding of the elemental steps of the catalytic hydrogenation of CO. Since the hydrogenation of CO leads to the formation of water, I also studied the interaction of CO and H_2O with TiO_x layer formed on Rh clusters.

2   Experimental

All my experiments were carried out on the same system under ultra-high vacuum (baseline pressure $<5\times10^{-9}$ mbar). The chamber was equipped with an Auger electron spectroscope (AES), a mass spectrometer, a Kelvin probe for measuring work function, an Ar^+ ion gun, and an EGN4 electron beam evaporator. I moved the sample to the correct position with manipulators.

3   New scientific results

3.1   The promotion effect of TiO_x layer on Rh particles and Rh film supported on TiO_2 single crystal.

In UHV condition I proved that the effect of TiO_x surface layer formed on TiO_2 (110) single crystal supported Rh particles was twofold. On the one hand, it prevented the uptake of CO by occupying the adsorption sites. On the other hand, the Rh-TiO_x interface, formed during the encapsulation process, promoted/enhanced the dissociation of CO, and by increasing the surface oxide layer, the amount of desorbed recombinant CO (γ-CO) went through a maximum value. I observed a similar phenomenon in the case of 20 ML thick Rh films, where the exact surface oxide concentration could be determined. In this case, the amount of γ-state at 0.2 ML coverage of Mo reached a maximum value, which is consistent with previous high-pressure studies, showing that the rate of hydrogenation of CO is maximal at low TiO_x coverage.

I successfully utilized the ultra-thin TiO_x layer as a carrier for Rh particles. The CO-TPD measurements on the Rh-TiO_x-Rh structure showed that the 0.4 ML thick Rh overlayer, prepared at 230 K, is highly active, though a slight increase in the deposition temperature of Rh (35 K), triggered a significant structural transformation. The rearrangement is accompanied by the diffusion of the TiO_x layer onto the Rh particles. The process is driven by the formation of a strong Rh-Rh bond and a reduction in surface free energy. Furthermore, adsorption experiments have confirmed that the CO-saturated Rh layer is stable at 230 K up to the molecular CO desorption temperature, indicating that the stability of the sandwich structure is strongly dependent on the presence of adsorbates.

3.2 Effect of Mo and MoOx layers on CO chemisorption properties of Rh particles and Rh films.

The Mo layer (0.15-2.7 ML) prepared by physical vapor deposition on TiO_2 single crystal is oxidized by the support already at room temperature and form a mixed oxide of $Ti_{1-x}Mo_xO_2$ in which the highest oxidation number for Mo is 2. The AES measurements have shown that on this surface the Rh growth occurs in a layer-by-layer manner. The CO-TPD measurements revealed that the MoO_x overlayer on 1 ML thick Rh film generated a new recombinative CO desorption state with Tp=700 K. I proved that the formation of β-CO can only be observed above certain Rh coverage (0.5-0.7 ML Rh) which can be attributed to Rh particle size effect and geometric factors governing the CO adsorption.

I showed that on pure MoO_2 film supported by TiO_2 single crystal the growth mode of Rh is 2D up to 0.7 ML coverage. The recombinant CO-state also appears in this case at Tp=720 K, but for this, higher Rh coverage is required (0.6-1 ML). By increasing the oxidation number of Mo, the mechanism of Rh growth become 3D even at low coverage, and the β-CO state does not appear even at 2 ML Rh coverage. This can be attributed to the fact that a significant part of the metal is encapsulated by MoO_x species at room temperature which is also confirmed by the CO titration series at $\theta_{Rh} = 0.4$ ML coverage.

MoO_xC_y and MoO_x layers formed on the Rh particles' and Rh films surface also promote CO dissociation (Tp = 700 K). In both cases, the amount of β-CO is reached its maximum value at 0.2–0.3 ML Mo coverage, supporting the assumption that the MoO_x–Rh interface plays a crucial role in this process. This interface has already been associated with enhanced reactivity towards CO hydrogenation in high-pressure studies.

3.3 The reaction of H_2, H_2O, and CO on the pure and on the Rh covered, reduced TiO_2 single crystals.

In my further adsorption experiments, I showed that the Rh-TiOx interface has high reactivity towards H_2 and H_2O molecules, which was manifested in their dissociation. By deuterium adsorption experiments, I proved that the desorption state of H_2 at TP = 540-570 K results from the recombination of OH groups originated from the decomposition of water at the metal-oxide interface.

The desorption of recombinant CO (T_P=780 K) was not affected by the co-adsorbed or the pre-adsorbed hydrogen, however, the pre-adsorbed water reduced the decomposition of CO, because of the oxidation of the Rh-TiO$_x$ interface. In addition, the pre-adsorbed and dissociated CO did not prevent the formation of a high-temperature H$_2$ state, resulting from water decomposition. The adsorption experiments have confirmed that the active centers of the reaction between CO and hydrogen are located at the Rh-TiO$_x$ interface. Furthermore, I proved that the hydrogen spillover (i.e. the diffusion of hydrogen atoms from the Rh nanoparticles into the TiO$_2$ single crystal) which is an important process for the storage and detection of hydrogen remains active/persists until the metal surface is completely covered with CO molecules or TiO$_x$ layer. In order to optimize the hydrogen spillover, the presence of these adsorbates must be minimized.

3.4 The dissolution of H into strongly reduced TiO$_2$.

I proved that in the case of very strongly reduced TiO$_2$, the H-atoms from the surface hydroxyl groups, formed by the dissociation of water, dissolve into the oxide, but upon heating, they diffuse again to the surface and desorb in the form of H$_2$O at T_p = 570, 670 and 750 K. The amount of total desorbed H-containing molecules shows a near saturation curve, indicating that the formation of these products is limited by the amount of surface and/or near-surface oxygen defects that react with H$_2$O molecules.

4 Publications related to the present thesis

1.   Promotion and inhibition effects of TiOx species on Rh inverse model catalysts
Bugyi, L.; **Szenti, I.**; Kónya, Z.
Applied Surface Sciience; 2014; 313; 432-439.
IF:2.711

2.   Interaction of Rh with Rh nanoparticles encapsulated by ordered ultrathin TiO_{1+x} film on TiO_2(110) surface
Berkó, A ; Gubó, R ; Óvári, L ; Bugyi, L ; **Szenti, I** ; Kónya, Z
Langmuir; 2013; 29. 15868-15877.
IF: 4.384

3.   Enhanced dispersion and the reactivity of atomically thin Rh layers supported by molybdenum oxide films
Szenti, I ; Bugyi, L ; Kónya, Z
Surface Science; 2015; 641; 60-67.
IF:1.85

4.   The promotion of CO dissociation by molybdenum oxide overlayers on rhodium
Szenti, I; Bugyi, L; Kónya, Z
Surface Science; 2017; 657; 1-9.
IF:1.38

5.   Reaction and Diffusion Paths of Water and Hydrogen on Rh Covered Black Titania
Szenti, I; Bugyi, L; Kónya, Z.
Topics in Catalysis; 2018; 61; 1362-1374.
IF:2.226

5 Presentations and posters related to the present thesis

1)   Promotion and inhibition effects of TiO_x and MoO_x species on the reactivity of atomically thin Rh films
Szenti I., Deák L., Kónya Z.
SIWAN7, Szeged International Workshop on Advances in Nanoscience,
Október 12-15., 2016 Szeged, Hungary

2)   The effect of atomically thin TiO_X layers on Rh model catalysts
Szenti I., Deák L., Kónya Z
1st Innovation in Science 2014 – Doctoral Student Conference
Május 2-3, 2014 Szeged

3) **Strukturális és kémiai változások atomi vastagságú ródium és fémoxid rétegekben adszorbeált gázok jelenlétében**
<u>**Szenti I.**</u>
Munkabizottsági ülés
Május 20. 2013 Budapest

4) **The impact of atomically thin Mo and MoO$_X$ films on the surface reactivity of Rh layers**
<u>**Szenti I.**</u>, Deák L., Kónya Z.
15th Joint Vacuum Conference
Június 15-20, 2014 Bécs, Ausztria

6 Other publications

1. **Fine tuning the surface acidity of titanate nanostructures**
D, Madarász ; <u>**I, Szenti**</u> ; L, Nagy ; A, Sápi ; Á, Kukovecz ; Z, Kónya
Journal of the International Adsorption Society; 2013; 19; 695-700
IF:1.735

2. **Exploiting the ion-exchange ability of titanate nanotubes in a model water softening process**
Madarász D, <u>**Szenti I**</u>, Sápi A, Halász J, Kukovecz Á, Kónya Z
Chemical Physics Letters; 2014;591;161-166
IF:1.95

3 **Localized growth of carbon nanotubes via lithographic fabrication of metallic deposits**
Tu, F ; Drost, M ; <u>**Szenti, I**</u> ; Kiss, J ; Kónya, Z ; Marbach, H.
Beilstein Journal of Nanotechnology; 2017; 8; 2592-2605
IF:2.968

4 **On the Principles of Tweaking Nanostructure Fabrication via Focused Electron Beam Induced Processing Combined with Catalytic Growth Processes**
Drost, M ; Tu, F ; Vollnhals, F ; <u>**Szenti, I**</u> ; Kiss, J ; Marbach, H
Small Methodes; 2017; 1; 17000095-17000105
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5 **Preparation of photocatalytic thin films with composition dependent wetting properties and self-healing ability**
Mérai L, Varga N, Deák Á, Sebők D, <u>**Szenti I**</u>, Kukovecz Á, Kónya Z, Dékány I, Janovák L.
Catalysis Today; 2019;328; 85-90.
IF:4.888 (2018)

6   Aging Impairs Cerebrovascular Reactivity at Preserved Resting Cerebral Arteriolar Tone and Vascular Density in the Laboratory Rat

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Frontiers in aging neuroscience; 2019;11; 301-313.
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7   Optimization of the Production Process and Product Quality of Titanate Nanotube–Drug Composites

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Nanomaterials; 2019; 9; 1406-1416
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8   Synergetic of Pt Nanoparticles and H-ZSM-5 Zeolites for Efficient CO_2 Activation: Role of Interfacial Sites in High Activity

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Frontiers in Materials; 2019; 6; 127-139
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9   Noble-metal-free and Pt nanoparticles-loaded, mesoporous oxides as efficient catalysts for CO_2 hydrogenation and dry reforming with methane

Sápi A, Rajkumar T, Ábel M, Efremova A, Grósz A, Gyuris A, Ábrahámné KB, **Szenti I**, Kiss J, Varga T, Kukovecz Á.
Journal of CO_2 Utilization; 2019; 32; 106-118
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10   Pore Structure as a Response to the Freeze/Thaw Resistance of Mortars

Netinger Grubeša I, Marković B, Vračević M, Tunkiewicz M, **Szenti I**, Kukovecz Á
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ACS applied materials & interfaces. 2019;11; 19331-8.
IF:8.456 (2018)

12   Optimal design of absorptive glass mat (AGM) separator with fastest electrolyte uptake using X-ray micro-computed tomography

Rawal A, Rao PK, Kumar V, Sharma S, Shukla S, Sebők D, **Szenti I**, Kukovecz A.
Journal of Energy Storage. 2019; 21; 505-514.
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13   Probing the three-dimensional porous and tortuous nature of absorptive glass mat (AGM) separators.

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Journal of Energy Storage. 2020; 27; 101003.
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14   Sulfur nanoparticles transform montmorillonite into an inorganic surfactant applicable in thermoplastics processing
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15   Fast optical method for characterizing plasmonic nanoparticle adhesion on functionalized surfaces
Mérai L, Janovák L, Kovács DS, **Szenti I**, Vásárhelyi L, Kukovecz Á, Dékány I, Kónya Z, Sebők D.
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16   Wetting and evaporation on a carbon cloth type gas diffusion layer for passive direct alcohol fuel cells
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