Final report on OTKA project 100793

1. Main tasks of the project

Our aims in this research project were twofold. First, mechanistic studies were performed on selected multi-component metal-oxide model systems in order to develop a molecular level understanding of the catalytic transformations of alcohols. For these studies ethanol steam reforming was chosen as the model reaction, although later the scope was extended towards photocatalytic methanol reforming also. Second, the knowledge in the materials science of multicomponent oxides was used to develop novel $Ti_{(1-x)}M_xO_2$-C (M= W, Mo; x= 0.2-0.4) mixed oxide-carbon composite supports for use as CO-tolerant anode electrocatalysts and oxygen reduction catalysts in polymer electrolyte membrane fuel cells. Because of changes in the research staff as well as in the research environment, the aims later involved also the exploration of the modification of the metallic element (platinum) of the fuel cell electrocatalysts by tin.

2. Main results of the project

2.1 Model studies of ethanol steam reforming

The first task of this research project was the development and detailed study of a model system for molecular level understanding of transformation of ethanol in the steam reforming reaction.

As the first step, comparative ethanol steam reforming tests were performed on $MgAl_2O_4$ supported Ni, Ni-Co and Ni-Co-Ce containing catalysts as well as on ceria supported Ni, Ni-Co and Ni-Fe catalysts.

The very strong positive effect of Co on the performance of the spinel supported catalysts initiated an in-depth investigation, which was originally not planned in this project. During experiments combining ethanol reforming and subsequent temperature programmed oxidation, it turned out that while the monometallic Ni- and especially the bimetallic Ni-Co containing catalysts suffered from extensive coke formation, addition of Ce in the form of a somewhat reduced oxide successfully eliminated this side process. Structural and electron spectroscopic studies indicated considerable exchange of Mg cations to Ni or Co, leading to the formation of spinel support doped with transition metal ions. Co turned out to preferentially occupy the exchangeable Mg sites forcing Ni to locations more accessible for reduction. As a consequence in the bimetallic case considerably larger fraction of Ni could be reduced to metallic state than in the monometallic case. From product analysis and *in situ* infrared spectroscopic measurements acetaldehyde formation, its decomposition to methane and CO, direct steam reforming of acetaldehyde and water-gas shift reaction (WGSR) were identified as key processes for hydrogen generation. Higher rate in direct steam reforming of acetaldehyde as well as in WGSR can be therefore traced to the increased metallic character of Ni, together with charge transfer processes at the interface between the Ni particles and the semiconducting support. The results of these investigations were published in a journal article [1]. Partly based on these results, one of the researchers of the project (G.P. Szíjjártó) has received his PhD degree from the George Olah Doctoral School of Budapest University of Technology and Economics in 2014.

Catalytic tests performed on Ni-containing ceria supported powder samples suggested that modification with Co or Fe results in inferior performance, while the Ni/CeO_2 system performs almost as well as our best $MgAl_2O_4$-supported catalyst. In addition, noticeable hydrogen generation started at lower temperatures than in the $MgAl_2O_4$-supported multicomponent catalyst, so the Ni/CeO_2 system fits well to the requirements of model studies.

The next step was to develop the Ni/CeO_2 model system. Because of the strongly insulating nature of bulk ceria, development of a thin film system featuring an ordered ceria surface was needed for the electron spectroscopic investigations. Possible electronic and chemical disturbance from the underlying catalytically active single crystalline metal support was avoided by depositing the epitaxial $CeO_2(111)$ overlayer on CaF_2-buffered Si(111). Ni nanostructures were prepared by evaporation onto the well-ordered ceria film. Electron spectroscopic data indicate clear reduction of ceria and slight oxidation of Ni, evidencing charge transfer between the metal and the support.

The interaction of the reactants of steam reforming, water and ethanol with these surfaces was characterized by photoelectron spectroscopy. Motivated by our preliminary understanding of the working mechanism of related real catalysts such as $MgAl_2O_4$ supported Ni, Ni-Co and Ni-Co-Ce systems, we decided to include possible intermediates and/or byproducts, acetaldehyde and acetic acid into this investigation.

First results found on the Ni-free ceria surfaces are summarized.

Acetic acid adsorbs dissociatively and forms relatively stable acetate species on ceria surfaces. Annealing experiments suggested gradual desorption without signs of transformation. On the Ni-loaded model catalysts acetate formation followed by further oxidization to carbonate species seems to be a minor reaction channel for transformation of ethanol; the presence of water vapour tends to suppress this route. Thus acetate appears rather as a spectator species and not a key participant of the ethanol steam reforming process.

At room temperature interaction of acetaldehyde with fully oxidized CeO_2 is very weak. Nevertheless, annealing of molecular acetaldehyde adsorbates formed during exposure at cryogenic temperatures leads to reduction of the ceria surface as evidenced by the appearance of Ce 4f signals in the valence band UPS spectra; this reduced ceria surface has some activity in oxidizing the remaining acetaldehyde adsorbates toward carboxylate species at higher temperatures. The weak adsorption and susceptibility for chemical transformation makes acetaldehyde to be a more likely important intermediate compared to acetic acid.

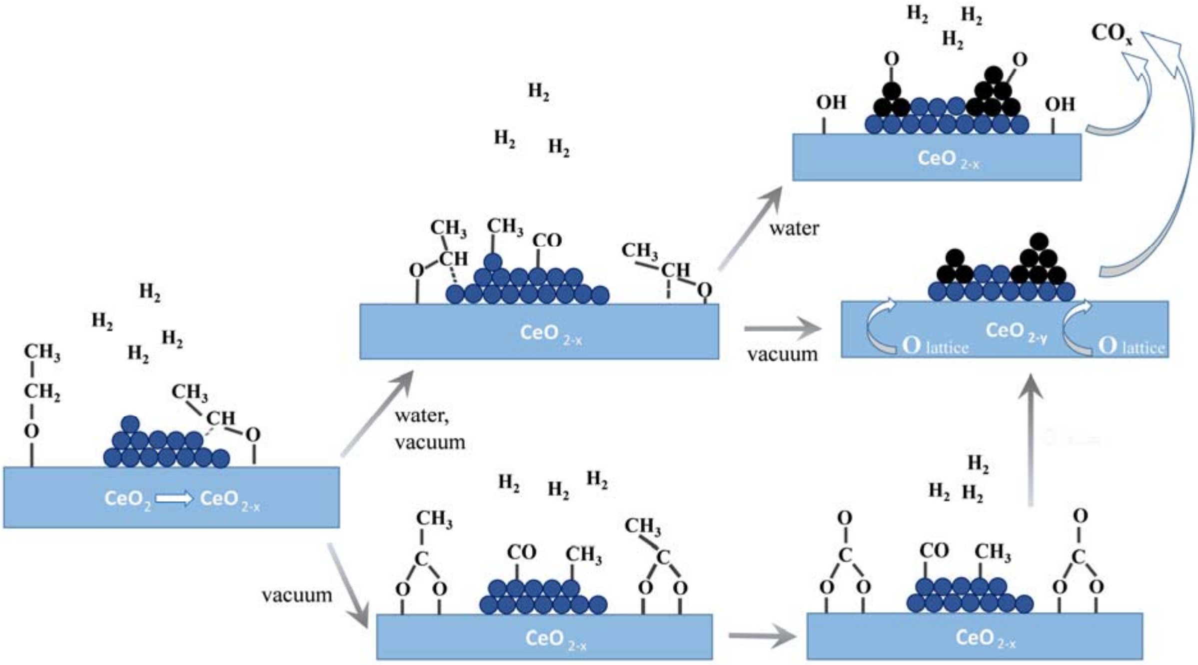
The dissociative adsorption of ethanol in the form of ethoxy groups and the subsequent reduction of the surface are well established facts. Our experiments demonstrated a competitive effect between O_2 and ethanol, indicating the key role of oxygen vacancies in ethanol adsorption; nevertheless, ethanol exposure of a fully oxidized CeO_2 surface at room temperature gradually creates enough adsorption sites for maintaining a strongly bound ethoxy monolayer. Theoretical work in collaboration with the group of prof. Kersti Hermansson at University of Uppsala, Sweden suggest a bond formation between the ethanol O atom and a Ce^{4+} ion and a hydrogen bond like bond between the alcoholic H and a surface O ion. Dissociative adsorption can be understood in terms of strengthening the latter bond and weakening the alcoholic O–H bond. Breaking the H-bond in either case highly destabilizes the adsorption. The calculated energetics predicts the predominance of the dissociated form above 220 K, in good agreement with the experimental data. Although annealing experiments suggested mainly recombinative ethanol desorption at relatively low temperatures, our measurements identified a gradual change in the electronic structure of the most strongly bound ethoxy species towards a more oxidized, acetaldehyde-like state.

At room temperature, water dissociates on both the fully oxidized and the partly reduced surfaces, nevertheless, reduced surfaces can bond more OH groups. Around 180 K the first adsorbed layer is dominated by dissociated water in case of reduced ceria, while molecular water dominates on fully oxidized surfaces. Upon further exposure, molecular multilayer adsorption is observed on both surfaces. The transition between molecular and dissociated water occurs at somewhat higher temperature (260 K) in case of the fully oxidized surface than on the reduced surface (230 K). Upon heating, hydroxyl groups disappear from the fully oxidized surface around 370 K while reduced ceria bonds OH groups even above 400 K. These findings indicate the role of the oxygen vacancies in dissociation of water and stabilization of the hydroxyl groups. Water exposure does not influence the oxidation state of ceria. On the other hand, oxygen exposure of a reduced surface saturated with OH groups results in rapid complete oxidation even at room temperature, accompanied by the desorption of the majority of the OH groups.

In the $Ni/CeO_2(111)$ system freshly deposited Ni is partly metallic and partly ionic (oxidized). Ethanol exposure has an effect on the oxidation state of Ni: annealing of the ethoxy-covered surface up to 420 K results in complete transformation of Ni into the metallic state. Completely oxidized nickel can be obtained by exposing the model surface to oxygen at temperatures above 500 K; large dose ethanol exposure of this system at or above 400-420 K again leads to full reduction of Ni to the metallic state. Ethanol dosing at lower temperatures around 370 K does not change the state of oxidized Ni. In the previous years it was demonstrated that CeO_2 and even TiO_2 becomes somewhat reduced upon alcohol adsorption, thus reduction of metal oxides in the presence of alcohols seems to be a universal process.

The presence of Ni nanoparticles facilitates the formation of acetate-like species from ethoxy adsorbates, which further oxidize into carbonates at higher temperatures; nevertheless, the presence of water vapour suppresses this reaction channel. However, the main reaction channel in either vacuum or in water vapor utilizes the bond breaking capabilities of Ni, leading to the loss of the oxygen functionality, dehydrogenation and condensation of the remaining carbon into graphitic aggregates. An important issue in ethanol reforming is the stability of these graphitic species, as on long term this coke formation can result in significant loss of the catalytic activity. Annealing in vacuum up to 540 K results in little change in the state of the graphitic material. Significant decrease of the carbon level occurs around 570 K, while complete carbon removal requires temperatures as high as 620 K. Carbon removal is accompanied by heavy reduction of the ceria. If the annealing experiment is carried out in oxygen, 520 K is enough for complete carbon removal, during which both the cerium oxide and the nickel becomes completely oxidized. Upon annealing in water vapor, the graphitic carbon signal starts to decrease around 540 K; rapid loss of the graphitic species was found around 620 K. The main difference with respect to the vacuum annealing was that the cerium oxide was reduced to a much smaller extent and was covered by hydroxyl groups; the presence of slightly oxidized carbon species was evident, while no oxidation of the Ni was seen. It means that apart from providing oxidizing agents for carbon removal, water also plays an important role in stabilizing the oxidation state of the catalyst at working temperature. It may be worth to note that in the case of the Ni/CeO_2 powder catalyst hydrogen generation became considerable above 600 K.

These observations compared to those available from studies on powder catalysts allowed to construct a general model for ethanol reforming. Accordingly, the catalytically active sites are complex metal cation-oxygen vacancy ensembles in the vicinity of metallic nanoparticles. These complex defect sites dissociate water and bond ethoxy groups; their interaction, probably with the help of the metallic sites, leads to formation of surface acetals, which may transform into acetaldehyde (the active intermediate, which becomes completely dehydrogenated later) or acetate (which is predominantly a spectator). The main proposed reaction steps are summarized on the following Scheme.



Our expectation was that vibrational spectroscopy analysis carried out by means of sum frequency spectroscopy (SFS) would enhance the understanding of these processes, so we have repeatedly attempted to carry out such measurements. Unfortunately, it turned out that the stability of the CeO_2 thin film sample is not enough to withstand the laser power levels required by the SFS measurement, so we were unable to collect meaningful vibrational data from the samples.

The majority of the results obtained in connection with the modeling of ethanol steam reforming catalysts were presented at international conferences and published in a journal article [2].

Apart from work on the Ni/CeO_2(111) model system, experiments on adsorption and transformation of alcohols on Ni-free or Ni-loaded TiO_2(110) by means of X-ray photoelectron spectroscopy were also carried out for comparison. These results still await for publication.

As far as room temperature adsorption of ethanol is concerned, there are no big differences between the 1×1 reconstructed surface, the somewhat more oxygen deficient 1×n or even the much higher reduced ion bombarded surfaces. In all cases dissociative adsorption can be observed. Ethanol adsorption on oxygen-rich TiO_2 surfaces is always accompanied by their slight reduction. In contrast to what was found for CeO_2 in the previous report, the adsorbed ethoxy layer is quite stable against oxygen exposure. Ethanol was found to desorb in a broad temperature range up to 700 K, without any evidence for its decomposition.

Similarly to the case of ethanol, methanol also adsorbs dissociatively on TiO_2. The adsorbed quantity seems to be independent from the oxygen vacancy concentration of the surface. The thermal behavior of the methoxy adsorbates is very similar to that of ethoxy: desorption in a broad temperature range extending up to 750 K can be observed. Nevertheless, the disappearance of the surface methoxy signals occurs at slightly lower temperature on the oxygen vacancy-rich (ion bombarded) TiO_2 sample.

Ni evaporated on the fully oxidized TiO_2(110) surface forms metallic particles even at low coverages, as indicated by the features of the Ni 2p core level spectra and the appearance of the Fermi edge. Nevertheless, a slight reduction of the oxide surface, along with a shift of the Ni 2p signals towards higher values with respect to bulk Ni suggests electron transfer from Ni towards the oxide. Upon annealing of the Ni-loaded TiO_2 surface, a sudden decrease of the Ni core level intensity, accompanied by reduction of the oxide, is observed around 700 K. Apart from Ni grain growth, the effect can be attributed to encapsulation of the Ni particles by partially reduced Ti-oxide. At 1000 K a thick oxide layer covers the Ni elements; at the same time the surface re-oxidizes due to oxygen diffusion from the bulk.

Although the amount of methoxy adsorbates at room temperature on the Ni-loaded TiO_2(110) surface is not different from what was found on Ni-free surfaces, their chemical behavior is clearly different. Slowly proceeding decomposition of methoxy and formation of hydrocarbon-like or graphitic species is evident even at this low temperature. At elevated temperatures transformation of methoxy into thermally stable carbonaceous species becomes faster, accompanied by only limited desorption. As far as hydrogen generation is concerned, this coke formation is an undesirable side process; nevertheless, our previous results on Ni-based alcohol reforming catalysts indicate that it can be eliminated in a multi-component approach.

2.2 Development of mixed oxide composite electrocatalysts for fuel cells

Another exciting energy related application of multicomponent oxide based catalysts is development of a novel type of electrocatalysts for fuel cells.

Fuel cells convert chemical energy of hydrogen-rich fuels into electricity without emission of greenhouse gases. An important type of fuel cells is the polymer electrolyte membrane fuel cell, which operates at relatively low temperature and utilizes either hydrogen or other fuels containing high amount of hydrogen (e.g. alcohols). An important and expensive part of these cells is the electrocatalyst, which is required both at the anode and cathode. The current anode electrocatalyst of choice, Pt/C with Pt loading as high as 40wt%, suffers from severe drawbacks regarding its stability (resistance to sintering and electrochemical corrosion) and tolerance to CO poisoning, which is important as a small amount of CO is inevitably present in fuels obtained by reforming.

Oxide supports are widely used in heterogeneous catalysis and have inherently higher stability than carbon in acidic and oxidizing environments. Titanium dioxide is non-toxic, possesses high mechanical, chemical and redox stability. Moreover, TiO_2 is also capable to stabilize metals in a highly dispersed state. However, TiO_2 is an n-type semiconductor and therefore for electrochemical applications the increase of electronic conductivity in TiO_2 is necessarily required. In addition, fine grained TiO_2 easily forms aggregates thus preparation of titania materials with large specific surface area is difficult.

Electrochemical studies revealed that transition metal oxides like W-, Mo- or Nb-oxides significantly enhance the CO-tolerance of the Pt/C electrocatalysts via the bifunctional mechanism. On the other hand, severe dissolution of these oxides at high potentials precludes their use in fuel cell applications.

Our idea in this research task was to combine the good stability of TiO_2 with the high conductivity and surface area of active carbon. Incorporation of W or Mo as isovalent dopants into the TiO_2 lattice was identified as a possibility to retain their beneficial co-catalytic properties, improve the conductivity of TiO_2 and mitigate the above mentioned leaching problems at the same time. As this task was the topic of the PhD thesis of one of the participants of the project, it enjoyed sustained interest, which was further increased by the arrival of Dr. Irina Borbáth to the research staff.

First we successfully prepared tungsten-doped rutile TiO_2 support material by utilizing descriptions found in the literature. High level of tungsten incorporation was achieved as demonstrated by both X-ray diffraction and X-ray photoelectron spectroscopy experiments. However, the electrocatalytic performance of the $Pt/Ti_{(1-x)}W_xO_2$ material was inadequate partly because the aggregation of the powder resulting in low specific surface area and partly because its still low conductivity. Thus retaining active carbon for its high surface area and excellent conductivity was judged to be inevitable.

The next step was to synthesize the mixed oxide in the presence of active carbon, which posed several challenges. Under less then ideal conditions significant amounts of non-incorporated tungsten (either metallic or oxidized, e.g. WO_2 or WO_3) remained in the catalysts; the lack of incorporation was often accompanied by formation of anatase TiO_2. Numerous co-precipitation and impregnation type synthesis routes were tested; a microwave-assisted solvothermal synthesis, a sol-gel process and a modified low-temperature sol-gel synthesis were thoroughly investigated. During these experiments it was established that tungsten incorporation requires rutile crystallites grown on the active carbon as starting material. A room temperature synthesis for these rutile crystallites was elaborated.

The genesis of the composite electrocatalyst was explored by *in situ* electron spectroscopic measurements. The precursory state of the catalyst (achieved by tungsten loading on the rutile nuclei on activated carbon) is characterized by the presence of hydrogen tungsten bronzes. An extended annealing in inert atmosphere results in growth and structural perfection of the rutile crystallites (as seen from *ex situ* XRD data), accompanied by reduction of tungsten and appearance of high amounts of W^{4+} species. A subsequent short reductive treatment ensures the incorporation of the W^{4+} species into the rutile lattice. Nevertheless, the annealing and reduction cycle has to be conducted with great care, as there is a clear tendency for over-reduction of W until the metallic state. Metallic tungsten species form nanoparticles, which, although becoming partially oxidized upon air exposure, are unstable under the electrocatalytic conditions.

Active carbon indeed successfully hindered the aggregation of the rutile particles into large chunks. The upper limit of reliable tungsten incorporation was found around a W/Ti ratio of 0.4 corresponding to $Ti_{0.7}W_{0.3}O_2$.

Loading of the 50 wt% $Ti_{(1-x)}W_xO_2$ – 50 wt% C composite material with Pt was achieved by the $NaBH_4$-assisted ethylene-glycol reduction method. The uniform distribution of highly dispersed Pt particles (2.3 ± 0.8 nm) in 40 wt% $Pt/50Ti_{0.7}W_{0.3}O_2$-50C anode electrocatalysts was verified via the TEM technique.

All composite supported electrocatalysts showed enhanced CO tolerance which was indicated by the appearance of a CO-oxidation related “pre-peak” between 150 and 540 mV and by a shift of the maximum of the main CO oxidation peak towards negative direction, from 820 mV to about 710 mV on the CO_{ads} stripping voltammogram. The electrocatalytic properties correlated well with the degree of tungsten incorporation. The mixed oxide exhibited a pronounced stabilizing effect against loss of electrochemically active Pt during aging tests. Comparison with a commercial CO-tolerant PtRu/C benchmark catalyst demonstrated the superior performance of the composite supported catalysts. These results were published at numerous national and international meetings and also in several journal articles [3, 4, 5].

Finally, a polymer electrolyte membrane fuel cell was assembled using the Ti-W mixed oxide catalyst at its anode. The cell was tested in a fuel cell test device; the performance in pure H_2 was equivalent to cells using commercial Pt/C reference catalysts, while in H_2 containing 100 ppm CO much superior results were obtained than in the case of the reference catalyst. This result is submitted for publication [6]. Based mostly on the results of this research task, one of the participants of the project (Dorottya Gubán) obtained her PhD degree from the George Olah Doctoral School of Budapest University of Technology and Economics in 2016.

A further step in the development of the mixed oxide composite electrocatalysts is to test other transition metals as doping elements. Thus the synthesis route was modified for Mo incorporation. By combined X-ray diffraction and photoelectron spectroscopy measurements it was revealed that the temperature of the inert gas annealing can be lowered with respect to that used for the W-doped system. Nevertheless, it was pointed out that by increasing the Mo content of the catalysts, the ratio of non-incorporated Mo outside of the rutile lattice also increases.

Enhanced initial CO tolerance of the Pt electrocatalysts prepared by using the $Ti_{(1-x)}Mo_xO_2$ – C composite support materials (x= 0.2-0.4, mixed oxide-carbon weight ratio: 50:50 and 75:25) were evidenced by the appearance of a CO-oxidation related “pre-peak” and by considerable shift of the maximum of the main CO oxidation peak towards less positive potential compared to the reference commercial Pt/C. The onset potential of H_2 oxidation also shifted to lower potential in comparison with the reference catalyst. According to the results of electrochemical measurements there is a good correlation between the Mo content of the samples and the extent of CO tolerance.

However, the difference in the electrochemical behavior of the samples with different Ti/Mo ratio gradually disappeared as a result of the accelerated aging process. The initially large amount of non-incorporated Mo being present in those samples with higher Mo content dissolved during the accelerated aging, so the extent and nature of the Pt-Mo interaction changed. From these results it can be concluded that although the high initial Mo concentration results in significant Pt-Mo interaction, the non-incorporated Mo is not stable and in long term use only the incorporated content is available and relevant.

These observations are described in a submitted paper [7] with generally supportive reviewer opinion.

The initial instability observed in the case of the Pt/ $Ti_{(1-x)}Mo_xO_2$ – C system is often overlooked during typical electrochemical experiments, as it occurs during the electrode conditioning (cleaning) stage, prior to data collection. Nevertheless, even in spite of this feature, we obtained better performance with the Pt/$Ti_{0.7}M_{0.3}O_2$-C electrocatalysts in a single cell test device using hydrogen containing 100 ppm CO compared to the reference Pt/C and PtRu/C catalysts [6].

The aim of introducing CO tolerance to the Pt/C electrocatalyst through the incorporation of oxophilic dopants can be achieved by a conceptually different approach also. A powerful method for anchoring a second metal exclusively to platinum in supported Pt catalysts is the utilization of Controlled Surface Reactions (essentially an atomic layer deposition technique combined with appropriate annealing treatments). In this project different Pt/C parent catalysts were modified by tin; this activity also formed the part of the PhD thesis work of Dorottya Gubán.

First commercial 40wt% Pt/C (40Pt/C, Quintech) catalysts were modified by tin by Controlled Surface Reactions during preparation of alloy-type Sn-40Pt/C electrocatalysts with Pt/Sn= 1.8-3.0 ratios and exclusive Sn-Pt interaction. As demonstrated by X-ray diffraction the incorporation of Sn onto Pt/C was achieved satisfactorily yielding a near-stoichiometric fcc Pt_3Sn alloy phase along with a certain amount of the $Pt_{(1-x)}Sn_x$ solid solution. The content and dispersion of the fcc Pt_3Sn phase within the electrocatalysts was controlled by tuning the reaction conditions of CSRs. No evidence of the presence of SnO_2 phases in the Sn-modified Pt/C samples was found.

The Sn-40Pt/C electrocatalysts were tested in both CO and methanol electrooxidation reactions. The superior CO oxidation ability was attributed to the facile formation of $Sn\text{-}OH_{ad}$, occurring at less positive potentials than Pt alone. The performance of the intermetallic Sn-40Pt/C catalysts in the CO and methanol electrooxidation reactions depended on the actual composition of the exposed surface; the results confirmed the importance of the Pt_3Sn phase in good electrocatalytic performance. The results of this work were published as a journal paper [8]. These results were also used in the PhD theses of Irina Borbáth, who received her PhD degree from the George Olah Doctoral School of Budapest University of Technology and Economics in 2013.

As the next step the platinum content of the catalysts was reduced to 20 wt%; the result of modification of commercial 20Pt/C (Quintech) and home-made parent catalysts was compared. According to *in situ* XPS and *in situ* XRD studies the exclusive incorporation of Sn onto the Pt sites was achieved resulting in exclusive formation of Pt-Sn alloy phase. No evidence of the presence of separated SnO_2 phase was found. However, it was established that after contact of the Sn-Pt/C catalysts with air Sn tends to segregate to the surface, where it oxidizes to a certain extent. Reversible interconversion of $PtSn \leftrightarrow Sn^{4+} + Pt$ in the presence of O_2 and H_2 was convincingly demonstrated by *in situ* XPS and *in situ* XRD studies. The electrocatalytic performance of these novel Sn-20Pt/C electrocatalysts was tested in CO oxidation and oxygen reduction reaction. Although initially the majority of Pt sites were blocked by segregated SnO_x, an electrode conditioning consisting of a few polarization cycles removed these species and only minor changes of the catalysts surface composition were observed after 20 cycles. Better performance in the CO electrooxidation for our Sn-20Pt/C catalysts compared to the state-of-art CO tolerant PtRu/C benchmark catalyst was demonstrated. Optimal surface composition of the home-made Sn-20Pt/C catalysts resulted also in increased activity in the oxygen reduction reaction compared to the Sn-20Pt/C prepared from the commercial parent catalyst; both tin modified catalysts performed better than the corresponding parent 20Pt/C catalysts. These results were presented at several national and international meetings and were published as a journal article [9].

Finally home-made 20 wt% Pt/C catalysts with significantly different morphology were prepared by varying the parameters of the Pt deposition by modified $NaBH_4$-assisted ethylene-glycol reduction method using ethanol as a solvent. Reaction conditions were established for the preparation of highly dispersed 20Pt/C catalysts. According to *in situ* XPS and *in situ* XRD studies upon using highly dispersed 20Pt/C catalyst the exclusive incorporation of Sn onto the Pt sites was achieved resulting in exclusive formation of Pt-Sn alloy phase. In contrast, the reductive treatment of the catalyst with lower Pt dispersion did not result in complete reduction of the tin content: while the major form of tin was attributed to the metallic Sn associated with Pt, 10 % of tin was still present in a form of Sn^{4+} surface species. The electrocatalytic performance of the novel catalysts was tested in the CO oxidation and the oxygen reduction reaction. Increased CO tolerance for all Sn-modified Pt/C catalysts compared to the parent 20Pt/C catalysts was demonstrated. The electrocatalytic performance of Sn-20Pt/C in the oxygen reduction is superior to that of the parent 20Pt/C catalysts, although the presence of separate, non-reducible SnO_x is not required for excellent activity. The results are under publication in the form of a journal article [10].

2.3 Photocatalytic reforming of methanol

A plausible extension of the scope of the project is to combine the knowledge gained on alcohol reforming or modification of Pt by Sn with our experience with TiO_2 based materials in order to develop novel catalysts for photocatalytic reforming of methanol. These efforts received renewed attention when Dr. Emília Tálas joined to the research staff.

First anatase TiO_2 nanoparticles were synthesized by a sol-gel method. The surface of the particles was modified by deposition of SnO_2 patches in monolayer thickness. Loading of the tin-modified samples by 0.5 wt % Pt increased the hydrogen production in comparison to 0.5 wt % Pt/TiO_2 samples. The improvement in the catalytic activity showed double maximum as the function of the tin content. In the limit of low tin contents isolated Ti-O-Sn linkages are envisaged, which provide highly effective channels for electron transfer from TiO_2 towards Pt. At considerably higher tin contents, the extended SnO_2 patches modify the bonding properties of the reactants, while the switch between the enhancement mechanisms results in a dip in the photocatalytic activity [11].

Further studies comparing the photocatalytic properties of the SnO_x-Pt/TiO_2 system prepared and activated by different methods in general confirmed the beneficial effect of tin. It was revealed that both the presence of Sn and the way of Pt co-catalyst formation influence the activity of this type of photocatalysts. The following benefits of Sn introduction were suggested: it can decrease the number of the unfavorable, relatively basic type of OH groups and the amount of the undesirable vacancies. Furthermore it can ensure a relatively high dispersion of Pt. As far as the cocatalyst formation is concerned, our studies revealed that activation by high temperature hydrogenation has clear negative effects, which can be related to at least two processes in this system: creation of unfavorable oxygen vacancies and appearance of alloy type Pt-Sn nanoparticles which transform into SnO_x covered Pt nanoparticles during air exposure. The latter means decreased number of active sites for reduction of H^+. On the contrary, cocatalyst formation by calcination avoids these problems. The results are under publication [12]. These observations will form the base for the PhD theses of Katalin Majrik, who spent some time on maternity leave during the project.

TiO_2, as a wide bandgap material, has limited potential in photocatalytic applications utilizing visible light. On the other hand, GaN doped with ZnO is reported to be a viable alternate in development of catalysts for photocatalytic methanol reforming by visible light. Our experiments with this system revealed that the proposed synthesis route leads to the formation of a ZnO-doped Ga-oxynitride phase, which, in the presence of a Pt cocatalyst, is indeed quite active in photocatalytic methanol reforming. Nevertheless, it was demonstrated that during oxidative activation the oxynitride started to transform into a nitrogen-free Zn-containing Ga-oxyhydroxide. Moreover, almost complete oxynitride to oxyhydroxide transformation was observed during the methanol photocatalytic reforming reaction, accompanied by complete reduction of the Pt co-catalyst to metallic state, while the activity of the catalysts was not deteriorated. These observations point to the importance of phase transitions under reaction conditions in the development of the active ensemble in the Ga,Zn-based photocatalysts [13]. A very similar oxide to oxyhydroxide transformation was observed in Pt/Ga_2O_3 methanol reforming photocatalysts under reaction conditions, again without noticeable activity change, demonstrating the photocatalytic activity of the Ga-oxyhydroxide phase [14].

3. Changes in research staff and its effects on the progress of the work

The original research team represented an optimal balance between surface chemists with expertise on catalyst modeling and experts of preparation and characterization of real catalysts. The first loss was the death of Prof. László Guczi in 2012. Later both Dr. Orsolya Hakkel (2014) and Katalin Majrik (2013) went on maternity leave; they were replaced by Dr. Tamás Keszthelyi (2015), Dr. Irina Borbáth and Dr. Emília Tálas (formally in 2016, although both of them worked on tasks related to the project already from the beginning of the research work). Finally, Dr. András Tompos also left the project in 2016 because of his other duties. All changes were approved by National Research, Development and Innovation Office. As a result, the balance of the research team shifted towards experts of heterogeneous catalysis, and the critical mass of expertise moved towards the fuel cell electrocatalyst related topics. Although interesting results were obtained and published in all topics included in the original proposal, the publication output necessarily reflects these changes.

4. Other relevant information

As a step of the MTA research network's infrastructural renewal, Research Centre for Natural Sciences was relocated to a new campus between the end of 2013 and the beginning of 2014. As a result of the relocation and subsequent difficulties in the Research Centre, execution of the research project suffered both scientific and financial delays. Accordingly, a 1 year extension for finishing the project was requested and obtained in 2015, while several budget modifications were also necessary.

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