

Ph.D. thesis

New scientific results

INVESTIGATIONS ON HYDROGENATION MODEL
CATALYSTS BASED ON NOVEL SUPPORT MATERIALS

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1. Introduction and objectives

Modern materials science has experienced major development recently. Nanotechnology became an applied science in a short time and new instruments and devices were developed specifically for this field. Specialization was facilitated by the relatively simple synthesis and beneficial properties of nanometer sized materials. Today, nanomaterials are utilized in as remote fields of application as human medicine, sensorics, catalysis and novel processing and waste management technologies. Therefore, it is evident that both metallic and nonmetallic nanomaterials are under intense study recently. Reducing at least one characteristic dimension of matter into the nanometer range results in changes in its physical and chemical properties. Modern surface analysis methods opened up the way towards studying atomically thin layers. It became possible to determine the orientation of surface atomic layers and to identify the types and roles of defect sites.

The primary objective of catalysis research has recently shifted from high conversion towards high selectivity processes, because consuming ~100 % of any starting material is completely futile when only a fraction of the products is valuable. Although in some processes it is possible to recycle the side-product or to utilize it in a secondary reaction, there are several technologies where the unwanted side-products can not be processed any further. In such cases the only economically feasible and environmentally friendly option is to avoid the formation of the side-product by relying on highly selective processes.

Even though metallic nanoparticles have been in use in catalysis since decades several open questions remained in this field. Single crystal studies are useful for investigating the catalytic activity of metals. On the other hand, they are costly, they are not performed under real-life process conditions and they do not provide any information about variations in the catalyst performance upon supporting the same metallic particle on different materials. Therefore, the primary objective of our work was to compare the catalytic performance of noble metal nanoparticle catalysts prepared using various supports but tested under identical reaction conditions.

Our first task was to characterize the adsorption behavior of all six-membered hydrocarbon rings on carbonaceous and silicate based mesoporous supports. These supports

were subsequently decorated by Pt and Rh nanoparticles of pre-designed morphology so that the performance differences between the resulting catalysts can be assessed.

In the second part of my research I attempted developing new catalyst support materials. The objective of this work was to make the operation of supported hydrogenation catalysts more controllable while simultaneously improving their functionality. My detailed studies in this field were on ZnO synthesized from rod-shaped zinc-glycerolate.

2. Experimental

The investigated catalyst supports were first characterized with respect to their adsorption properties using a manually operated volumetric adsorption apparatus. Adsorption isotherms of all possible six-membered C₆ hydrocarbon rings were recorded at 273 K.

Several methods were utilized for the synthesis of the studied nanoparticles, thus it was possible to prepare nanoparticles of varied size and morphology. Particle size distribution curves were derived from the analysis of multiple transmission electron microscopic images.

Support materials were prepared by well-known methods obtained from the literature, with the exception of high surface area mesoporous carbon (CMH) which was developed in our own laboratory. The structure of the supports was characterized by nitrogen adsorption, XRD, IR spectroscopy and thermal analysis, whereas their morphology was investigated by transmission and scanning electron microscopy.

Catalyst activities were investigated in the model reactions of cyclohexene hydrogenation/dehydrogenation and ethylene hydrogenation/dehydrogenation. Gas chromatography and mass spectrometry were utilized to monitor the progress of the reactions.

3. New scientific results

T.1 Adsorption behavior of six-membered C6 hydrocarbon rings

1.a. We have undertaken a detailed study on the correlation between the molecular structure of all six-membered C6 hydrocarbon rings and their adsorption characteristics on selected carbonaceous supports and on SBA-15. Carbon nanotubes exhibit clear adsorption preference towards more aromatic molecules, whereas on SBA-15 the adsorption process is more sensitive to minor pressure variations when the adsorbate is saturated. It is anticipated that this finding will contribute to the rational design of optimal catalysts for a particular reaction.

1.b. Our new mesoporous carbon support (CMH) featured a neutral behavior insofar as adsorption on its surface is governed by size effects only and is not influenced by the electronic structure of the adsorbate. Therefore, CMH appears to be particularly well suited for studying the effects of e.g. catalytic metal nanoparticle variations without the distortions introduced by preferential reactant or product adsorption sensitivity on the support.

T.2 Studies on the ethylene hydrogenation activity of Rh/CMH and Pt/CMH catalysts

2.a An important asset of using mesoporous carbon CMH as catalyst support is its high oxygen tolerance at elevated temperatures (800 K). This allows preparing Rh/CMH and Pt/CMH catalysts by impregnating the CMH precursor with the metal precursors and carbonizing the system. The oxygen tolerance of CMH allows the subsequent oxidative removal of unwanted carbonaceous deposits from the metal surfaces without damaging the structure of the support. Without this special stability it would be necessary to complicate Rh/CMH or Pt/CMH synthesis by first preparing CMH and metallic nanoparticles separately and then combining them in a second step.

2.b We have found that the duration of activation affects the ethylene hydrogenation activity of Rh/CMH and Pt/CMH catalysts more than the oxygen content of the activation gas mixture does. A possible explanation of this phenomenon is that the carbonaceous deposit blocking the catalyst metal surface burns off slowly. Therefore, even at low oxygen

concentrations it is more favorable to have the reaction run for a longer time because this will result in a larger available metal surface area.

T.3 Effect of the structure of carbonaceous supports on cyclohexene hydrogenation

3.a The behavior of catalytically active Ni particles supported over various supports was compared in cyclohexene hydrogenation. Ni nanoparticles of different size (as determined by independent XRD and TEM measurements) were formed when using the same synthesis method on various supports with identical chemical composition (pure carbon) but different structure. The cyclohexene hydrogenation activity of the prepared catalysts differed considerably as well. On this basis we suggest that the interaction between Ni nanoparticles and carbonaceous supports of different structures is heavily dependant on the structure of the support.

3.b Cyclohexene hydrogenation TPR was applied to demonstrate that the differences reported in 3.a for Ni/carbon catalysts are also observable in the temperature dependence of the hydrogenation reaction. Ni/active carbon loses its hydrogenation activity at the lowest temperature, Ni supported on pristine and on shortened carbon nanotubes can maintain hydrogenation for 10-15 K more (the two nanotube types feature very similar TPR profiles), whereas the Ni/graphite system exhibits hydrogenation activity even at temperatures 100 K above that of Ni/active carbon. At this temperature the performance of the other three catalysts is dominated by dehydrogenation reactions. Summarizing, graphite appears to be a suitable support material for high temperature catalytic hydrogenation tasks.

T.4 Significance of H₂ amount in the catalytic hydrogenation of ethylene

4.a We investigated the hydrogenation of ethylene over noble metal nanoparticles supported on SBA-15. When the amount of H₂ in the system is small, ethylene conversion over Rh/SBA-15 remains low and can not be significantly improved by increasing the reaction temperature to above 400 K. This phenomenon can be explained on the basis of literature data by the high ethylidene coverage of the Rh surface. Increasing the H₂ amount represses ethylidene formation and results in a more pronounced hydrogenation activity. On

the other hand, the Pt/SBA-15 system exhibits a different behavior. Since ethylidene formation over Pt is repressed even at low H₂ concentration, this catalyst has a higher hydrogenation activity. Over Rh/SBA-15 the dehydrogenation reaction route becomes preferred at 550 K and hydrogenation performance deteriorates above this temperature, whereas hydrogenation can be clearly detected over Pt/SBA-15 at temperatures close to 700 K. This huge difference could arise from the fact that the surface ethylidene species actually plays a more important role in dehydrogenation than in hydrogenation.

4.b When increasing the H₂:C₂H₄ ratio gradually from 2 to 10 we observed increases in the ethylene conversion and in the activation energy of ethylene hydrogenation over both Rh/SBA-15 and Pt/SBA-15. The change in the activation energy is more pronounced for Rh (from 38.41 kJ/mol to 56.49 kJ/mol) than for Pt (from 46.17 kJ/mol to 51.31 kJ/mol). We explain this observation by the qualitative (di- σ -form vs. π -form) and quantitative (ethylidene amount on the surface) differences between the appearance of ethylene-derived species on the two different metals.

T.5 Development of a novel, ZnO based hydrogenation catalyst

5.a We demonstrated by converting ZnO nanorods into zinc-glycerolate (ZnGly) microstacks that it is possible to transform ZnO into ZnGly in such a way that the product partially inherits the morphology of the parent ZnO. Since ZnO can be synthesized in a large morphological variety, our new and previously unpublished method opens up the way towards preparing ZnGly microstructures in several interesting shapes.

5.b. Morphologically controlled ZnGly microstacks can be converted back to ZnO by thermal treatment. We compared the ethylene hydrogenation activity of Pt/ZnO prepared from such ZnO with that of Pt/ZnO obtained from a commercial ZnO powder and found them to be different. The catalyst obtained via the ZnGly pathway exhibited a behavior similar to Pt/SBA-15 insofar as ethylene conversion over it increased linearly with the amount of H₂. On the other hand, the amount of available H₂ had a negligible effect on the hydrogenation activity of Pt/ZnO prepared from commercial ZnO. This finding agrees well with our previous results discussed in T3a/b for carbonaceous supports: when designing a hydrogenation catalyst utilizing supported metallic nanoparticles, one should always consider that supports

4. Publications related to the thesis

1. E. Horváth, R. Puskás, **R. Rémiás**, M. Mohl, A. Kukovecz, Z. Kónya, G. A. Somorjai and I. Kiricsi
„A novel catalyst type containing noble metal nanoparticles supported on mesoporous carbon – Synthesis, characterization and catalytic properties”
Topics in Catalysis, 2009, **52**, 1242
IF: 2.36
2. A. Sápi, **R. Rémiás**, Z. Kónya, A. Kukovecz, K. Kordás, I. Kiricsi
„Synthesis and Characterization of Nickel Catalysts Supported on Different Carbon Materials”
Reaction Kinetics & Catalysis Letters, 2009, **2**, 379
IF: 0.584
3. **R. Rémiás**, A. Kukovecz, M. Darányi, G. Kozma, S. Varga, Z. Kónya, I. Kiricsi
“Synthesis of Zn-glycerolate microrods from ZnO nanorod sacrificial template”
Eur. J. Inorg. Chem. 2009, 3622
IF: 2.597
4. **R. Rémiás**, A. Sápi, A. Kukovecz, Z. Kónya, I. Kiricsi
“Adsorption of C6 hydrocarbon rings on mesoporous catalyst supports”
Chem. Phys. Lett. 2009, submitted

Impact factor total: 5.541

5. Presentations at conferences

Oral presentations

R. Rémiás, A. Gazsi, É. Molnár, T. Tóth, Á. Kukovecz, Z. Kónya, I. Kiricsi
13rd Zeolite Forum, Polanczyk, Poland
Study of catalysts containing Pt-nanoparticles on SBA-15 in a model hydrogenation reaction

R. Rémiás, Z. Fodor, Á. Kukovecz, Z. Kónya, I. Kiricsi
14th Zeolite Forum, Kocierz, Poland
Adsorption of possible model compounds for hydrogenation/dehydrogenation reactions on SBA-15

Posters

R. Rémiás, A. Gazsi, É. Molnár, T. Tóth, Á. Kukovecz, Z. Kónya, I. Kiricsi
8th Pannonian International Catalysis Symposium
Hydrogenation activity of Pt/SBA-15 catalysts in the conversion of cyclohexene to cyclohexane

É. Molnár, **R. Rémiás**, Á. Kukovecz, G. Tasi, Z. Kónya, I. Kiricsi
28th European Congress on Molecular Spectroscopy
New experimental method for IR spectroscopic investigation of reactions taking place on supported metal surfaces

R. Rémiás, Á. Kukovecz, Z. Kónya, I. Kiricsi
29th European Congress on Molecular Spectroscopy
A study on the metal nano(Pt, Rh)/SBA-15 catalyst system

R. Rémiás, Á. Kukovecz, Z. Kónya, I. Kiricsi
6th International Mesostructured Materials Symposium
Catalytic hydrogenation of cyclohexene on Rh/SBA-15 systems

E. Horváth, R. Puskás, **R. Rémiás**, Á. Kukovecz, Z. Kónya, I. Kiricsi

9th Pannonian International Symposium On Catalysis

Synthesis and characterization of noble metal nanoparticles supported in the ordered pore system of mesoporous carbon