

New Heterogeneous Catalysts for the Selective Reduction of NO_x under Lean Conditions

Final Report

Michael D. Amiridis
Professor of Chemical Engineering

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, SC 29208

May 2004

DOE Patent Clearance Granted

MP Dvorscak

1-2-05

Mark P. Dvorscak

Date

(630) 252-2393

E-mail: mark.dvorscak@ch.doe.gov

Office of Intellectual Property Law

DOE Chicago Operations Office

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT DE-FG02-96ER14666

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

--Contents of Final Report--

A. Research Results 2000-2004.

- A1. Cluster-derived Pt-Au Bimetallic Catalysts
- A2. Cluster-derived Pt-Ru Bimetallic Catalysts
- A3. Bimetallic Catalysts Prepared by Surface Redox Reactions
- A4. NO_x Storage Reduction Catalysts

B. Publications for 2000-2004.

A. Research Results 2000-2004.

The original goal of this program was the identification and design of new noble-metal-based catalysts for the selective catalytic reduction of nitric oxide by hydrocarbons under excess oxygen (i.e., "lean") conditions (HC-SCR). Work conducted in the first funding cycle of this award (i.e., 1997-20000) was successful in allowing us to develop an understanding of the fundamental surface chemistry taking place during the adsorption and reaction of nitrogen oxides and propylene on the surface of supported noble metal catalysts. Both experimental results collected in our own group as well as molecular simulation results published by Professor Neurock suggested that in order to improve the performance of the Pt catalysts – in terms of the nitrogen selectivity and the temperature window of operation – it was necessary to introduce a second metal. However, synthesizing such catalysts with the metals of interest (i.e., Pt-Au, Pt-Ru, Pt-Rh, etc.) with some degree of control of the structure and composition of the resulting supported metal particles is in itself a research challenge. Consequently, the bulk of our efforts during the second funding cycle of this award (covered by this report) was shifted to the use of organometallic cluster precursors for the synthesis on novel bimetallic catalysts. During this time we have also continued to maintain an interest in NO_x abatement, but have redirected our efforts from the HC-SCR process to the more promising from a commercial standpoint NO_x Storage Reduction (NSR) approach.

The following paragraphs contain the highlights of the research results obtained during the 2000-2003 time period. Additional details can be found in the publications listed at the end of this report.

A1. Cluster-derived Pt-Au Bimetallic Catalysts

A substantial amount of our efforts has been focused on the synthesis and characterization of supported bimetallic Pt-Au catalysts prepared from organometallic cluster precursors. The Pt-Au system represents a significant synthetic challenge because of the high miscibility gap of Pt and Au in the bulk and the tendency of Au to agglomerate even under mild conditions. As a result, when Pt-Au catalysts are prepared via conventional impregnation techniques from individual Pt and Au precursors, the end results is a material in which the two metals are mostly segregated and little catalytic synergism exists. In our work we have used primarily a Pt₂Au₄(^tBu)₈ cluster as a precursor, following the early work of Professor Pignolet. The kinetic results obtained with silica-supported cluster-derived Pt-Au catalysts for the HC-SCR reaction indicate that the addition of Au significantly alters the catalytic properties of Pt. These cluster-derived Pt-Au catalysts were found to be more active than monometallic Pt at higher temperatures (Figure 1) and exhibited an increased selectivity towards the production of N₂. In contrast, Pt-Au catalysts prepared by co-impregnation from individual precursors exhibited behavior identical to that of monometallic Pt.

Similar results were also obtained by the use of two additional reactions, namely the oxidation of propylene and the isotopic homoechange reaction between ¹⁶O and ¹⁸O (Figure 2). In both cases the cluster-derived catalysts exhibited substantially different behavior than the catalysts prepared from individual precursors. The results further indicate in these cases that the presence of Au in

the cluster-derived catalysts inhibits the ability of Pt to activate oxygen, which given the structure-sensitive nature of the two reactions, suggests a substantially smaller Pt ensemble size.

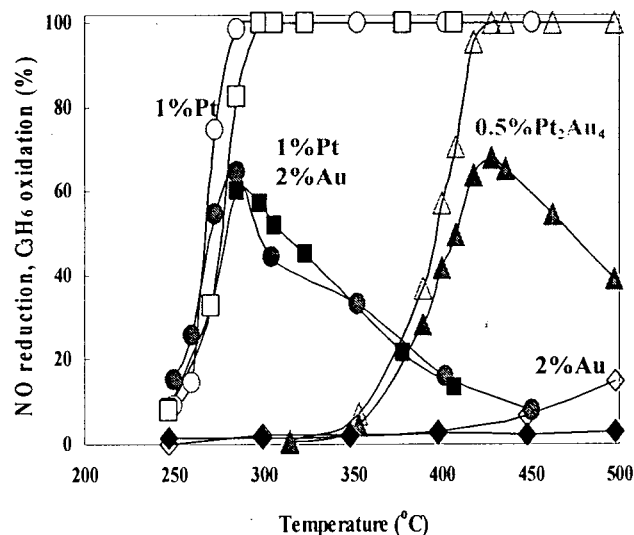


Figure 1

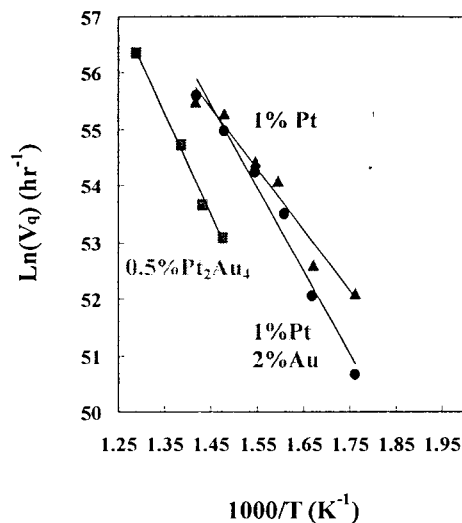


Figure 2

Average particle sizes and particle size distributions were obtained for all fresh and spent catalyst samples employed in our studies using transmission electron microscopy. The results indicate that although the cluster-derived catalysts have slightly smaller particles (3.4 nm) than the co-impregnated ones (4.5 nm), this difference can not account for the significant differences observed in the catalytic behavior. Extensive characterization studies were also performed using FTIR spectroscopy of adsorbed CO. The spectra obtained (Figure 3) indicate that in the cluster derived catalyst Au is capable of chemisorbing CO (characteristic peak at 2110-2120 cm⁻¹),

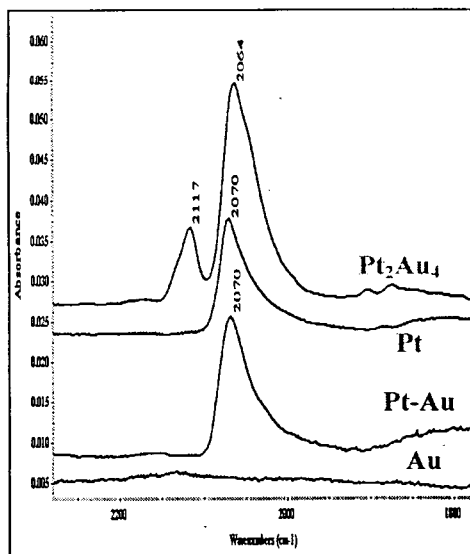


Figure 3

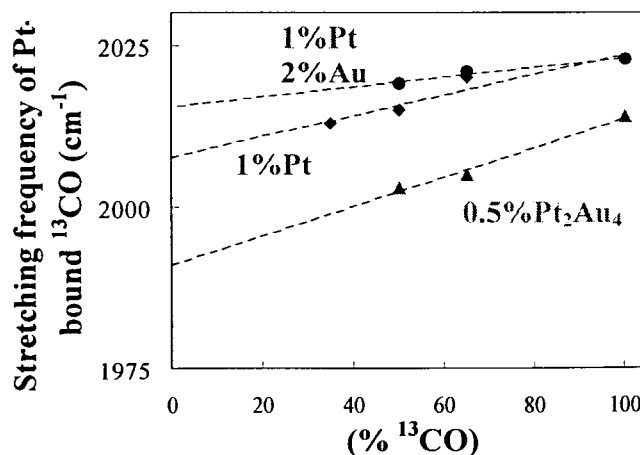


Figure 4

suggesting the presence of finely dispersed Au. IR spectra obtained with different $^{12}\text{CO}/^{13}\text{CO}$ mixtures also revealed a red shift in the singleton frequency of CO bound to Pt for the cluster-derived catalysts (Figure 4), which along with the new CO-Au peak are indications of electronic modification of Pt and the presence of bimetallic Pt-Au particles.

Similar results were also obtained with different supports. Kinetic and FTIR results suggest that in addition to silica we have also successfully synthesized bimetallic Pt-Au nanoparticles on alumina and titania. In all of these cases we have observed CO chemisorption on Au (Figure 5; characteristic IR peaks in the 2110-2120 cm^{-1} region), which suggests that Au nanocrystallites capable of uptaking CO have been stabilized on all these supports. While small Au crystallites have been previously obtained by groups utilizing different synthetic techniques on certain supports (i.e., titanium or iron oxides), it is generally considered a challenge to stabilize such Au nanocrystallites on widely-used supports such as alumina and silica. Our success in synthesizing these Au nanocrystallites, allowed us to explore some mechanistic issues for the oxidation of CO as discussed below.

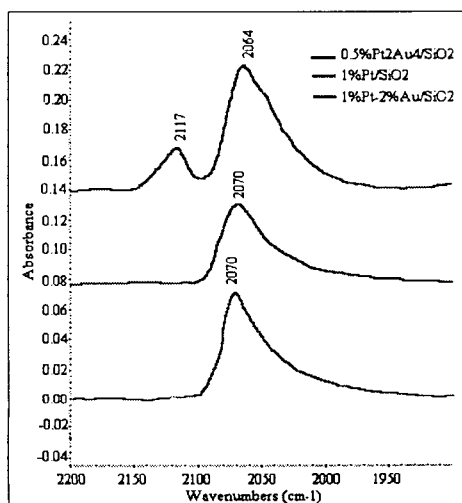


Figure 5a

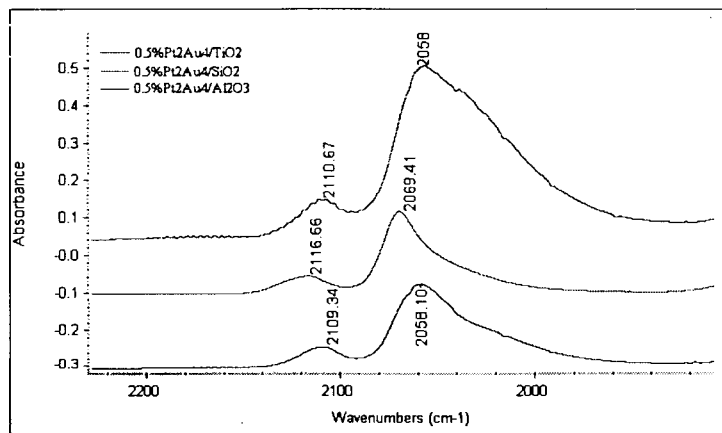


Figure 5b

We are also investigating the ligand removal process through the use of *in-situ* FTIR spectroscopy. So far, we have examined the behavior of the $[\text{Pt}_2\text{Au}_4(\text{C}\equiv\text{CBu}^t)_8]$ cluster supported on Al_2O_3 and TiO_2 , and have conducted treatments in helium, hydrogen and oxygen at various temperatures, monitoring the process continuously via *in-situ* FTIR spectroscopy. CO was also used as a probe to examine the availability of adsorption sites. The results indicate that when the helium or oxygen are used, temperatures as high as 300 $^\circ\text{C}$ are required to complete the ligand removal process. However, in a hydrogen atmosphere the process is completed at temperatures as low as 100 $^\circ\text{C}$. These recent results suggest that substantial additional control

over particle size may be exercised by the careful choice of ligand removal (i.e., “activation”) conditions. For applications (such as the low temperature oxidation of CO) where no exposure to high temperatures is required under reaction conditions, such treatments will yield more dispersed catalysts with apparent catalytic advantages.

We have also examined the effect of the nature of the ligands used to stabilize the organo-bimetallic clusters on the final catalytic properties of the materials obtained. This is important in the case of the Pt-Au system, because most known Pt-Au organo-bimetallic clusters are stabilized by phosphine ligands (i.e. $[\text{Pt}(\text{Au}(\text{PPh}_3)_8)(\text{NO}_3)_2]$, $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6](\text{NO}_3)_2$, and $[\text{Pt}(\text{AuPPh}_3)_2(\text{PPh}_3)_2](\text{NO}_3)_2$) and we were concerned that the presence of phosphorus may have adverse effects on the catalytic performance of these materials. Consequently, we prepared bimetallic Pt-Au catalysts from a phosphine-ligated cluster (i.e. $[\text{Pt}(\text{AuPPh}_3)_2(\text{PPh}_3)_2](\text{NO}_3)_2$) and compared the results obtained with those obtained previously with catalysts derived from an acetylide-ligated cluster (i.e., $\text{Pt}_2\text{Au}_4(\text{C}\equiv\text{C}^i\text{Bu})_8$) with the same Pt:Au stoichiometry. Similar results were obtained in both cases, suggesting that the presence of phosphorus had no adverse effects on the performance of these materials for the selective catalytic reduction of NO. The implication of these results is that a relatively large number of known phosphine-ligated Pt-Au clusters can be used for the synthesis of Pt-Au catalysts.

Our conclusion has been that in all the probe reactions described above, Pt remained the active site, while Au contributed either by affecting the Pt ensemble or by modifying the properties of Pt. In an attempt to probe the reactivity of Au in these cluster derived bimetallic catalysts as well, we have also investigated the low temperature oxidation of CO. The kinetic results obtained for this reaction (Figure 6) are in agreement with the work of Haruta and co-workers regarding the activity of Au nanocrystallites supported on titania (i.e., lightoff at temperatures near room temperature as shown in Figure 6a), although a completely different synthetic approach was used

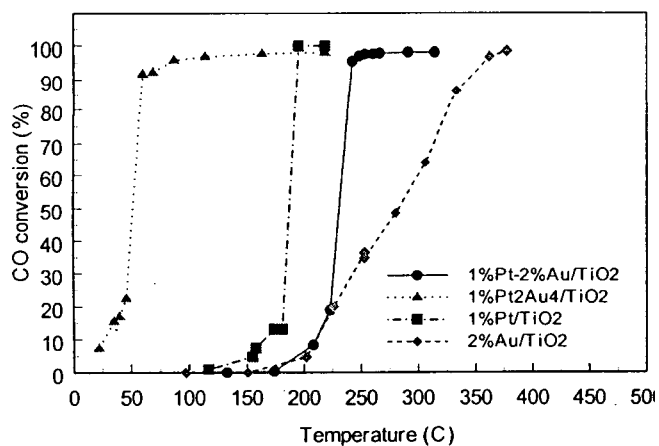


Figure 6a

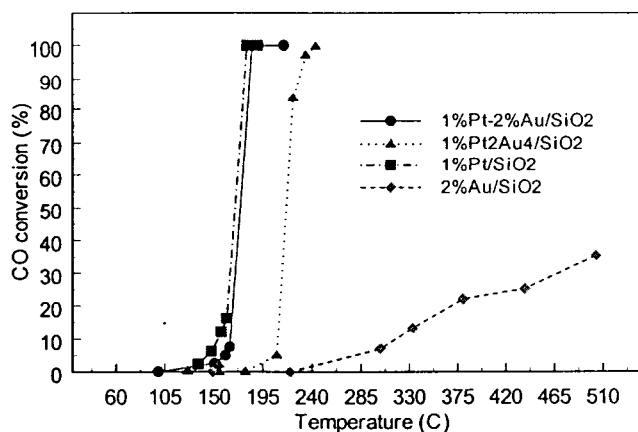


Figure 6b

in Haruta's case. We should also point out that Haruta's kinetic measurements were conducted at a space velocity of $18,000 \text{ hr}^{-1}$, while a space velocity of $120,000 \text{ hr}^{-1}$ was used in our case.

Our results further support Haruta's thesis regarding the role of oxygen supplied by the support. This can be clearly demonstrated with the silica-supported Pt-Au cluster-derived system. Although in this case the catalyst has Au nanocrystallites capable of chemisorbing CO (Figures 5a and 5b), it does not show any low temperature activity for the oxidation of CO (Figure 6b). We also observed differences on the effect of water between the bimetallic Pt-Au cluster-derived catalysts and the monometallic Au catalysts (as reported by Haruta) suggesting that some mechanistic differences may exist. This part of our work is ongoing and we are currently in the process of completing *in-situ* FTIR studies expected to help us develop a better understanding of the low temperature CO oxidation process.

Finally, we should point out that based on the results described above, we have also made an attempt of obtaining a cluster-derived carbon-supported Pt-Au catalyst with a high metal loading (10wt% total noble metals) for use as an electrocatalyst in a PEM fuel cell. This material has not been structurally characterized yet, but initial performance data – obtained in a collaborative effort with Professor Weidner – indicate substantial CO tolerance under air-bleed conditions. We are in the process of obtaining patent protection for this material and use.

A2. Cluster-derived Pt-Ru Bimetallic Catalysts

We have also synthesized alumina- and magnesia-supported Pt-Ru catalysts from a $[\text{Pt}_2\text{Ru}_4(\text{CO})_{18}]$ cluster precursor. These materials have been imaged with the help of Dr. Penycook at ORNL though the use of HRSTEM. Atomic resolution images obtained clearly show the formation of 20-30 atom agglomerates even after very mild treatments (Figure 7a). Individual metal atoms were also observed. The agglomeration process appears to proceed at a smaller scale on magnesia, in which case some intact clusters can be observed (Figure 7b). Based on these results, we have initiated a comprehensive characterization program and we are in the process of obtaining images after a series of systematic treatments.



Figure 7a

Figure 7b

The catalytic properties of alumina-supported Pt-Ru catalysts were probed by the selective oxidation of CO in the presence of hydrogen. The kinetic results indicate no difference in the

initial activities of cluster-derived and conventionally prepared Pt-Ru catalysts when a reduction treatment is applied prior to exposure to reaction conditions. However, the cluster-derived catalyst is stable, while a slow deactivation is observed with the conventionally prepared sample. In contrast, when the samples were oxidized prior to exposure to reaction conditions, the cluster-derived catalyst exhibits much higher activity than either the conventionally prepared one or the corresponding monometallic materials. Our working hypothesis is that bimetallic interactions between Pt and Ru in the cluster-derived samples stabilize Ru in a highly dispersed state and prevent sintering. We are in the process of exploring this hypothesis further, as well as continuing the characterization of the Pt-Ru system, by the use of characterization techniques such as EXAFS and XPS, which recently became available to us through successful proposals for beam/instrument time at BNL and PNNL, respectively.

A3. Bimetallic Catalysts Prepared by Surface Redox Reactions

In collaboration with the catalysis group at the CNRS Center in Poitiers (France), we have also explored an alternative approach for the synthesis of bimetallic catalysts that involves the utilization of a surface redox reaction, which takes place in the liquid phase between a prereduced parent monometallic catalyst (or a reducer adsorbed on this parent metal) and a solution containing an oxidized form of the second metal. This approach has been successful in the past in yielding stable supported bimetallic particles for different metal combinations. Pt-Au and Rh-Ge catalysts were prepared according to this approach in France and were characterized in our group. The results suggest that in the case of the Pt-Au system, the redox approach fails to yield stable bimetallic catalysts and following oxidation and reduction treatments of the resulting materials, Pt and Au segregate, while at the same time Au irreversibly agglomerates. A similar agglomeration of Rh is observed in the Rh-Ge system upon exposure of these catalysts to air even at room temperature. However, if the catalysts are maintained under reducing conditions, the Ge addition leads to the creation and stabilization of smaller Rh^{+1} clusters at the expense of larger Rh^0 surfaces. The effect becomes more pronounced at increased Ge loadings. At these higher Ge loadings a charge transfer is also taking place between Rh and Ge. Bimetallic Rh-Ge catalysts thus prepared were found to exhibit a higher selectivity during the hydrogenation of citral.

A4. NO_x Storage Reduction Catalysts

We have redirected our NO_x abatement efforts in the direction of Pt- and BaO-containing NO_x Storage Reduction (NSR) catalysts. Our decision was based on limitations that we have reached with the Pt-based catalysts for the HC-SCR reaction with regards to their potential commercial application and a widely-accepted belief among industrial researchers that it is more probable that NSR catalysts will be able to satisfy the requirements for commercial deployment in this area. Nevertheless, our previous work on HC-SCR catalysts is of great relevance to these systems since some of the steps of the process remain the same.

We have studied the mechanism of NO_x adsorption and reaction on a typical 1 wt.% Pt/20 wt.% BaO/Al₂O₃ NSR catalyst by the use of *in situ* Fourier Transform InfraRed (FTIR) spectroscopy. Parallel studies were also conducted with the individual components of the NSR system (i.e., 1 wt.% Pt/Al₂O₃ and 20 wt.% BaO/Al₂O₃) in an effort to identify the role and importance of each

component in the NSR process. Finally, the role of SO_2 was also investigated, since it has been reported that it represents a poison for the NSR process. Our results indicate that at 350 °C, NO_x is stored on the NSR catalyst primarily in the form of surface barium nitrite and bulk barium nitrate species. In the presence of Pt, a conversion of the nitrite to the nitrate is taking place during the storage phase. This step is accelerated in the presence of gas phase oxygen and at elevated temperatures. Both barium nitrite and nitrate species are reduced in the presence of propylene, although at different rates. Our working hypothesis is that the surface nitrite species plays the most important role under cyclic operation, since the rate of reduction of the nitrate appears to be limited by the diffusion process from the bulk to the surface. The reduction of the nitrite and nitrate species is catalyzed by Pt and does not proceed at any significant rate over the $\text{BaO}/\text{Al}_2\text{O}_3$ sample. Finally, we observed the formation of surface and bulk barium sulfates when SO_2 was introduced as a component of the NO-containing gas phase mixture. These species are stable on the catalyst surface under reduction conditions and inhibit the NO_x storage process.

We have also initiated work in this area utilizing Pd and SrO as the noble metal and storage components. Initial results indicate a faster rate for the oxidation of NO over Pd – as compared to Pt – during the storage phase. However, a faster rate of nitrite reduction was observed over Pt during the reduction phase. Finally, although SrO exhibits a lower storage capacity than BaO, it is not as severely poisoned by SO_2 . These results provide the basis for some of the research plans outlined in the attached renewal proposal.

B. Publications in 2000–2003 acknowledging support from this grant.

B1. Journal Publications

D.K. Captain and M.D. Amiridis, "NO Reduction by Propylene over Pt/ SiO_2 : An In-situ FTIR Study", *Journal of Catalysis*, **194**, 222-232, (2000).

C.M. Parler, J.A. Ritter and M.D. Amiridis, "Infrared Spectroscopic Study of Sol-Gel Derived Mixed-Metal Oxides", *Journal of Non-Crystalline Solids*, **279(2-3)**, 119-125, (2001).

C. Mihut, B.D. Chandler and M.D. Amiridis, "Bimetallic Pt-Au Cluster-Derived Catalysts for the Selective Catalytic Reduction of NO by Propylene", *Catalysis Communications*, **3(3)**, 91-97, (2002).

D.K. Captain, C. Mihut, J.A. Dumesic and M.D. Amiridis, "On the Mechanism of the NO Reduction by Propylene over Supported Pt Catalysts", *Catalysis Letters*, **83(3-4)**, 109-114, (2002).

C. Mihut, C. Descorme, D. Duprez and M.D. Amiridis, "Kinetic and Spectroscopic Characterization of Cluster-Derived Supported Pt-Au Catalysts", *Journal of Catalysis*, **212(1)**, 125-135, (2002).

M.D. Amiridis, C. Mihut, M. Maciejewski and A. Baiker, "The Selective Catalytic Reduction of NO by Hydrocarbons over Pt- and Ir-based catalysts", *Topics in Catalysis*, **28**(1-4), 141-150, (2004).

S. Yu and M.D. Amiridis, "*In situ* FTIR Studies of the Mechanism of NO_x Storage and Reduction on Pt/Ba/Al₂O₃ Catalysts", *Catalysis Today*, in press.

G. Lafaye, C. Mihut, C. Especel, P. Marecot and M.D. Amiridis, "FTIR Characterization Studies of Alumina-Supported Bimetallic Rh-Ge Catalysts Prepared by Surface Redox Reactions", submitted to *Langmuir*.

O. S. Alexeev., S. Chin, and M. D. Amiridis, "Kinetic and Spectroscopic Characterization of Cluster-derived Pt-Ru Catalysts", in preparation for the *Journal of Physical Chemistry*.

S. Yu and M.D. Amiridis, "*In situ* FTIR Studies of Pt- and Pd-Containing NSR Catalysts", in preparation for *Applied Catalysis B: Environmental*.

B2. Peer-reviewed conference proceedings

D.K. Captain, C. Mihut and M.D. Amiridis, "Selective Catalytic Reduction of Nitric Oxide over Supported Platinum Catalysts", *Proceedings 5th International Conference on the Protection and Restoration of the Environment*, 1007-1014, (2000).

S. Yu and M.D. Amiridis, "*In situ* FTIR Studies of NO_x Storage Reduction Catalysts", accepted *Proceedings 7th International Conference on the Protection and Restoration of the Environment*.