



## SELECTIVITY, ACTIVITY, AND METAL-SUPPORT INTERACTIONS OF RH BIMETALLIC CATALYSTS. PROGRESS REPORT, 15 NOVEMBER 1981-15 AUGUST 1982

YALE UNIV., NEW HAVEN, CT. DEPT. OF CHEMICAL ENGINEERING

AUG 1982



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## SELECTIVITY, ACTIVITY, AND METAL-SUPPORT INTERACTIONS OF Rh BIMETALLIC CATALYSTS

#### Progress Report

for Period 15 November 1981 - 15 August 1982

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August, 1982

#### Prepared for

THE U. S. DEPARTMENT OF ENERGY AGREEMENT NO. DE-AC02-81ER10829

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## ABSTRACT

We report on a detailed investigation of the effect on  $TiO_2$  support on Rh-Ag interaction as exhibited in catalytic activity. The temporal evolution of activity over Rh-Ag/ $TiO_2$  for ethane hydrogenolysis and hydrogen chemisorption as a function of temperature, Ag to Rh ratio, the Rh particle size, Rh loading, and ambient gas were studied. Preliminary extended X-ray absorption fine structure (EXAFS) analysis of  $Rh/TiO_2$  catalysts indicate that 100% exposed (dispersed) catalyst prepared by ion exchange may be atomically dispersed after low temperature reduction.

## Introduction

In our previous Progress Report, the investigation of the effects of metalmetal interaction on activity and selectivity in three intergroup VIII systems, Rh-Ir, Rh-Pt, and Ir-Pt, were discussed in detail. Some further work and an analysis of the mechanistic implications have recently been published in the thesis of T. C. Wong(1). The abstract of this work is attached. Two topics which comprise a major part of our effort in this reporting period are summarized below. The first topic is a study of deactivation and regeneration of hydrogenolysis activity over Rh-Ag bimetallic catlaysts. The second topic is the extended X-ray absorption fine structure (EXAFS) analysis of Rh/TiO<sub>2</sub> interaction of an impregnated and an ion exchanged catalyst. These results are preliminary and constitute necessary background experiments before we move onto the EXAFS of Rh-Ag/TiO<sub>2</sub>, work which we plan to complete by the end of the current grant year.

#### Rh-Ag Bimetallic Catalysts

We will summarize our results here; a more complete discussion can be found in Reference 2, which is attached to this report. We have defined two kinds of effects of TiO<sub>2</sub> on Rh: a direct effect, which changes the activity and selectivity of pure Rh on TiO<sub>2</sub>, and an indirect effect, which effects the metal-metal interaction, e.g., Rh-Ag, and thus indirectly influences the activity and selectivity of Rh(3).

The direct effect of TiO<sub>2</sub> on group VIII metals which results in negligible H<sub>2</sub> adsorption on catalysts reduced at 773K has been called the strong metalsupport interaction(4). This strong metal-support interaction may be reversed by oxidation at 673K; reduction at 473K results in the normal group VIII chemisorption properties. By measuring the activity of Rh/TiO<sub>2</sub> catalyst reduced at

low temperature as a function of dispersion (percent exposed) we have shown that there exists a specific Rh interaction with  $TiO_2$  after low temperature reduction even when the catalyst exhibits normal hydrogen chemisorption(5). By comparing Rh-Ag supported on  $SiO_2(6)$  to Rh-Ag supported on  $TiO_2(5)$ , we demonstrated that the nature of the Rh-Ag interaction is effected by the support. On  $SiO_2$ , Rh-Ag interact by what is effectively Ag chemisorption onto Rh particles with Ag forming islands or patches, while on  $TiO_2$ , the Ag spreads more uniformly. The latter form of interaction produced dramatic decreases in the specific ethane hydrogenolysis rate.

In Reference 2 (attached), the time evolution of activity for ethane hydrogenolysis and hydrogen chemisorption on TiO<sub>2</sub> supported pure Rh and Rh-Ag bimetallic catalysts supported on TiO<sub>2</sub> were investigated. This comparative study allows us to determine separately the activation energy for the direct effect (Rh-TiO<sub>2</sub> interaction) and indirect effect (effect of TiO<sub>2</sub> support on Rh-Ag interaction). The activation energy for these two processes are comparable and in both cases is interpreted as an activation energy for metal particle movement over the surface of TiO<sub>2</sub>. In the direct effect the Rh particles move to find an oxygen vacancy  $-Ti^{3+}$  pair which results in charge transfer from Ti<sup>3+</sup> to Rh(7), while the indirect effect involves metal particle interaction of the different metals so that they may interact (probably both Rh and Ag particles move). We have systematically varied the Ag to Rh ratio, the Rh particle size and the ambient gas to elucidate the nature of the indirect metal-support effect on Rh-Ag interaction(2).

#### EXAFS of Rh/T102

To date, the only EXAFS results of Rh/TiO2 are those reported by Katzer et al.(8). It was stated that EXAFS measurements of Rh/Al2O3 and Rh/TiO2 reduced at 473K show that samples which exhibit CO/Rh chemisorption ratios of

 $\sim 2.0$  and exhibit only dicarbonyl infrared bands are not atomically dispersed as had been previously claimed. These catalysts have Rh-Rh coordination numbers of 4 ± 1, but after reduction at 673K, there is a modest increase in the coordination numbers. We are in the process of re-examining the question of Rh dispersion on TiO<sub>2</sub> using EXAFS.

The EXAFS of four samples are shown in Figures 1-7. In each Figure, the upper lefthand quadrant shows the X-ray absorption K edge of Rh. In the upper righthand quadrant, the oscillatory part of the absorption coefficient normalized to the structureless background absorption and weighted by  $k^3$  (where k is the wave vector) is shown. The Fourier transform magnitude is presented in the lower lefthand quadrant and the inverse transform of the Fourier transform magnitude nearest that of Rh foil nearest neighbor distance is shown in the lower righthand quadrant (the Fourier filtered peak is indicated by an arrow on each Figure). We have followed the analysis procedure outlined by Lee et al. (9) using a computer program written and supplied by B. M. Kincaid. The results shown in Figure 1 are for the Rh foil, our reference material, from which we obtain an empirical phase shift. When this phase shift is applied to the inverse transform of the Fourier filtered peak, it can be used to extract a Rh-Rh distance. In the foil, we assign a value of 2.69 Å to the nearest Rh-Rh distance. In Figure 2 are the results for Rh<sub>6</sub>(CO)<sub>16</sub>, a model compound which was used to test our procedure. The Rh-Rh distance we calculate from the EXAFS analysis of Rh<sub>6</sub>(CO)<sub>16</sub> is 2.759 ± .007, which is within 0.02 Å of the weighted metal bonding distance measured by X-ray diffration, 2.776 Å(10).

We have built an EXAFS cell that allows spectra to be obtained in the temperature range of 77-773K and in situ reduction and/or oxidation of the catalyst. It is also possible to obtain spectra under reaction conditions. The cell is very simple in design. The main cavity can be flushed with an inert or reactive gas continually, the sample being hald in place by Al foil clamped between

two metal plates. A leak-tight seal is not made, but the entire sample chamber is enclosed in a larger compartment, also furnished with Al foil windows, and this larger enclosure is continually flushed with He.

Two catalysts were examined. A 76% dispersed (measured by hydrogen chemisorption) catalyst was prepared by impregnation and a 100% dispersed catalyst was prepared by ion exchange. In Table 1, the Rh-Rh distance as a function of catalyst treatment has been estimated. For the model compound we have used, Rh6(CO)16, the procedure of amplitude transferrability(11) was used to estimate the coordination number. A value of 6 was obtained compared to the known value of 5. This illustrates the considerable difficulties that must be overcome with this approach. Short data length in k space and low signal-to-noise ratio both effect the amplitude of the Fourier transform relatively more than they influence the phase. Moreover, the relative disorder in the model (Rh foil) and unknown (catalyst) systems, the relative mean-free-paths in the two systems, and the inhomogeneities in the sample can all lead to erroneous coordination numbers(9). Because of these problems, we have not yet attempted to estimate coordination numbers for any catalyst. This work will await the preparation of a new reference,  $Rh_6(CO)_{16}$  deposited on TiO<sub>2</sub> at about 1% by weight, and improved signal-to-noise data for our catalyst.

Only qualitative conclusions can be drawn from our EXAFS data in their current state. First, the ion exchanged catalyst (see Figure 5) is atomically dispersed before reduction, <u>i.e.</u>, no distance remotely close to that expected for Rh-Rh is observed. Very likely this atomic dispersion remains after low temperature reduction (see Figure 6), but there is clear evidence for Rh particle formation after a reduction at 723K, even though hydrogen chemisorption indicated complete dispersion. The reduction in disorder after reduction at high temperature relative to low temperature reduction is apparent for both impregnated and ion exchanged catalysts. There is a substantial difference

in the structure for peaks shorter than the nearest neighbor Rh-Rh when the ion exchanged and impregnated catalyst reduced at high temperature are compared, <u>i.e.</u>, there are two such major peaks in the impregnated catalyst, and three for the ion exchanged. It is not possible to assign these to Rh-O or Rh-Ti until we obtain proper references. However, this is a line of investigation which we will pursue. We have discovered that certain kinds of the ion exchanged Rh/TiO<sub>2</sub> catalysts are extraordinary alkane isomerization catalysts(12). Normal supported Rh catalysts promote alkane hydrogenolysis to the exclusion of isomerization. The catalyst which we are currently investigating has almost no hydrogenolysis, a property which we hypothesize is due to essentially atomically dispersed Rh interacting with TiO<sub>2</sub>.

### Effort Devoted to Project

The principal investigator has devoted approximately 15% of his time during the academic year and 45% of the summer during the term of this project. Two graduate students are appointed as research assistants on this project, and all of their research effort is devoted to this project. It is anticipated that the level of effort will be the same for the remainder of the current term, <u>i.e.</u>, until 14 January 1983. We acknowledge access to Cornell High Energy Synchrotron Source where the EXAFS data were obtained.

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FIGURE 1, RH FOIL



FIGURE 2, RH<sub>6</sub>(CO)<sub>16</sub>



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Catalyst	Treatment	Rh-Rh Distance Å	Approximate Coor. No.
Foil	None	2.69	12
Rh6(CO) <sub>16</sub>	None	2.76	6
76% Disp. Rh on TiO <sub>2</sub>	H <sub>2</sub> , 473K, 2 hrs.	2.69	
76% Disp. Rh on TiO <sub>2</sub>	H <sub>2</sub> , 763K, 2 hrs.	2.72	
100% Disp. Rh on TiO <sub>2</sub>	None	2.97†	
100% Disp. Rh on TiO <sub>2</sub>	H <sub>2</sub> , 473K, 2 hrs.	2.65*	
100% Disp. Rh on TiO <sub>2</sub>	H <sub>2</sub> , 723K, 2 hrs.	2.67	

<sup>†</sup>This is not a Rh-Rh distance, but a Rh-X, where X has not been identified.

\*This sample gave a very weak edge. Because of the low signal/noise (see Figure 6), the peak at the position expected for Rh-Rh is very likely a noise peak.

### ABSTRACT

# N-BUTANE AND NEOPENTANE HYDROGENOLYSIS AND ISOMERIZATION OVER SUPPORTED METAL ALLOYS, RHODIUM-IRIDIUM,

RHODIUM-PLATINUM, IRIDIUM-PLATINUM, AND MECHANISTIC IMPLICATIONS

Teik Chen Wong Yale University 1982

N-Butane and neopentane hydrogenolysis and isomerization were studied over supported bimetallics of rhodium, iridium and platinum. A kinetic scheme and an analogy argument with the diffusion limited Type C selectivity of porous catalysts were used to reason that hydrogenating desorption is rate controlling for neopentane/hydrogen on iridiumplatinum. C-C cleavage is probably rate determining on rhodium and rhodium-rich bimetallics and is the case for n-butane/hydrogen on all catalysts. The isomerized intermediate is unstable on iridium and stable on platinum and explains observations of high isomerization selectivity over platinum and conflicting literature reports on iridium. The catalytic site is supposed identical for both reactions and requires an atomically rough surface by a reasoning from alloy solid-state theory. Derived rate equations and preferential segregation of solute atoms to this high energy defect site suggest a hydrogenolysis intermediate less extensively dehydrogenated than previously deduced. There is rhodium enrichment on rhodium-iridium, slight platinum enrichment on iridium-platinum and doubted rhodium enrichment on rhodium-platinum. These are rationalized by regular solution Gibbsian theory extended to small particles. Surface compositions and dispersions were determined by hydrogen and carbon monoxide chemisorption, and x-ray photoelectron spectroscopy on rhodium-iridium and iridium-platinum. Reactions were studied in a pulse reactor and qualitative features reproduced in a flow reactor. The order of activity is rhodium > iridium >> platinum. There is suppression of activity in butane hydrogenolysis and less suppression in neopentane hydrogenolysis; with the suppression being iridium (on rhodium) > platinum (on iridium) > platinum (on rhodium). Isomerization (neopentane) selectivity is in the order platinum > iridium >> rhodium and isomerization activity, iridium > rhodium >> platinum. Iridium shows sharp drops in isomerization selectivity with conversion. Alloying has no influence on the position of fission in butane hydrogenolysis and minor effects on isomerization.



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September 7, 1982



Richard Kropschot, Director Office of Basic Energy Sciences/HQ ER-10, Germantown

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