**Catalyst Laboratory of National Taiwan University- 2002 graduate**

**C. A. Lin (Ph.D)**

**Thesis: Novel Non-oxide Supported Pt Catalysts for VOC Deep Oxidation**

In stead of silica and alumina, the novel non-oxide material was used as the support of deep oxidation catalyst in the research.

Activated carbon dispersed Pt and adsorbed reactant well due to its high specific surface area. The activated carbon was pretreated at 400 and 800°C in nitrogen for 2 hours respectively. Then half of the activated carbons after different thermal pretreatment were soaked in HF for 2 hrs. Higher temperature pretreatment graphitized the surface of activated carbon more, as observed in XPS(X-ray Photon Spectroscopy) and SIMS(Secondary Ion Mass Spectroscopy). The HF pretreatment can lower the ash content on the surface of activated carbon, as proved by EDX(Energy Dispersion X-ray Spectroscopy). The TGA(Thermogravimetric Analysis) and TPD(Temperature-Programmed Desorption) spectra indicated activated carbon can adsorb a huge amount of moisture, aromatics, paraffins, methane and alcohols. The oxygen atom adsorbed on Pt/AC showed higher activity than that adsorbed on Pt/alumina, as proved in TPR spectra. The oxygen atom adsorbed on Pt/AC800 owned the highest activity of those on other Pt/AC catalyst.

Pt/AC800 and Pt/AC800HF gave higher activity in benzene and toluene oxidation than Pt/AC400 and Pt/AC400HF due to their higher activity of adsorbed oxygen atoms and higher graphitized surface to adsorb benzene and toluene. Pt/AC400 and Pt/AC400HF displayed better activity in xylene oxidation than Pt/AC800 and Pt/AC800HF. Two extra-methyl groups on xylene was presumed to reduce the adsorption of xylene on the graphitized activated carbon surface. The oxidation activity of Pt/AC was higher than the traditional Pt/alumina catalyst. But, the Pt/AC catalyst decomposed dramatically when we increased the reactant concentration to 2000 ppmv.

Activated carbon dispersed Pt and adsorbed reactant well due to its high specific surface area. The activated carbon was prepared by incipient wetness method and the composition of Pt was about 0.37%.

**Y. C. Fan**

**Thesis: Deep Oxidation of Alcohols Using Pt/BN Catalyst**

The thesis is devoted to study catalytic oxidation of 1000-4000 ppmv methanol, ethanol, isopropanol using Pt/BN catalyst, compared with both Pt/Al2O3 and commercial Pd/Pt/Al2O3/CeO2 catalyst. Pt/BN and Pt/Al2O3 were prepared by incipient wetness method and the composition of Pt was about 0.37%.

After reaction tests, it was shown that up to 60% methanol could be oxidized to carbon dioxide under room temperature, showing better activity compared with Pt/Al2O3 and Pd/Pt/Al2O3/CeO2 catalyst. That is due to the Pt-O bond on Pt active sites.

Using power law, the reaction order of alcohol is equal or greater than 1, which indicates the rate of alcohol molecules adsorbed on Pt active sites is slow. Besides, the reaction order of oxygen is increased from negative to zero followed by increasing temperature. Oxygen atoms have priority to adsorb on Pt active sites and the tendency decreases as temperature increases.

As the number of carbon of an alcohol increases, the oxidative temperature difference of the three kinds of catalysts decreases. However, Pt/BN catalyst can still oxidize alcohol at lower temperature than that of Pt/Al2O3 catalyst. When the oxidative temperature is over 100°C, Pt/BN catalyst shows poor activity than that of Pd/Pt/Al2O3/CeO2 catalyst resulting from the reactivity of lattice oxygen of CeO2.
**H. Y. Chou**

**Thesis: Photoreduction of Carbon Dioxide via Nano Ag/TiO₂ Catalysts**

The main purpose of this study is to reduce the amount of carbon dioxide by artificial photosynthesis, and derive a reasonable calculation of photoefficiency.

The photocatalytic reduction of carbon dioxide in aqueous solution is carried out by the catalysts suspended in 300ml 0.2M NaOH solution at 295K and ambient pressure. After the solution is saturated by bubbling CO₂(99.9999% V), it is irradiated by a UV lamp(λ=254nm or 365nm). The major liquid phase reduction product analyzed by gas chromatography is methanol. Besides, we can detect a little of oxygen.

The procedure of catalyst preparation is adding CuCl₂ or Cu(CH₃COO)₂ or AgNO₃ to the solution containing Ti(OCH₃)₄, n-C₃H₈OH and CH₃COOH, resulting in a sol consisting of Cu/TiO₂ or Ag/TiO₂.

In order to get the best catalyst of photocatalytic reduction of carbon dioxide, we still use 2% Cu/TiO₂ as the photocatalyst. We change the precursor(copper chloride or copper acetate) and the time of adding precursor(0 hour or 8 hour), and find out the best result is 2% Cu/TiO₂ prepared from 0 hour adding copper chloride. Besides, 2% Ag/TiO₂ is the best loading amount of silver on TiO₂.

We also try to change the wavelength of light source, such as 254nm and 365nm UV light. Under 254nm irradiation, the reaction yield tendency of 2% Cu/TiO₂ and 2% Ag/TiO₂ is approximately the same. But under 365nm irradiation, the reaction yield of 2% Cu/TiO₂ is higher than that of 2% Ag/TiO₂. The yield of 365nm irradiation is much lower than that of 254nm irradiation. Besides, the highest P.E. we get 0.7% ; ϕapp : 2.74% in this system.

**C. Y. Chien**

**Thesis: Ceramic Membrane Modified via Chemical Vapor Deposition and its Characterization**

The objective of this study is to reduce pore size of tubular alumina membrane under 2nm using TEOS via chemical vapor deposition(CVD) route. Consequently, we can promote the applications and increase the value of tubular alumina membrane from Chung-Shan Institute of Science and Technology(CSIST).

The system assembly: gas permeability, CVD reaction, and characterization of SiO₂ membrane are included in this work. Tubular alumina membranes from CSIST consist of two kind of pore sizes, 0.02μm and 0.006μm. The permeabilities of pore size 0.02μm clean membrane is 50-90 for He, and 30-50 for N₂. As to clean membrane of pore size 0.006μm, He and N₂ permeabilities are 20-50 and 10-30 respectively. After modified by CVD, the permeability of all tube membrane decreases with deposition time. The He/N₂ selectivity of 0.006μm clean membrane can be enhanced to 17, compared with 1.96 before CVD. Based on Knudsen diffusion, H₂/N₂ selectivity may achieve up to 24.4. The thickness and microstructure of SiO₂ layer are observed by scanning electron microscopy(SEM). Nitrogen adsorption and mercury intrusion estimated the pore size distribution and porosity. Chemical state and quantity analysis of SiO₂ and Al₂O₃ was recognized through XPS and EDX.

**S. C. Tsai**

**Thesis: Mathematical and Computer Simulation of Methanol Steam Reforming Using Palladium Membrane Reactor**

In this research, we simulated a methanol steam reforming reaction process in a palladium membrane reactor. We attempted to find the optimal conditions for maximum hydrogen yield. The conditions were: the pressure difference of the two sides of the membrane; the thickness of the membrane; the temperature of the external heat source; and the feed ratio. We first established the mathematical model for this system based on mass and energy balance, and thus obtained a set of initial-value ordinary differential equations. The programming language for the computer simulation is FORTRAN. We use the Fourth-Order Runge-Kutta Method to calculate the values of the variables at different positions of the reactor.

The major findings are:

1. An increase of the difference between the inner-outer pressures results in an increase in the hydrogen yield.
2. When the system is in high temperature, it is beneficial for hydrogen yield.
3. The hydrogen yield increases significantly when the thickness of the membrane decreases.
4. Optimal feed ratio is determined by the rate of the feeds, and the length of the reactor (or contact time).

If we want to obtain more hydrogen yield, we need to increase the pressure-difference and the temperature of heat source, and find the optimal feed ratio which depends on the feed rate and the reactor length.