Catalyst Laboratory of National Taiwan University- 2003 graduate

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**Thesis : Nano Metal-loaded Titania Catalysts for CO\textsubscript{2} Photocatalytic Reduction**

Copper or silver-loaded titania photocatalysts were prepared via modified sol-gel process. These catalysts were applied to the catalytic of CO\textsubscript{2} photoreduction. Methanol was favorably produced in aqueous solution under UV irradiation. The relationship between process conditions, catalyst properties, and photocatalytic activity was under investigation. Various sol-gel procedures, precursors, sol-mixing periods, post-treatments were proceeded to look for specific modified titania to methanol yield. The anatase titania nanoparticles were formed after drying and calcination. Metal loading inhibits the growth of TiO\textsubscript{2} crystal size. Metal particles were small and well dispersed in TiO\textsubscript{2} matrix. Parts of metal islands loaded on the surface of TiO\textsubscript{2} particles. The optimal Cu on surface was 50% for better photocatalytic activity. It revealed that the major copper and silver states was Cu\textsuperscript{+} and Ag\textsuperscript{0} on Cu/TiO\textsubscript{2} and Ag/TiO\textsubscript{2} catalysts, respectively. The status of Cu\textsubscript{2}O remained as the Cu loading amount was increasing. However, the portion of Ag\textsuperscript{0} diminished and changed into Ag\textsuperscript{+} as increasing Ag-loaded amount. The increasing temperature resulted in sintering and aggregation of small Ag particles under H\textsubscript{2} flow.

During the sol-gel period, the sol-mixing time and metal precursor were major factors affecting the characterization of catalysts. For CuCl\textsubscript{2} -1h or -3h procedures, higher activity were observed for the optimum Cu distribution and appropriate OH group on TiO\textsubscript{2} surface. More absorbed HCO\textsuperscript{-} on more positive surface was also a benefit to photocatalysis. The amounts of OH group on TiO\textsubscript{2} surface increased with the mixing time of metal precursor. Using copper acetate (Cu\textsubscript{2}O), higher OH ratio on surface was believed to the reason of higher catalysis performance. The similar surface Cu ratios remained for CuAc\textsubscript{2} different mixing time. The additive of NaOH promoted both to the solubility of CO\textsubscript{2} and the absorption of OH in TiO\textsubscript{2} surface.

The methanol yield under 24-h UV (254nm) irradiation was about 600 μmol/g for CuCl\textsubscript{2} -1h and CuCl\textsubscript{2} -3h catalysts. The photocatalytic results under UV (365nm) irradiation revealed that lower metal-loaded amount for higher methanol yield. The methanol yield of 0.5% Cu/TiO\textsubscript{2} catalyst was 40 μmol/g.

C. Y. Chen

**Thesis : The Research of Activity and Selectivity of Pt/BN on Crotonaldehyde Hydrogenation**

The thesis is aimed to study the hydrogenation reaction of Pt/BN catalyst. We compared the hydrogenation activity and selectivity with a traditional catalysis, Pt/Al\textsubscript{2}O\textsubscript{3}. The study used the hydrogenation of benzene as activity test and crotonaldehyde as selectivity test.

In benzene hydrogenation, Pt/BN catalyst showed a higher TOF (Turnover Frequency) than that of Pt/Al\textsubscript{2}O\textsubscript{3} catalyst. The TOF was about 0.09s-1 of Pt/BN and about 0.03 s\textsuperscript{-1} of Pt/Al\textsubscript{2}O\textsubscript{3} at 60°C. The differences of TOF between Pt/BN and Pt/Al\textsubscript{2}O\textsubscript{3} can be referred to the active sites estimated by hydrogen chemisorption. Hydrogen spillover is known due to the acidic sites of Al\textsubscript{2}O\textsubscript{3} support. The increases of active sites on Pt/Al\textsubscript{2}O\textsubscript{3} due to spillover hydrogen, thus might overestimate its dispersion. As a result, the TOF of Pt/BN was higher than that of Pt/Al\textsubscript{2}O\textsubscript{3}.

The reaction order derived from our experimental data gave near 0.4 of hydrogen partial pressure and 0.07 of benzene. The mechanism of benzene hydrogenation can be estimated by non-linear regression of experimental results. It fitted best when the first hydrogen addition was assumed to be the rate-determining step (RDS).

The crotonaldehyde hydrogenation is preferred to the formation of butanol based on thermodynamic equilibrium at room temperature. Pt/BN showed 100% selectivity of butanal at room temperature while Pt/Al\textsubscript{2}O\textsubscript{3} showed about 70% selectivity of crotyl alcohol, 25% of butanal and 15% of butanol. The selectivity of crotyl alcohol is much higher in Pt/Al\textsubscript{2}O\textsubscript{3} than in Pt/BN because of the higher charge density of Pt on Al\textsubscript{2}O\textsubscript{3} than on BN. However the abundant acidic sites on Al\textsubscript{2}O\textsubscript{3} cause a poor selectivity of crotyl alcohol at high conversions. In the study we conclude that Pt/BN is preferred in the C=O hydrogenation and Pt/ Al\textsubscript{2}O\textsubscript{3} is preferred in not only the C=O but also C=C hydrogenation.
C. F. Lo

Thesis: Nano Thin Film of TiO\textsubscript{2} coating and TiO\textsubscript{2}-Coated Optical-Fiber Reactor Design

Titania solutions were prepared by thermal hydrolysis, sol-gel method, and obtained from P25-suspension, Hombikat XXS100 and Hombikat UV100WP TiO\textsubscript{2} solution (Sachtleben Chemie GmbH Com., Germany). The TiO\textsubscript{2} films were coated on glass plates and optical fibers by the dip-coating method. The thickness of films ranged from 60~600 nm after calcinations at 500°C. Process parameters for coating TiO\textsubscript{2}, such as the concentration of TiO\textsubscript{2} solution, the rate of dipping and the times of coating were studied. The films became thicker, and the crystal size increased by increasing the concentration of TiO\textsubscript{2} solution, the dipping rate and the numbers of coating. However, films were found crack or aggregate when the film thickness was thick.

From SEM micrographs, AFM surface profiles and the ASTM adhesion tests, the films coated by thermal hydrolysis and Hombikat XXS100 solution were among the best, following by the films coated by sol-gel, P25-suspension, and Hombikat UV100WP solution. From the result of XRD, the anatase phase was found for all films. Furthermore, the wavelength of absorption was under 400nm from the UV-Vis spectra. For TiO\textsubscript{2} superhydrophilicity property, it was found that the contact angle of water decreased to near zero under UV-light irradiation, and recovered to the initial contact angle in darkness. An optical-fiber reactor (OFR) with TiO\textsubscript{2}-coated fibers was designed and assembled to transport UV light to fiber-supported TiO\textsubscript{2} and conducted a photocatalytic reaction. Gas-phase ammonia was decomposed in the OFR under UV-light irradiation showing a good photocatalytic reactivity of TiO\textsubscript{2}-coated fibers.

C. H. Chen

Thesis: Preparation and Characterization of Visible Light Driven Nano-size V-loaded TiO\textsubscript{2}

The object of the thesis is the synthesis of visible-light responded TiO\textsubscript{2} photocatalysts. The V-doped TiO\textsubscript{2} was synthesized by modified sol-gel method. The prepared photocatalysts were characterized by X-ray diffractometer (XRD), Ultra violet-visible spectrophotometer (UV-VIS), electron microscopy, N\textsubscript{2} adsorption method, X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The photocatalytic activity was evaluated by the degradation of crystal violet and methylene blue under visible light.

In the results of XRD, V-doped TiO\textsubscript{2} was found to be mainly preserved in its anatase phase form after calcinations at 700°C, and the average crystal size was below 10nm calculated by Scherrer’s formula. Furthermore, the TEM micrographs showed the primary particle’s size of V-doped TiO\textsubscript{2} were 6~10nm. Therefore, the catalysts were nano-size particles and maintained high photoactivity anatase-phase even after calcinations at high temperature.

The increase of vanadium amount promoted the crystal growth of V-doped TiO\textsubscript{2}, and resulted in the “red-shift” in the UV-VIS spectra. It indicated that the photocatalysts probably absorbed long-wavelength visible light. In the analysis of XAS, the results showed the vanadium in the TiO\textsubscript{2} structure was in the status of V\textsuperscript{4+} instead of V\textsuperscript{5+}, and implied that vanadium substituted Ti\textsuperscript{4+} site or embedded in the vacancy of structure. The XPS could not detect vanadium indicating only few vanadium on the surface of catalysts, furthermore, there were also no peak of vanadium oxide in the XRD patterns. Therefore, vanadium should well disperse inside the TiO\textsubscript{2} structure.

The photocatalytic activity was evaluated by the degradation of crystal violet and methylene blue under visible and ultra-violet light irradiation. Degussa-P25 had higher photoactivity than that of V-doped TiO\textsubscript{2} under ultra violet source. However, V-doped TiO\textsubscript{2} and P25 were similar in photoactivity under visible light. Therefore, the pure TiO\textsubscript{2}, like P25, could be activated effectively by the existence of ultra-violet light, while the V-doped TiO\textsubscript{2} could not be activated. As the results, V-doped TiO\textsubscript{2} possessed better absorption ability of visible light. The low photoactivity of the V-doped TiO\textsubscript{2} photocatalysts were due to poor quantum efficiency. The future work should pay more effort to solve this problem.