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SHORT COMMUNICATION

TPR STUDY OF ELECTROLESS PLATED COPPER CATALYSTS

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Abstract – An electroless copper plating method, an impregnation method, and a precipitation method were used to prepare copper/alumina catalysts with different loadings. Temperature-programmed reduction (TPR) was employed to characterize the reducibility of copper catalysts prepared by different methods. The experimental results showed that the copper catalyst prepared by electroless plating method had the lowest reduction temperature, followed by the catalyst prepared by the precipitation method, and the catalyst prepared by the impregnation method had the highest reduction temperature.

Key words : Copper, Alumina, Electroless Plating, TPR

INTRODUCTION

The catalytic dehydrogenation of alcohols to ketones has gained much importance in the past two decades because of the increasing demands for valuable solvents and organic intermediates. Most of the catalysts used for dehydrogenation reactions are high-dispersion copper-based catalysts, and generally an impregnation or precipitation method is used to prepare supported metal catalysts. At higher degrees of loading, however, evaporation of solvent or precipitation is required to deposit the active material on a support; as a consequence, these methods may not give a catalyst with uniform distribution of active material on the support [Sivaraj and Kanta Rao, 1988]. The electroless plating technique has been studied by many researchers from the chemical or electrochemical viewpoint and was reviewed in several articles [El-Raghy and Abosalama, 1979; Kikuchi et al., 1986]. Electroless copper plating refers to chemical deposition of copper on a substrate without an external electric current. Copper is autocatalytically deposited on the substrate surface by the oxidation-reduction reaction. Due to the redox mechanism of the electrochemical reaction, it is expected to give a uniform distribution of active material on the support with better physical and chemical properties. A previous study has shown that the dehydrogenation activity of the copper/alumina catalysts prepared by the electroless plating method is better than that of catalysts prepared by the impregnation method and the precipitation method [Chang and Saleque, 1993]. Although the electroless plating technique has been thoroughly studied in the past thirty years and successfully applied in the electrochemical industry for the manufacture of electronic parts, computer parts, printed circuit boards, etc., further study of the characterization of the newly developed electroless copper catalysts still remains and needs to be carefully examined by advanced instrumentation.

Temperature-programmed reduction (TPR) is a powerful characterization technique recently developed in the study of both amorphous co-precipitated oxides and supported metal catalysts [Jenkins et al., 1977]. It allows one to study the influence of support materials, of pretreatment procedures, and of applications of promoters on the reducibility of solid samples under dynamic conditions by continuously monitoring the consumption of hydrogen while a known heating program is being conducted on the sample [Monti and Baiker, 1983]. In this communication temperature-programmed reduction is used to characterize the electroless plated copper/alumina catalysts and to study the effects of copper loading on the reduction profile. We also investigated the variations of reduction property of alumina-supported copper catalysts prepared by different methods.

EXPERIMENTAL

1. Catalyst Preparation

1-1. Impregnation Method

Copper/alumina catalysts of varying composition (6.16-25.52 wt% Cu) were prepared according to the method described by Lo Jacono et al. [1982]. The copper catalysts were prepared by impregnation of alumina with a comparable volume of a titrated solution of copper nitrate for 24 h. The soaked paste was dried at 110 °C, ground, and then calcined at 400 °C for 24 h.

1-2. Deposition Precipitation Method Using Urea as Hydrolyzing Agent

Copper/alumina catalysts of varying composition (2.36-20.02 wt% Cu) have been prepared using the urea hydrolysis procedure [Sivaraj et al., 1986; Sivaraj and Kanta Rao, 1988]. In a typical experiment, a solution containing the required amounts of copper (II) nitrate, γ-alumina, and urea was heated at 90-95 °C. After precipitation was completed (pH 7-7.5) the solids were filtered, washed with distilled water, and dried at 110 °C for 24 h. The oxide catalysts were obtained by calcining the catalyst at 400 °C for 24 h.

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1-3. Electroless Plating Method

1-3-1. Pretreatment of Alumina

The reagents used in the experiment were analytical grade and made by Merck or Riedel-de Haen. The main purpose of pretreatment was to remove the fats and oils and to provide Pd nucleating centers on the surface of the alumina. The γ-alumina (Merck), having particle size 50-100 μm and BET surface area of 138 m^2/g, was used as the substrate for the electroless plating process. The raw alumina was subjected to alkaline cleaning (1 N NaOH) at 65-70 °C for 5-15 min, then acid cleaning (25 vol% H_2SO_4) at 30-35 °C for 3-15 min, sensitizing (20 g/*l* $SnCl_2$ and 40 g/*l* HCl solution) at 25-30 °C for 8-10 min, activating (0.25 g/*l* $PdCl_2$ and 0.5 ml/*l* HCl solution) at 40-45 °C for 20-25 min, and finally drying at 110 °C for 15-20 h. To exclude the effects of Pd and surface condition, a sufficient amount alumina was activated at a time. The pretreated alumina was heated at 250 °C for 12 h with sufficient hydrogen flow.

1-3-2. Electroless Copper/Alumina Catalysts

The pretreated alumina was transferred to the chemical copper plating solution. The plating bath contained 0.04 M $CuSO_4 \cdot 5H_2O$, 0.08 M EDTA·4Na, 0.08 M HCHO and 5 ppm pyridine as a stabilizer [Chang and Saleque, 1994]. The plating bath temperature was maintained at 70 °C and the pH was adjusted to 12.5, with constant agitation for 30 min. The plated alumina was separated by filtration and then washed several times with distilled water. The clean plated alumina, i.e., catalysts of varying copper loadings (8.44-24.56 wt% Cu), were obtained by changing the volume of the chemical copper plating solution.

2. Characterization of Catalysts

In the TPR experiment, 10 % H_2/Ar served as the reducing gas, with a heating rate of 10 °C/min and temperature ranging from 25 to 500 °C. The consumption of H_2 was detected by a TCD analyzer and was then analyzed through an on-line IBM PC.

The copper contents of the catalyst were individually determined with a Polarized Zeeman atomic absorption spectrophotometer, after the sample had been dissolved in a mixture of hydrochloric acid and nitric acid, and it was diluted to obtain the required concentration range. The copper surface area was determined by the decomposition of nitrous oxide [Chang et al., 1994] according to the reaction:

$$N_2O(g) + 2\,Cu \rightarrow (Cu\text{-}O\text{-}Cu)s + N_2(g)$$

BET surface area and pore size distribution were determined from multipoint BET isotherms (Micromeritics 2010) using nitrogen as adsorbate at − 195 °C.

RESULTS AND DISCUSSION

The BET surface area decreased with increasing copper loading for the copper/alumina catalysts prepared by the impregnation method, the precipitation method, and the electroless plating method as shown in Fig. 1. Since the alumina particles were subjected to a pretreatment procedure before electroless copper plating was conducted, they were etched by alkaline cleaning as well as acid cleaning and consequently created new surface. Therefore, the surface area of uncoated alumina for electroless plating was higher than that for impregnation and precipitation. The remarkable reduction of BET surface area is mainly attributed to the copper dilution effect because it is based on one gram of catalyst (alumina+copper), and is partially due to the plugging of micropores of support by copper deposition [Chang et al., 1996].

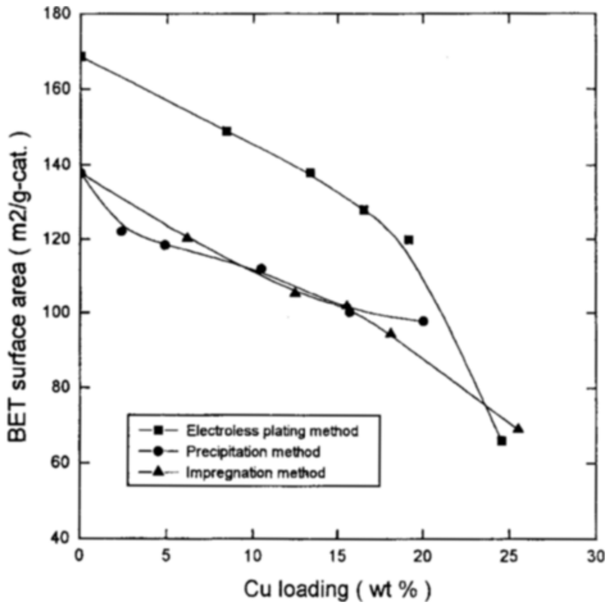

Fig. 1. Effect of copper loading on BET surface area.

Fig. 2 depicts the variations of copper dispersion and copper surface area with copper loading for the electroless plated copper catalysts. The copper dispersion monotonically decreased with increasing copper loading, while the copper surface area attained a maximum value at a copper loading of about 18 wt% Cu. At the beginning of electroless plating, the copper surface area was proportional to the number of

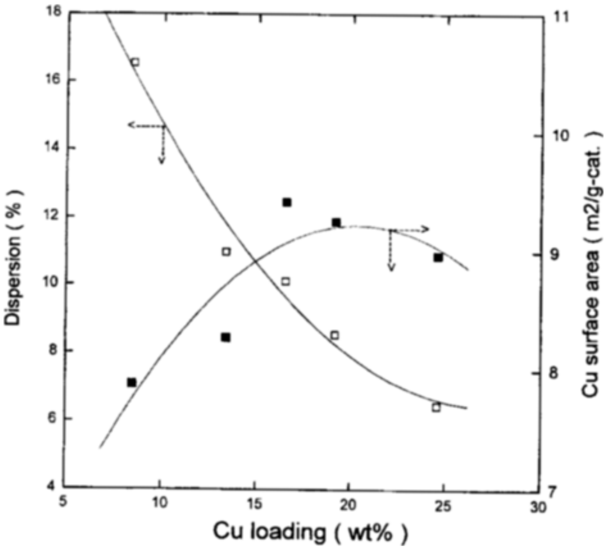

Fig. 2. Effect of copper loading on copper surface area and copper dispersion for the electroless plated copper catalysts.

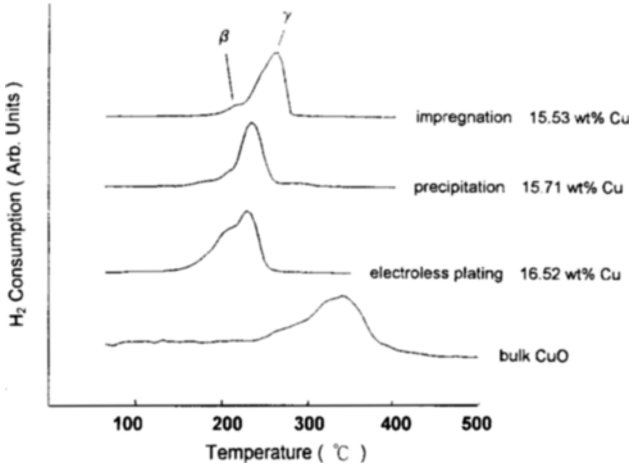

Fig. 3. The TPR profiles of copper/alumina catalysts prepare by different methods.

sparsely distributed fine copper crystallites, which increased with copper loading. Up to a certain loading, the copper crystallites finely covered the whole substrate surface and formed a thin film that caused the exposed copper atoms to maximize. Further copper deposition caused the formation of copper agglomerates and reduced the number of exposed copper atoms. The result coincides with the analysis of SEM images and was also observed by Sivaraj et al. [1990].

Fig. 3 shows that two peaks β and γ appeared on the TPR profiles and their relative intensities depended on the preparation method. The β-peak, which represented highly dispersed copper entities that might include isolated copper ions, weak magnetic associates, or two- and three-dimensional clusters [Tikhov et al., 1992], was attributed to reduction of octahedrally coordinated Cu(+2) ions. The γ-peak was attributed to reduction of bulk-like CuO [Strohmeier et al., 1985]. It is found that the unsupported cupric oxide had the largest reduction peak at about 330 °C. For the copper catalyst prepared by electroless plating method, the maximum reduction peak was about 213 °C. For the copper catalyst prepared by the impregnation method, the largest reduction peak shifted to 254 °C. For the copper catalyst prepared by the urea hydrolysis precipitation method, however, the γ-peak appeared at 218 °C and the β-peak shrunk to a shoulder.

The TPR profiles of electroless copper catalysts without calcination, after calcination at 300 °C, and 400 °C are shown in Fig. 4. The TPR of copper catalyst without calcination clearly shows two separated peaks, representing isolated small copper crystalites and bulk copper oxides, respectively. After calcination, the two peaks gradually merge into one peak, especially at high copper loadings. This may indicate that at the temperature above the Hüttig temperature (ca. 135 °C), surface atoms of small copper crystallites may redisperse and form large copper oxide clusters.

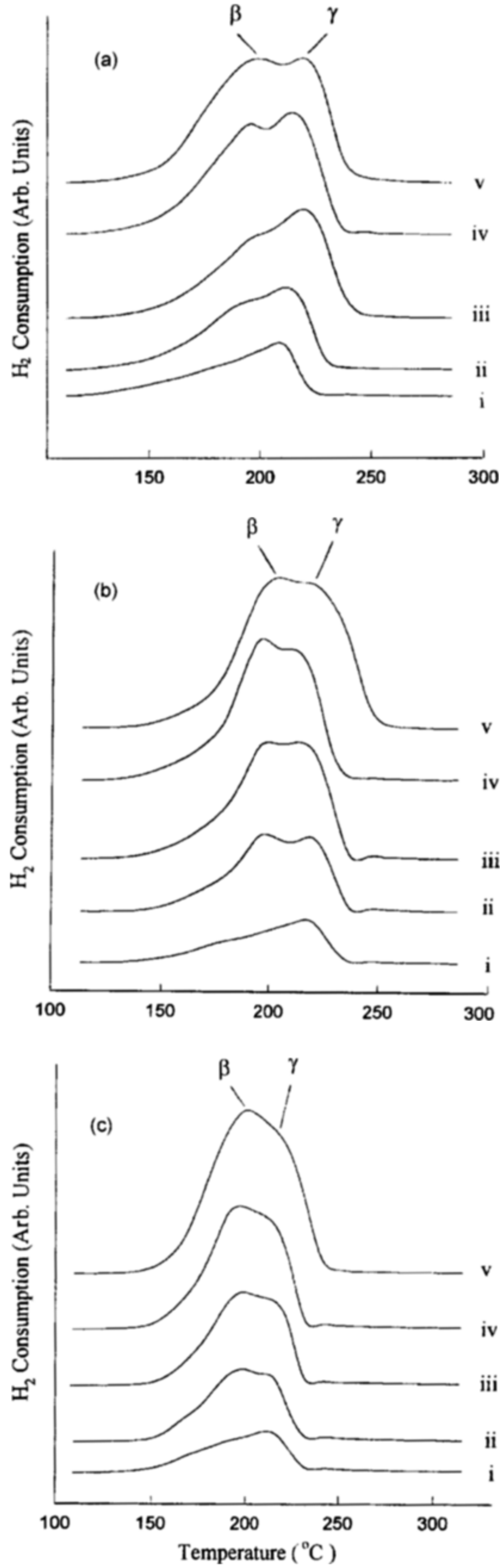

Fig. 4. TPR profiles of the electroless plated copper catalysts. (i) 8.44 wt% Cu, (ii) 13.36 wt% Cu, (iii) 16.52 wt% Cu, (iv) 19.17 wt% Cu, (v) 24.56 wt% Cu
(a) original, (b) calcined at 300 °C, (C) calcined at 400 °C

CONCLUSION

The alumina-supported copper catalyst is easier to reduce than the unsupported cupric oxide. Among the various copper/alumina catalysts prepared by different methods in this study, the catalyst prepared by the electroless plating method had the lowest reduction temperature, followed by the catalyst prepared by the precipitation method, and the catalyst prepared by the impregnation method had the highest reduction temperature.

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