

PROPERTIES OF POLYMER SUPPORTED Ni-Cu BIMETALLIC CATALYSTS PREPARED BY SOLVATED METAL ATOM IMPREGNATION

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ABSTRACT

D-72 resin supported nickel-copper catalysts prepared by solvated metal atom impregnation (SMAI) were studied by magnetic measurements and X-ray photoelectron spectroscopy (XPS). The Ni particles on the catalysts are very highly dispersed and display superparamagnetic behaviour. Ni-Cu alloy clusters were found to be formed. The surface compositions are different from the bulk concentrations. In contrast with the surface enrichment in copper generally observed on conventional Ni-Cu catalysts, the surfaces of these catalysts are enriched in nickel. The nickel is in both zero and valent states, while copper is mainly in metallic state. Catalytic data show that the formation of Ni-Cu alloy clusters has a profound effect on the catalytic activities of the catalysts in the hydrogenation of furfural. The activity of the Ni:Cu ratio of one bimetallic catalysts is much higher than that of the Ni or Cu monometallic catalyst.

INTRODUCTION

As one of the methods for preparing supported metal catalysts, solvated metal atom impregnation (SMAI) into oxide and polymer supports attract much attention nowadays. This technique has been developed by Klabunde's, Ozin's and our research group. It provides a number of advantages, as compared with the traditional methods^[1,2,3].

Bimetallic catalysts are a subject of considerable interest in recent research not only because of the activity but also the activity of the bimetal species differs from that of their components. For example, Ni-Cu bimetallic catalyst remarkably modifies the activity of Ni in the hydrogenation of benzene and butadiene and the selectivity in the isomerization of n-hexane.

Since 1960 much work has been done on the characterization of nickel-copper alloys and nickel-copper alloy catalysts, such as impregnation, incipient wetness impregnation and deposition precipitation. Each of them has its merits and demerits.

Here we present an alternative method, viz. solvated metal atom impregnation at low temperature (-78°C), as described in the previous papers^[3,4]. This technique allows zero valent ultrafine metal particles to be dispersed on catalyst's supports under very mild conditions. Some unusual features of the Ni-Cu/D-72 SMAI catalysts have been found.

EXPERIMENTAL

1. Preparation of the catalyst

D-72 supports the of catalytic supports D-72 (particle size 0.3—1.2) were transformed into Na form using 5%NaOH solution, washed with water and acetone successively, then dehydrated at 80°C and evacuated ($1.33 \times 10^{-5}\text{Pa}$) for 3 h. Toluene was used as the matrix was carefully dehydrated and degassed by three freeze-thaw cycles.

The K-927500 stationary metal atom reactor employed for SMAI catalyst preparation is the product of Martin-Kontes Company, U.S.A. The design of the equipment has been described elsewhere^[5]. In a typical experiment, 1g mixture of Ni and Cu metal chips (mole ratio Ni/Cu= 1) was put into a W-Al₂O₃ crucible, weighed and placed at the proper position in the metal atom reactor. The reactor was degassed by heating to a dull red heat. The reactor vessel was cooled to -196°C with liquid nitrogen, and then began to add toluene ($\sim 10\text{ml}$) to coat the reactor wall. Afterwards, the crucible was warmed to white heat and metal vaporization began. A total of 1g metal and 130ml toluene were cocondensed for 2h., yielding a purple matrix at -196°C . After completion of the cocondensation the reactor was isolated from vacuum and the liquid N₂ Dewar flask was replaced by the dry-ice-acetone bath. The matrix slowly warmed and melted down to the reactor bottom. The dark solution was transferred to the precooled (-78°C) Na form D-72 resin through a stainless steel tube. The resin was impregnated with the solution of solvated metal atom / cluster for 10h. at -78°C under magnetic stirring and N₂ atmosphere, and a black metal-toluene /D-72 slurry was obtained. The slurry was gradually warmed to room temperature. The excess toluene was removed under N₂ flush via syringe, and the metal-toluene /D-72 catalysts were dried under vacuum at room temperature for several h. at $\sim 10^{-5}\text{Pa}$. The dried Ni-Cu/D-72 powders were stored and handled in a nitrogen filled glove box (Vacuum/Atmosphere HE-43-2 Drilab).

2. Magnetic measurements

Magnetic measurements were performed using the Faraday method in an electromagnet (magnetic field up to 8KO_e). The temperature could be either varied between room temperature and 100°C or fixed at 77, 195 and 293K. Samples were degassed at 100°C for 4h. in the sample cell before measuring the mass susceptibility.

3. X-ray photo-electron spectroscopy

The XPS spectra were recorded on a PHI-5300 spectrometer using ALK_α radiation (1486.6eV). The instrument was operated at pressure below 1×10^{-8} torr. Samples were mounted on the holder using double-sided type. Sample preparation and introduction into the spectrometer were performed under N₂ atmosphere. The C_{1s} signal was used as an internal reference for the determination of binding energies.

4. Catalytic activity tests

The catalytic activities of Ni-Cu/D-72 catalysts were measured via the static high pressure hydrogenation of furfural. In an inert-atmosphere glove box, a 160 ml stainless steel vessel was charged with a stirring bar, the catalyst (~0.3g) and 10ml furfural. The vessel was then covered, removed from the box and flushed with H₂, and finally pressurized to 3MPa H₂. The vessel was heated in an oil-bath with constant vigorous magnetic stirring to 130°C and allowed to remain here for 5 h. The vessel was then cooled to room temperature, depressurized, and the contents were examined using a SP-501 gas chromatography.

RESULTS AND DISCUSSION

1. Magnetic measurements

Fig.1 shows the variation of nickel specific magnetization with applied field for monometallic Ni and bimetallic Ni-Cu catalysts prepared by SMAI technique. The low nickel specific magnetization in both catalysts are typical of superparamagnetic systems. As expected from the Langevin equation

$$\frac{\sigma}{\sigma_s} = \coth \frac{MH}{KT} - \frac{KT}{H} \quad (1)$$

where σ is specific magnetization at H and T , σ_s specific magnetization at saturation, H applied field, T absolute temperature, K Boltzmann constant, M magnetic moment of particle. A superimposition of magnetizations at different temperatures for 2.2%Ni-1.1%Cu catalyst was observed by plotting against H/T (see Fig.2).

As the nickel magnetization in Ni-Cu bimetallic catalysts were, in all cases, lower than that of the Ni monometallic catalyst and the increase of the mole ratio Cu/Ni

leads to a lower magnetizations of the samples, we conclude that the decreased nickel magnetic moment of the former is due to Ni-Cu alloy cluster formation [6].

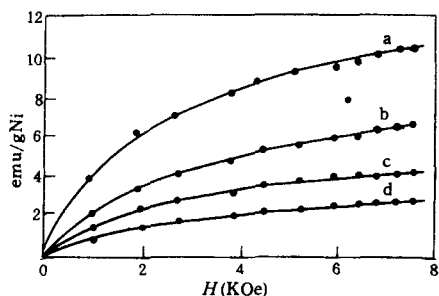


Fig. 1 The specific magnetization (δ) of D-72 supported Ni-Cu and Ni SMAI catalysts as a function of field strength (H) at 293K. (a) 1.6%Ni; (b) 1.8%Ni-0.6%Cu; (c) 2.2%Ni-1.1%Cu; (d) 0.9%Ni-0.9%Cu

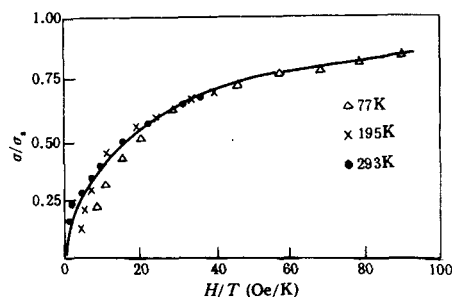


Fig. 2 Plot of σ/σ_s vs. H/T for D-72 supported 2.2%Ni-1%Cu SMAI catalyst

Table 1 Sizes of Ni particles for SMAI Ni-Cu/D-72 catalysts from magnetic measurements

Catalyst	Size of Ni particles	
	$d_{HF}(\text{nm})$	$d_{LF}(\text{nm})$
0.9%Ni-0.9%Cu	1.2	1.5
2.2%Ni-1.1%Cu	1.4	1.7
1.8%Ni-0.6%Cu	1.5	1.9

The sizes of Ni particles in the samples calculated from the results of magnetic measurements in high field (HF) and low field (LF) areas by formulas (2) and (3) are listed in Table 1. The formulas are derived from HF and LF approximation of the Langevin equation, and d values correspond to diameters of metal particles as if they adopt a spherical shape [7]. Superfine Ni particles $< 2.0\text{nm}$ were observed for all the samples. These results clearly demonstrate that the SMAI procedure leads to very highly dispersed monometallic and bimetallic catalysts.

$$d_{HF} = \left[\frac{6K}{\pi I_s} \left(1 - \frac{\sigma}{\sigma_s} \right) \cdot \frac{T}{H} \right]^{1/3} \quad (2)$$

$$d_{LF} = \left[\frac{18K}{\pi I_s} \cdot \frac{\sigma}{\sigma_s} \cdot \frac{T}{H} \right]^{1/3} \quad (3)$$

2. XPS studies

The XPS binding energies of Ni-Cu/D-72, Ni/D-72 and Cu/D-72 catalysts are summarized in Table 2. Fig.3 and Fig.4 show Ni_{2p} and $\text{Cu}_{2p_{3/2}}$, CuLMM Auger

lines for these catalysts respectively. It can be seen from Table 2 and Fig.3 that the $Ni_{2p_{3/2}}$ binding energies and band shapes of Ni monometallic and Ni-Cu bimetallic catalysts are different. The $Ni_{2p_{3/2}}$ line of all Ni-Cu samples have a peak (854.1—854.3eV) which can not be observed in Ni only catalyst. We think this peak may be attributed to the presence of Ni(1+) compounds, probably (Ni-Cu)O, in Ni-Cu catalysts. Further works are needed to prove this assumption. Nevertheless, it is clear that the XPS spectrum of $Ni_{2p_{3/2}}$ for Ni/D-72 catalyst is affected by the incorporation of Cu. Similarly, the incorporation of Ni into Cu/D-72 catalyst affects Cu valent state greatly. The $Cu_{2p_{3/2}}$ binding energies and band shapes of Ni-Cu catalysts are different from that of Cu only catalyst, with the latter having the shake-up structure, suggesting there are Cu(2+) species (CuO) in it. Such shake-up satellite peaks have been attributed to either $3d \rightarrow 4s$ or a ligand to metal ($O_{2p} \rightarrow Cu_{3d}$) transition which is not observed for Cu(1+) compounds and metallic Cu^0 (8.9). In addition, the full width at half maximum (FWHM) $Cu_{2p_{3/2}}$ line of CuO is about twice that of Cu_2O or Cu. This broadening is caused by the multiple splitting of Cu(2+)^[8]. The $Cu_{2p_{3/2}}$ binding energies and band shapes can not be used to distinguish between Cu_2O and Cu because they are essentially identical. However, the Cu LMM Auger lines of CuO and Cu^0 are separated by 2.0eV and their band shapes are different, allowing easy distinction between the two species. The lack of any shake-up satellite structure in Cu_{2p} spectra of Ni-Cu catalysts indicates the absence of any CuO or other Cu(2+) compounds.

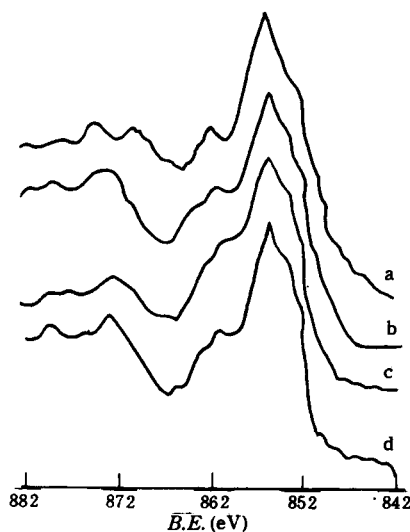


Fig. 3 Ni_{2p} XPS spectra of D-72 supported Ni-Cu and Ni SMAI catalysts (a) 1.6%Ni; (b) 0.9%Ni-0.9%Cu; (c) 2.2%Ni-1.1%Cu; (d) 1.8%Ni-0.6%Cu

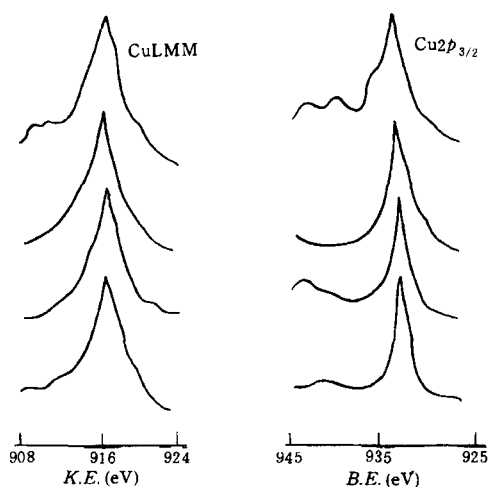


Fig. 4 XPS spectra of $\text{Cu}_{2p_{3/2}}$ and CuLMM Auger lines for D-72 supported Ni-Cu and Cu SMAI catalysts (a) 1.2%Cu; (b) 0.9%Ni-0.9%Cu; (c) 2.2%Ni-1.1%Cu; (d) 1.8%Ni-0.6%Cu

Table 2 Binding energies of SMAI Ni-Cu catalysts

Sample	$\text{Ni}_{2p_{3/2}}$			$\text{Cu}_{2p_{3/2}}$		CuLMM Auger		
	Ni^0	$\text{Ni}(1+)$	NiO	Cu^0 or Cu_2O	$\dot{\text{C}}\text{uO}$	Cu^0	Cu_2O	CuO
0.9%Ni-0.9%Cu	852.5	854.3	855.4	932.1		918.5	916.5	
2.2%Ni-1.1%Cu	852.4	854.2	855.4	932.2		918.4	916.4	
1.8%Ni-0.6%Cu	852.5	854.3	855.5	932.2		918.5	916.5	
1.6%Ni	852.7		856.4					
1.2%Cu				932.4	934.2	918.6	916.6	917.6

Table 3 Comparison between bulk and surface compositions for SMAI Ni-Cu/D-72 catalysts

Sample	Bulk composition			Surface composition		
	Ni(at.%)	Cu(at.%)	mole ratio	Ni(at.%)	Cu(at.%)	mole ratio
			Ni:Cu			Ni:Cu
0.9%Ni-0.9%Cu	0.92	0.89	~1:1	8.18	2.00	~4:1
2.2%Ni-1.1%Cu	2.22	1.09	~2:1	2.41	0.60	~4:1
1.8%Ni-0.6%Cu	1.90	0.63	~3:1	1.30	0.37	~4:1

Quantitative analysis of the Cu and Ni surface atom concentration have been done using the $\text{Ni}_{2p_{3/2}}$ and $\text{Cu}_{2p_{3/2}}$ lines. The peak areas were obtained by computer integration and corrected for instrumental parameters and photoionization cross-section^[10]. We have compared the bulk compositions of Ni-Cu/D-72 catalysts obtained from elemental analysis with their surface compositions obtained from XPS analysis (see Table 3). It is clear that surface of SMAI Ni-Cu/D-72 catalysts are enriched in nickel, in contrast with the surface enrichment in copper or the uniform

composition generally observed in conventional Ni-Cu catalysts^[10].

Table 4 Catalytic activities of SMAI Ni-Cu/D-72 catalysts in hydrogenation of furfural

Catalysts	Mole ratio Ni/Cu	Weight of catalyst(g)	Furfural conversion(%)	gNih (mmol*)	gM.h (mmol)
0.9%Ni-0.9%Cu	1:1	0.50	30	1596	796
2.2%Ni-1.1%Cu	2:1	0.49	35	786	524
1.8%Ni-0.6%Cu	3:1	0.51	26	671	504
1.6%Ni		0.51	16	474	474
1.2%Cu		0.50	3		121

* Data for Ni-Cu catalysts were calculated with neglecting Cu contribution

3. Hydrogenation of furfural

The catalytic activity data of Ni-Cu/D-72, Ni/D-72 and Cu/D-72 catalysts in hydrogenation of furfural are summarized in Table 4. The most striking feature is that the activity of Ni is increased as it is incorporated with Cu, and when the mole ratio Cu/Ni increases the activity of the catalyst increases. It is interesting that the most active Ni-Cu/D-72 catalysts studied has a Ni:Cu ratio of one.

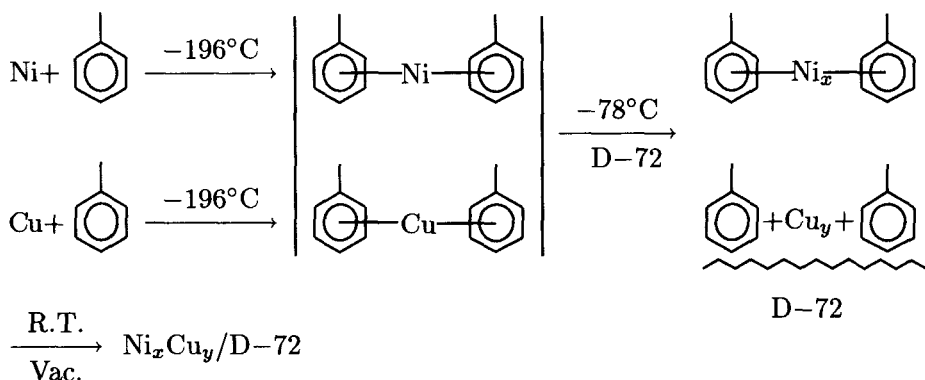
Magnetic measurements show that Ni-Cu alloy clusters are formed on Ni-Cu/D-72 bimetallic SMAI catalysts and that Ni particles are highly dispersed. XPS results suggest that Ni and Cu are present both in metallic and oxidized states, and metallic state Cu⁰ content increases with Ni incorporation. Furthermore, the relative intensity of Ni_{2p_{3/2}} and Cu_{2p_{3/2}} line relative shows that Ni enrichment occurs in the surface region within the escape depth of photo electrons. The activity test results also provide evidence that Ni-Cu entities are present on our catalysts. The bimetallic catalysts exhibit higher activities in furfural hydrogenation than either Ni or Cu monometallic catalyst.

A closer look at the SMAI process is needed in order to understand these results.

In the process of SMAI catalyst preparation, both Ni and Cu vaporize monoatomically, and cocondense with excess toluene. Upon warming and melt down, some clustering occurs, but the cluster growth process competes with the reaction between the growing clusters and the toluene solvent. This process may be illustrated in Scheme 1.

In the case of bimetallic SMAI systems, the decomposition sequence of the arene complexes may play an important role in controlling the geometrical arrangement and valence states of the final metal particles. It is known that Ni-toluene complex is stable to about -50°C, whereas Cu-toluene complex is much more unstable^[11]. That is because (toluene)_n-Cu decomposes more easily than (toluene)_n-Ni. As a consequence it would be expected that Cu clustering would precede Ni, and that Ni

would deposit on the outside of the Cu clusters. This is consistent with XPS results which show that our Ni-Cu bimetallic catalyst surface are enriched in nickel and that incorporation of Ni into Cu catalyst decreases the degree of oxidation of Cu to Cu(2+) by trace oxygen because the Ni particles form a protective partial "coating" around the Cu clusters.



Scheme 1 The SMAI process for preparing Ni-Cu/D-72 catalysts

Keywords:

Polymer support; Ni-Cu catalyst; Solvated metal atom impregnation

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