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Silica supported Pt/Ni alloys prepared via co-precipitation method

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ABSTRACT

Pt/Ni alloyed nanoparticles have been prepared via co-precipitation method on crystalline silica support. The respective salt solutions were reduced using sodium borohydride ($NaBH_4$) in an inert atmosphere at 353 K. Various Pt/Ni molar ratios were studied. H_2-TPR studies revealed that total reduction of the metal ions occurred during the reduction stage while H_2-TPD profiles show that there are four different types of the catalysts. Catalytic studies of these bimetallic catalysts demonstrate enhancements in the activity compared to Ni_{100}. Catalyst with the best activity, $Pt_{72}Ni_{28}$, exhibits specific metal sites not seen in other catalysts. The existence of these metal sites is explained as due to the interaction between Pt and Ni nanoparticles. STEM analysis strongly indicates that the nature of the interaction is the formation of alloys between the metal particles while XPS demonstrates that Pt segregation occurs on the surface of the bimetallic particles.

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1. Introduction

Supported metal nanocatalysts have been given great attention for many years. They play significant roles in various industries such as in portable electronic products, production of nylons [1] and most importantly in fuel cells [2,3]. With the rapid development of technology, the demand for such active materials has increased considerably. This has led to numerous studies among others on the synthesizing and characterization of better efficiency catalysts. Various metals, supports and synthesis conditions have been investigated. This has inadvertently brought about the increasing interest in supported alloys as one of the main studied catalyst materials. Nevertheless, these catalyst materials still lack comprehensive fundamental understanding. For this reason, much work has been focused on studying not only the properties of these materials but also their synthesis conditions.

Traditionally, supported alloys are usually synthesized using two or more metal precursors/metals at extreme temperatures. This technique is well known and has been reported comprehensively [4–6]. This classical approach is recognized for its simplicity and clean resultant alloyed material, nevertheless it has several disadvantages. One of the major drawbacks of this method is the increase in particle size with increasing temperature and heating periods [7]. These treatments are employed to ensure the formation of crystalline alloys as well as for drying and activation purposes. This phenomenon has been described in several systems such as for alloy electrocatalysts [4], $Pt_{70}Co_{30}$ and the Pt/Ru supported on carbon [5]. It is this shortcoming that eventually led to the development of other methods of alloying in the catalyst preparations.

Generally, chemical reduction, electroplating as well as mechanical milling [8] are some of the alternative (non-classical) alloying techniques employed. Chemical reduction methods use reducing agents such as borohydrides [9–13], hydrazine [14–16], formaldehyde [17–18] and alcohols [18–20]. This chemical reduction method has been reported to produce both dispersed and small sized particles at low temperatures. The main reason for such favorable features is the enhanced reduction rate of the precursors [15]. Even so, it is noted that although this method is capable of efficiently synthesizing the bimetallic nanoparticles, it does not guarantee the formation of crystalline alloys and the particle is still prone to oxidation. Hence, many researchers have employed thermal treatments at high temperatures for long durations even after reduction of the metal salts [11,16,21]. This method was employed by Mattei [22] who reported the synthesis of non-alloyed bimetallic particles with core-shell morphology while other researches [15,23] demonstrated the formation of alloyed bimetallic nanoparticles with similar morphology. Though this non-classical method may prove to enhance catalytic activity via the formation of smaller particles when compared to the classical methods, the thermal treatments used may hinder the actual potential of the catalyst due to the increase in particle size during alloy formation as previously mentioned. Therefore understanding the factors that govern the alloy formation and their manipulation is significant.

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Several aspects can influence the formation of supported alloys. Among them are the miscibility of the metal components, the chemical interaction that occurs with the host matrix and the reduction technique or reducing agent that ultimately influences the nucleation and growth of the nanoparticles [22]. Researches have also observed that other synthesis conditions can be manipulated to induce or enhance alloying of elements. In a recent paper by Antolini and coworkers [10], the effect of reduction temperature as well as $NaBH_4$ concentration on the extent of alloying was reported. Their investigations showed that for Pt/Co nanoparticles, a higher degree of alloying was observed when the metal salts were reduced at temperatures ranging from 0 to 40 °C and with lower concentrations of $NaBH_4$. Similar reaction temperatures have also been used to synthesize Ni/Pd and Ni/Pt alloys employing hydrazine as the reducing agent [14].

Our previous work has revealed that size and shape of supported nickel prepared by a chemical method depended on the reduction conditions [16], the nature of the support [24] and presence of a metal additive [25]. By using hydrazine as the reducing agent, it is found that crystalline silica promoted the reduction of nickel while amorphous silica inhibits the nickel reduction by giving rise Ni ion-silica surface species [24]. In a similar chemical reduction method [25], whereby the bimetallic system is silver (Ag) and Ni, the presence of Ag sharply increased the catalytic activity of Ni. Although silver is known as an inactive catalyst it was found that in the presence of silver, Ni/Ag core-shell groupings are formed which led to an increase in metallic surface area of nickel and consequently to a sharp increase in catalytic activity.

In this work, it is our objective to understand the surface characteristics of the catalysts and describe how it affects the catalytic activity of the supported bimetallic nanoparticles. We, hereby, report the synthesis of Pt/Ni nanoparticles on crystalline silica using sodium borohydride as a reducing agent. The formation of NiB and PtB also considered as metal–metalloid alloys have been reported to promote hydrogenation activities [26]. Catalysts were prepared via co-precipitation technique. The nature of the as prepared catalysts was characterized by transmission electron microscopy (TEM), scanning tunneling electron microscopy (STEM), selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS). Surface characteristics of the samples were investigated using dynamic flow methods such as H_2 temperature programmed desorption (H_2-TPD) and H_2 temperature programmed reduction (H_2-TPR) analysis. The catalytic activity of the prepared catalysts is evaluated via the hydrogenation of benzene to cyclohexane.

2. Experimental

2.1. Materials

All materials were used without further treatment. Crystalline silica (99.99%) was obtained from Chempur. Platinic chloride ($H_2PtCl_6{\cdot}H_2O$) was purchased from Sigma, nickel (II) sulphate ($NiSO_4{\cdot}6H_2O$) from R & M Chemicals and sodium borohydride ($NaBH_4$) from Riedel de Haen.

2.2. Preparation of catalysts

All the catalysts were prepared via co-precipitation technique. An amount of crystalline silica was weighed and suspended in a mixture of 30 ml of distilled water and 8 ml of ethanol. The suspension was purged with argon at 353 K. Subsequently, various amounts of Pt (0.05 M, 10 ml) and Ni (0.084 M, 100 ml) salt stock solutions were added to the suspension to obtain various mol/mol ratios of Pt:Ni. The various ratios are Ni_{100}, Pt_8 Ni_{92}, $Pt_{21}Ni_{79}$, $Pt_{72}Ni_{28}$ and Pt_{100} (calculated based on AAS analysis). In all cases, the Ni salt solution was added prior to Pt salt solution. The resultant mixtures were homogenized for a duration of 10 min before the addition of 8 ml of 0.2 M fresh cold $NaBH_4$. The reaction was allowed to continue for an additional 15 min before filtering and washing with distilled water. All catalysts were then dried under vacuum conditions.

2.3. Characterization of catalysts

The TEM, STEM-EDX and SAED of all the samples were obtained using a CM20 Philips transmission electron microscopy operating at 20 kV. Fresh catalysts were redispersed in ethanol and a drop of the solution was placed onto carbon coated copper grids. The XRD spectra were recorded in the 2θ range of 10–100° with a Cu Kα radiation. XPS measurements (for C 1s, Si 2p, O 1s, Ni 2p and Pt 4f) were conducted using an ESCALAB MK II VG with Mg Kα and Al Kα radiations.

H_2-TPR experiments were performed on all of the fresh catalysts. Typically, 50 mg of the catalyst was weighed and placed in a reactor. The catalyst was heated at a constant rate of 5 K min^{-1} from room temperature to 1123 K while purging with a mixture of hydrogen and argon (1000 ppm H_2). The total gas flow rate was previously determined as 90 ml min^{-1}. The resultant effluent gas was analyzed on line using an Agilent G2890A microchromatograph operated at 333 K. In the case of H_2-TPD experiments, 50 mg of the catalyst was placed in the reactor. This was then activated at 473 K in pure hydrogen for the duration of 15 min followed by purging with argon (100 ml min^{-1}) for approximately 45 min and finally cooled to room temperature. H_2-TPD analysis was carried out using similar temperature program and detection as for the TPR analysis described earlier.

2.4. Catalytic activity measurements

A series of experiments were conducted to determine the conditions in which optimum activity is achieved. Catalysts were subjected to various heating rates (2, 5, 10 and 15 K min^{-1}) and subsequent activation at 100 or 200 °C in a flow of 100 ml min^{-1} of pure hydrogen. The condition in which optimum activity is obtained was then used to activate the catalysts as described below.

Typically as much as 50 mg of the samples were weighed and placed in a U-shaped reactor. The catalysts were then activated in a flow of 100 ml min^{-1} of pure H_2. Samples were heated to 473 K at a heating rate of 10 K min^{-1}. Upon reaching 473 K, the samples were maintained at the same temperature for another 15 min. Catalysts were then cooled to room temperature and the catalytic activity measurements were conducted by contacting the catalysts with a reaction mixture of 10/40/150 ml min^{-1} benzene/hydrogen/helium. The extent of dilution of the reaction mixture with helium was previously chosen to enable comparison of catalytic activity of the prepared catalysts. The reaction products were fed into a 5730A Hewlett–Packard gas chromatography equipped with a flame ionization detector and 8 m molecular sieve column. Various other temperatures were studied to evaluate the catalytic activity.

2.5. Determination of fractal dimension

The particle's dispersion onto and within the crystalline silica support is evaluated using the fractal technique. Fractal dimensions, D_F, of the samples were determined based on the method described by Liang [27]. This approach involves choosing several centre points in a TEM image of a sample and drawing circles with a radius of r_1, r_2, r_3, …, r_i. Following this, the micrograph is manually digitized using ones and blanks to indicate the presence and absence of par-

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