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Preparation and characterization of Pt-promoted NiY and CoY catalysts employed for 4-nitrophenol reduction

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ABSTRACT

The reduction of 4-nitrophenol (4-NP) by $NaBH_4$ was used as a probe reaction to investigate the promotion effect of platinum to CoY and NiY catalysts. Subsequent catalysts preparation by ion exchange method, they were characterized by XRD, FTIR, TEM, EXD and surface area measurements at −196 °C. The metal particle size calculated from XRD patterns and TEM images was ≈20 nm for PtY and ≈8–14 nm for Pt-promoted CoY and NiY catalysts. The catalytic efficiency toward the hydrogenation reaction was in the order of PtY < NiY < CoY < PtNiY < PtCoY. Using Pt-promoted CoY catalyst, the reaction rate of 4-NP reduction at 28 °C was found to be 54 times higher than that of PtY catalyst. Moreover, after reduction of the employed catalysts, a significant improvement in the catalytic performance was observed toward the hydrogenation reaction. The specific rate constant of the hydrogenation reaction in the presence of reduced PtCoY was 3.7, 50 and 201 times more than that in the presence of unreduced PtCoY, CoY and PtY catalysts, respectively. Both of the catalysts promotion with platinum and their reduction extremely decreased the apparent activation energy (E_a), whereas it decreased in case of reduced PtCoY to ≈one third of its value in case of PtY. The catalytic activity was found to have a logarithmic relation with the catalyst mass.

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1. Introduction

Faujasite zeolites have many potential properties with their novel cage structure, high surface area and their high affinity for adsorption of enormous reactants and products while being used as supports for catalysts in several reactions. Precious metals-loaded faujasite zeolites have attracted much attention as they are interesting host–guest materials. Specifically, it is of interest to investigate the activity of platinum supported on NaY zeolite for the development of these catalysts for the industrial applications of organic pollutants removal by hydrogenation reactions. Bimetallic platinum with a second metal such as $PtFe/Al_2O_3$ [1], $PtCo/Al_2O_3$ [2], supported PtNi [3,4], and Pt-Cr/ZSM-5 [5] have been prepared using different preparation methods such as successive impregnation, incipient wetness and competitive ion exchange methods. They have been used in some reactions such as CO oxidation, isomerization reactions and alkane conversion. Although, the interaction between the noble metals and the zeolitic structure can lead to the generation of electronic deficient sites which have high activity toward hydrogenation reactions, seeking of higher activity and cheaper cost catalysts never ends. The presence of transition metal as a second element (d electrons are available) can increase the Pt electronic density and, consequently, enhance the catalytic activity [5]. In the previous oxide promoted catalysts, the activity is likely to be controlled *via* the Pt-promoter interface and so it is essential that the oxide and Pt should be associated together to increase the catalytic activity [6] with high dispersion. Such dispersion is difficult to be achieved by traditional preparation methods such as impregnation, incipient wetness or co-precipitation. One of the ways to attain high dispersion is to use ion exchange method which can homogenously distribute ions on the surface. In a previous work [7], we used successive ion exchange method to prepare PtFeY catalyst and study its catalytic activity toward CO oxidation. As far as we know, Pt was not used as promoter to CoY and NiY catalysts using ion exchange method. Therefore, it will be interesting to use such method to prepare Pt-promoted CoY and NiY catalysts and investigate their catalytic activity toward the removal of hazardous materials.

Upgrading water quality is getting more interest with increasing the industrial applications. Phenolic compounds are considered as priority pollutants since they are harmful to organisms even at low concentrations [8,9]. Among various phenolic compounds, 4-nitrophenol (4-NP) is one of the frequently occurring by-products, which is toxic to the environment. On the other hand, 4-NP is

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reduced to form 4-aminophenol (4-AP) which has great commercial importance as an intermediate for the preparation of analgesic and antipyretic drugs [10–12]. In view of the hazardous effect of 4-NP and the growing demand for 4-AP, direct catalytic reduction of the former to the later becomes important.

$NaBH_4$ has the potential to be a useful hydrogen storage compound ($NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$). The speed of releasing of hydrogen can be raised by adding metal containing catalysts [13]. Reduction of 4-NP with $NaBH_4$ in the aqueous medium is kinetically inert reaction, and generally it occurs in the presence of metal containing catalysts such as colloids of platinum nanoparticles [14,15].

Reduction of 4-NP to 4-AP with an excess amount of $NaBH_4$ has often been used as a model reaction to examine the catalytic performance of metal nanoparticles [16]. It has been extensively studied involving various noble metal nanocatalysts such as Au, Ag, Pt and Pd [17]. Compared with Au, Pt, Pd and Ag cobalt and nickel are not expensive. Moreover, they can be used as binary metallic system with precious metals such as Pt to enhance its activity. Based on our literature survey, the use of Pt-promoted CoY and NiY catalysts for the 4-NP reduction has not been reported. So, employing these catalysts for such reaction is interesting in view point of applied and industrial importance.

The apparent lesser reports on the metal oxides-promoted PtY catalyst for the 4-NP reduction hearten the author to prepare Pt-promoted CoY and NiY catalysts using successive ion exchange method and characterize the prepared catalysts with different techniques. The catalysts will be employed in the reduction of the hazardous organic pollutant 4-NP to form the useful 4-AP.

2. Experimental

2.1. Catalyst preparation

All the employed reagents in this study were of analytical grade. To prepare platinum, cobalt and nickel supported NaY solids, 4 g of NaY zeolite (Toyota Company Ltd., Japan. CBV, SAR = 5.1) were soaked in 0.01 M solution of $Pt(NH_3)_4Cl_2{\cdot}H_2O$ (Mitsuwa's Pure Chemicals), $Ni(NO_3)_2{\cdot}6H_2$ and $Co(NO_3)_2{\cdot}6H_2$ (Aldrich), respectively. The mixtures (pH ≈ 6.2) were stirred for 24 h at room temperature, and then the solution was filtered off. This was repeated three times to increase the degree of ion exchange. After filtration, the suspensions were washed with de-ionized water, dried, and finally calcined at 500 °C in air for 3 h. The resulted solids were inferred as PtY, CoY and NiY for platinum, cobalt and nickel supported NaY zeolite, respectively.

The binary systems PtCo and PtNi catalysts supported on NaY zeolite were prepared by successive ion exchange method. In two separated beakers, 2 g of the previously prepared powders CoY and NiY were added to 0.01 M of $Pt(NH_3)_4Cl_2{\cdot}H_2O$ solution at pH 10. Then, the mixtures were stirred at 80 °C for 1 h, filtered, washed with distilled water, dried at 100 °C for 24 h and finally calcined at 500 °C for 3 h. The obtained solids were referred as PtCoY and PtNiY for Pt-promoted CoY and NiY catalysts, respectively.

2.2. Catalyst characterization

The parent NaY and the prepared catalysts were characterized by various techniques such as X-ray diffraction (XRD), FTIR, surface texture parameters measurements, TEM and elemental analysis by EDX technique.

XRD patterns of parent NaY and the prepared samples were collected at room temperature with an X-ray diffractometer, D8 Advance (Bruker axs), with a Cu Kα radiation source (30 kV and 20 mA) in the 2θ range of 5–60°. Hall-equation–Scherer's formula $D = 0.9\lambda/\beta\cos\theta$ [18] was used to determine the average crystallite size (D) of the obtained powders; where λ represents the X-ray wavelength (1.54 Å), θ is the Bragg's angle and β (in radians) is the pure full width of the fraction line at half of the maximum capacity.

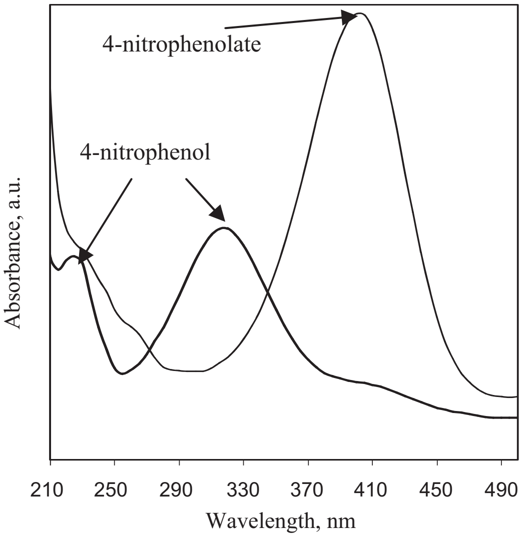

Fig. 1. UV–vis absorption spectra for the change of 4-NP to 4-AP in the presence of $NaBH_4$.

IR spectra were recorded in the solid state as KBr pellet on JASCO FTIR-600 Plus with a spectral resolution of 2 cm^{-1} and accumulation of 100 scans at room temperature.

N_2 adsorption–desorption isotherms were used to examine the porous properties of each sample by using nitrogen as the adsorbent at −196 °C. The measurements were carried out in a Quantachrome AS1Win. (Quantachrome instruments Version 2.01). Before analysis, all samples were pretreated in vacuum at 300 °C for 2 h. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on adsorption data in the partial pressure (P/P_0) range of 0.02–0.25. The total pore volume was determined from the amount of nitrogen adsorbed at P/P_0 = *ca.* 0.95. Pore size and pore volume were obtained *via* *t*-plot analysis of the isotherm data.

Transmission electron microscope (TEM) micrographs of the prepared catalysts were measured using JEOL JEM-1010 transmission electron microscope at an accelerating voltage of 60 kV. Samples were previously ground and ultrasonically dispersed in water. The solids were then deposited over a thin carbon film supported on a standard copper grid.

EDX analysis of the prepared samples was accomplished to estimate the weight ratio (wt%) of the metal ions by using an X-ray energy dispersive spectroscopy (JOEL, Model: JSM-5600, Japan).

2.3. Catalytic reduction of 4-nitrophenol

The performance of 4-NP reduction in the presence of $NaBH_4$ was investigated in batch mode. Typically, 100 ml aqueous solution of 4-NP (0.72 mmol) was mixed with $NaBH_4$ (1.5 mmol) as a reducing agent. The concentration of the $NaBH_4$ was chosen to exceed the concentration of the 4-NP by far. It is known that the light yellow 4-NP exhibits a strong absorption peak at 317 nm (Fig. 1), however, after addition of $NaBH_4$ to its aqueous solution (increase of alkalinity), 4-nitrophenolate ions (dark yellow) are formed with a new absorption band at 400 nm [19–21].

$$\text{4-nitrophenol} + NaBH_4 \rightarrow \text{4-Nitrophenolate}$$

The temperature of the mixture (4-NP + $NaBH_4$) was kept constant at the desired temperature using water bath ($t \pm 1$ °C) and

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