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Characterization and functionalities of Pd/hydrotalcite catalysts

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ABSTRACT

A series of palladium supported on calcined hydrotalcite (CHT) catalysts with varying palladium (Pd) loadings (1.0–8.0 wt%) were prepared by impregnation method. Their catalytic performance was evaluated for the reductive amination of phenol to aniline that showed a tremendous interest in the chemical industry. The catalysts were characterized by BET surface area, XRD, TEM, XPS, TPR of H_2, TPD of CO_2 and CO chemisorption. BET surface area decreased continuously with increase in Pd content. XRD results confirmed the changes in the crystalline phases with altering Pd content. TEM results showed the formation of fine particles at lower loadings and agglomerates at higher loadings. TPR profiles revealed that the reducibility increases with increase of Pd loading. CO_2 TPD results illustrate the catalysts basicity increases with increase of Pd loading up to 4.0 wt% and decreases at higher loadings. Pd dispersion, metal area and crystallite sizes were determined by CO chemisorption method. Pd dispersion and metal area decreases with increase of Pd content and crystallite sizes. The results demonstrated that the Pd dispersion and basic properties are depending on the Pd loading. The catalytic performance clearly showed that the increase Pd loading the conversion of phenol increased up to 2.0 wt% and level off beyond the loading. The catalytic properties are well correlated with the active Pd sites determined by CO chemisorption, dispersion and basicity.

1. Introduction

Supported precious metal catalysts have been used widely for many industrial applications such as synthesis of fine chemicals, petrochemicals and pharmaceuticals. Among the precious metal catalysts, supported palladium catalysts have been applied extensively for variety of reactions [1–5]. The catalytic property of active palladium phase can be greatly influenced by the nature of supported oxide, promoter and the dispersion of the active component [6,7]. Support plays a vital role on the dispersion and stability of active metal; in addition, it can influence the catalytic properties. Different kind of materials like metal oxides, zeolites, molecular sieves, mesoporous materials, and polymeric materials, have been used as a catalyst support for anchoring palladium metal catalysts [8,9]. However, the nature of active species of catalysts is still the subject of extensive investigation by many researchers. The CHT is an important class of basic mixed oxide, is being tried as support for dispersing noble metals.

Hydrotalcite based materials have attracted considerable interest in recent years for their potential use as catalyst and catalyst supports [10,11]. Jiang et al. [12] reported that the catalytic activity of $Pd/MgAl_2O_4$ spinal is better active than those of Pd/Al_2O_3 catalyst for the synthesis of 2,6-diisopropylaniline and Padmasri et al. [13] also reported that palladium supported on hydrotalcite catalytic systems showed superior catalytic activity for hydrodechlorination of CH_2F_2. The high catalytic activity of supported anionic clays (hydrotalcite) is due to its unique properties as compared to that of other classical supports. Hydrotalcite is stable below 300 °C and transform in to mixed Mg-Al oxides (calcined Mg-Al hydrotalcite referred as CHT) upon heating to 500–600 °C, shows basic catalytic behavior [14,15]. Calcined hydrotalcite-type anionic clays are widely used in catalysis, because of their high surface area, basicity, structural stability, homogeneous dispersion of active metal, and better resistance to sintering. Di Cosimo et al. [16] reported that Mg_yAlO_x catalyst showed an excellent acid–base property for the alcohol condensation reactions. In the same way, phenol reductive amination reaction is also depending on the acid–base properties of catalysts. Few literatures are available on the synthesis of aniline from phenol via vapor-phase reductive amination [17–20].

Aniline and their derivatives are highly versatile building blocks for various organic substrates and are essential precursors for

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the synthesis of variety of biologically active compounds such as pharmaceuticals and agrochemicals [21]. It can also be used in the production of rubber additives, dyes and pigments etc. [22]. Commercially, aniline can be synthesized by the reduction of nitrobenzene and ammonolysis of chlorobenzene/phenol [17,23]. The reductive amination of phenol with ammonia and hydrogen to form aniline in a single step is an interesting route in modern organic chemistry with great synthetic potential for the application in academia and industry. First time, we are attempting the synthesis of aniline from phenol over palladium supported on CHT catalysts. To better understand the catalytic nature of supported Pd catalysts an in-depth study of their surface chemistry would be necessary.

In the present investigation, we report the effect of palladium loading on CHT for the reductive amination of phenol to aniline. A detailed characterization studies and their relation to catalytic performance is reported in this work. The main goal of this work is to estimate the dispersion of Pd on CHT as a function of loading, and also to understand the relation between the Pd dispersion and the phenol reductive amination functionality. A comparison is also made with Pd supported on other supports such alumina and magnesia for the vapor phase reductive amination of phenol to aniline.

2. Experimental

2.1. Catalyst preparation

Mg-Al hydrotalcite support was prepared by co-precipitation method. Briefly, solution ***A*** was prepared by dissolving $Mg(NO_3)_2.6H_2O$ (1.0 mol) and $Al(NO_3)_3·9H_2O$ (0.5 mol) in distilled water. Solution ***B*** was prepared by dissolving NaOH (3.5 mol) and anhydrous Na_2CO_3 (0.943 mol) in distilled water. Solution ***A*** was added to solution ***B*** in about 6 h at room temperature under vigorous stirring. The precipitate was washed thoroughly with distilled water until pH reached to neutral. The white crystalline material was dried in an oven at 373 K for 24 h and calcined in air at 773 K for 5 h to get its oxide form; this is termed as calcined Mg-Al hydrotalcite (CHT). A series of supported palladium catalysts with Pd loadings from 1.0 to 8.0 wt% were prepared by impregnation method using an acidified solution of $PdCl_2$ (Aldrich) on CHT (surface area = 218 m^2/g) support. The samples were dried at 383 K for overnight and subsequently calcined at 773 K for 5 h in air. And also 4.0 wt% palladium supported on γ-Al_2O_3 (ENGELHARD, surface area = 175 m^2/g) and MgO (S.D. Fine Chem Ltd, surface area = 65 m^2/g) catalysts were prepared by the same procedure as above mentioned.

2.2. Catalyst characterization

X-ray powder diffraction patterns were obtained with a Siemans D-5000 diffractometer using nickel filtered Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 30 mA and a secondary graphite monochromator. The measurements were recorded in steps of 0.045° with a count time of 0.5 s in the 2θ range of 2–65°. Identification of the phase was made with the help of Inorganic Chemistry Diffraction Database (ICDD). TEM images were obtained with a Tecnai-12, FEI (Netherlands) transmission electron microscope, operating at an accelerating voltage from 20 to 120 kV and magnification value is 6,00,000×. BET surface area of the catalyst samples was measured on a Pulse Chemisorb 2700 (Micromeritics) unit by nitrogen physisorption at 77 K.

CO chemisorption was measured by a dynamic method on Auto Chem 2910 (Micromeritics, USA) instrument. Prior to measurements, 100 mg of the sample was reduced in a flow of hydrogen (50 mL/min) at 573 K for 2 h and flushed with pure He flow (50 mL/min) for 1 h at same temperature. After flushing, the temperature was brought to 303 K (room temperature), pulses of CO (using 9.96% CO balance helium mixture) were injected from a calibrated on-line sampling valve onto a He stream passing over the reduced sample at room temperature. Saturation was assumed to be completed after three successive peaks showed the same peak areas. CO uptake was calculated using the GRAMS/32 software.

The XPS of catalysts was measured on a Kratos-Axis 165, XPS spectrometer with Mg Kα radiation ($h\nu$ = 1253.6 eV) at 75 W. The Pd 3d, Mg 2p, and Al 2p core-level spectra were recorded, and the corresponding binding energies were referenced with C 1s line at 284.6 eV (accuracy within (0.2 eV)). The background pressure during the data acquisition was kept below 10^{-10} bar.

Temperature-programmed reduction studies were carried out on AutoChem 2910 (Micromeritics) instrument. In a typical experiment, 150 mg of oven-dried sample (dried at 383 K for 12 h) was taken in a U-shaped quartz sample tube. The catalyst was mounted on a quartz wool plug. Prior to TPR studies, helium gas was passed with a flow rate of 50 mL/min at 473 K for 2 h to degas the sample. After pretreatment, the sample was cooled to ambient temperature, and TPR analysis was carried out in a flow of 5% H_2–Ar (50 mL/min) from ambient temperature to 873 K at a heating rate of 10 K/min. H_2 consumption and T_{max} positions were calculated using the GRAMS/32 software.

Temperature-programmed desorption of CO_2 studies were also conducted on Auto Chem 2910 (Micromeritics, USA) instrument. In typical TPD studies, about 100 mg of the oven-dried sample (dried at 383 K overnight) was placed in a U-shaped quartz sample tube. Prior to TPD studies, the catalyst sample was reduced at 573 K for 1 h by passing very pure hydrogen (99.99%, 50 mL/min) through it and subsequently flushed with pure helium (50 mL/min) for 30 min to remove an excess hydrogen. After reducing, it was saturated with CO_2 with flow of 10% CO_2–He mixture at 303 K with a flow rate of 75 mL/min and was subsequently flushed at 378 K for 1 h to remove physisorbed CO_2. Desorption was carried out from ambient temperature to 1073 K at a heating rate of 10 K/min. The amount of CO_2 desorbed was calculated using GRAMS/32 software.

2.3. Catalytic activity

The catalytic tests were performed in a down flow fixed bed glass reactor (i.d. = 12 mm, length = 250 mm) in vapor phase at atmospheric pressure. Reductive amination of phenol was used as a model reaction to test the catalytic performance of supported palladium catalysts. In a typical experiment, 0.5 g of catalyst particles diluted with an equal amount of quartz grains having the same size were loaded into the reactor. The catalyst was packed between two quartz wool plugs in the middle of the reactor. Also the upper and lower portions of the catalyst bed were filled with quartz grains. Before reaction, the catalyst was reduced in flowing of hydrogen at 573 K for 3 h. The liquid feed of premixed cyclohexane and phenol (2:1, w/w) was added from a calibrated motorized syringe. The liquid was vaporized in a preheating zone. The reaction was performed with feed rate 2.53 μmol/sec and feed ratio 1:6:6 (feed:H_2:NH_3 mole ratio) at 523 K. The liquid products were analyzed by a HP-6890 gas chromatograph equipped with a flame ionization detector using HP-5 capillary column.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of pure CHT and various Pd/CHT catalysts are shown in Fig. 1 [24]. In all samples, XRD pattern is showing