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Active palladium catalyst preparation for hydrogenation reactions of nitrobenzene, olefin and aldehyde derivatives

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ABSTRACT

A series of Pd/FeO_x catalysts were prepared using co-precipitation method via controlling the washing operation after co-precipitation of the catalyst precursors. The prepared catalysts were tested by the hydrogenation reactions of nitrobenzene, benzaldehyde and styrene, respectively. The highest activity could be obtained when the catalyst precursors were washed for ten times containing ~2.2 ppm chlorine concentration in the aqueous phase. XPS characterization suggested that a suitable $Pd^0/Pd^{\delta+}$ ratio might be important for the high activity. TEM characterization showed that smaller nano-Pd particles can be generated and TPR characterization suggested the formation of more easily reducible Pd species when the catalyst precursors were washed for 10 times. Less or over-washing of the catalyst precursors result in coagulation of the nano-Pd particles. The washing operation, chlorine concentration, catalyst structure and catalytic performance can be related reasonably. The current results should promote the controllable preparation of active Pd-based catalysts.

1. Introduction

It is well accepted that the presence of chlorine in noble metal catalysts normally results in aggregation of nanoparticles, and the chlorine might be adsorbed on the active sites of the catalyst, which often causes deactivation of the catalyst. Therefore, it is well adopted that the removal of chlorine from the catalyst is essential to gain active catalysts [1–9]. However, there is no direct evidence to prove that the low activity is caused by the presence of chlorine. It cannot be concluded definitely that it is the essential step to obtain active catalysts by removing the chlorine completely. Recently, much effort was focused on this field and the role of chlorine in active catalyst fabrication was explored. For example, the presence of chlorine had little impact on the activity of the unwashed and un-calcined supported nano-Au catalysts [10]. During the preparation of nano-Au-based catalysts, active Au/FeO_x catalysts for CO oxidation could be prepared by co-precipitation method even the chlorine was maintained in the catalyst precursor if the catalyst was dried at low temperature. Moreover, the presence of chlorine could be an effective promoter to enhance the performance of catalysts for some reactions [11–15]. For example, in the styrene epoxidation reaction on Au (1 1 1), the introduction of chlorine significantly improved the selectivity of styrene oxide by inhibiting over-oxidation, and the rate of styrene oxide formation was increased, too [16]. Also, the addition of chlorine could optimize the redox characteristic of surface molybdenum oxide species, i.e. depression of the reduction potential of Mo^{6+}, which leads to increased selectivity of ethylene on Mo/Si:Ti catalysts in the oxidative dehydrogenation of ethane [17].

In the last years, the controllable preparation of active supported nano-Au or Pd catalysts was explored in our group by controlling an optimum chlorine concentration in the aqueous solutions containing the catalyst precursors. During the preparation of Au/Fe_2O_3 catalyst with co-precipitation method, we have found that the activity of Au/Fe_2O_3 for CO oxidation and for reductive N-alkylation of nitrobenzene were varied with the chlorine concentration in the aqueous solutions containing the catalyst precursors, and the catalytic activity of Au/Fe_2O_3 reached the maximum at an appropriate chlorine concentration, i.e. 1–3 ppm [18]. We also prepared a series of Au/NiO_x catalysts with co-precipitation method by tracing the chlorine concentration in the washing step and tested by the total oxidation of CO. The results indicated that Au/NiO_x catalysts prepared from aqueous solutions with 4–8 ppm chlorine can be active catalysts and the temperature for CO total oxidation was <0 °C. The catalytic activity dropped sharply if the chlorine concentration was >8 ppm or <4 ppm [19]. The Pd/$Fe(OH)_x$ catalysts with

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different activities for the hydrogenation of nitrobenzene can be controllably prepared by tracing the chlorine concentration in the aqueous solutions containing the catalyst precursors, and the catalytic activity dropped dramatically if the chlorine concentration was >18 ppm or <8 ppm [20]. Catalyst characterizations suggested that catalysts prepared from aqueous solutions containing different chlorine concentration possess different structure. Typically, much bigger nano-Au or Pd particles were formed if the catalyst precursors were over or less washed, in which the catalysts were prepared from solutions with lower or higher chlorine concentrations.

In this work, a series of nano-Pd/FeO_x catalysts were prepared with co-precipitation method by controlling the washing operations of the catalyst precursors. The variation of chlorine concentration during the washing operation was also studied. We chose the selective hydrogenation of nitrobenzene, benzaldehyde and styrene as model reactions to investigate whether the activity of Pd/FeO_x can be tuned by the washing operation or the chlorine concentration of catalyst precursor solutions.

2. Experimental

2.1. Catalyst preparation

The Pd/Fe_2O_3 catalysts were prepared by co-precipitation method. Typically, 26 mmol (10.5 g) $Fe(NO_3)_3{\cdot}9H_2O$ and 1.5 mL H_2PdCl_4 (2.8 M) were dissolved in 4 mL water and were dropwise added into 150 mL Na_2CO_3 solution (0.47 M) in ~0.5 h under vigorous stirring. After it was further stirred for 1 h, the reaction mixture was centrifuged and the recovered precipitates were re-dispersed into 300 mL distilled water and were further ultrasonically washed for 1 h. Then, the reaction mixture was separated into 6 pieces and all of them were ultrasonically washed again by deionized water respectively (50 mL × 4, 50 mL × 6, 50 mL × 8, 50 mL × 10, 50 mL × 12 and 50 mL × 14). All these samples were centrifuged and the resulting slurries were dried at 100 °C for 6 h, and were further calcined at 400 °C in static air. The temperature was ramped from room temperature at a rate of 15 °C/min to the final temperature and maintained for 5 h. In the end, 6 pieces of dark-brown Pd/Fe_2O_3 catalyst samples (~0.3 g × 6) were obtained and denoted as cat-1 to 6.

The Pd/Fe_3O_4 catalysts were obtained by treating the cat-1 to 6 under hydrogen flow. The temperature was ramped from room temperature at a rate of 15 °C/min to 200 °C and maintained for 1 h under hydrogen flow (20 mL/min). In the end, 6 pieces of black Pd/Fe_3O_4 catalyst samples were obtained and denoted as cat-1-r to 6-r.

2.2. Catalysts characterization

The TEM analysis was carried out on a FEI-TF20 field emission transmission electron microscope. The catalyst samples were dispersed in ethanol, and the solution was mixed ultrasonically at room temperature. A part of solution was dropped on the grid for the measurement of TEM images. XRD measurements are conducted by an X'Pert PRO (PANalytical) diffractometer. The XRD diffraction patterns were scanned in the 2θ range of 10–80°. X-ray photoelectron spectroscopy (XPS) analysis was measured using a K-Alpha-surface analysis instrument with Al Kα radiation (1361 eV). Nitrogen adsorption–desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Pd content of the catalysts was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device. The Cl^- ion concentration in the aqueous phase containing the catalyst precursors was tested at 25.0 °C through potentiostatic scanning on a CHI660D electrochemical workstation. A Cl^- ion electrode was used as a working electrode and a platinum wire and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. Before analysis, a series of Cl^- ion standard solutions including 2.0 ppm, 4.0 ppm, 8.0 ppm, 40.0 ppm, 200.0 ppm and 400.0 ppm were prepared using NaCl as the Cl^- ion source. The potentiostatic scanning was carried out at interval of 0.1 s for 1 min in the standard solutions, and the corresponding average potential value (mV) was obtained, which were repeated three times. The electrode system was calibrated with a 5.0 ppm standard solution and the chlorine determination could be carried out through potentiostatic scanning when it is in the range of 5.0 ± 0.5 ppm. The test limit about this method is ~1 ppm. For the temperature-programmed reduction (TPR) measurement, 13 mg of catalyst balanced with 37 mg SiO_2 was placed in a quartz tube, and it was heated up to 350 °C under 5 mL/min O_2 flow (10 °C/min) and maintained 100 min. The sample was then cooled down to 25 °C under 50 mL/min Ar flow and maintained for 1 h at room temperature. Then the catalyst was heated up to 350 °C under 20 mL/min H_2 (10%, balanced with N_2) at a rate of 10 °C/min. The amount of hydrogen uptake was monitored on-line by a TCD detector and recorded as a function of temperature.

2.3. Catalytic activity test

Typically, 1.0 mmol nitrobenzene, styrene or benzaldehyde, 10 mg catalyst and 2 mL EtOH were added into a glass tube (50 mL), respectively. Then, it was exchanged with H_2 and the reaction was carried out in the presence of H_2 at atmospheric pressure (H_2 balloon) at the given temperature. After reaction, 154 mg biphenyl and 10 mL EtOH were added for quantitative analysis by GC-FID (Agilent 7890A).

3. Results and discussion

3.1. Catalytic activity study

The influence of washing times on the catalytic performance of Pd/Fe_2O_3 for the hydrogenation of nitrobenzene is examined first, and the results were shown in Fig. 1. It could be seen that the conversion of nitrobenzene increased with the increasing of washing times until the washing times was up to 10, and then the conversion of nitrobenzene decreased with more washing times.

Meanwhile, taking into account that other factor that might affect the catalytic performance, we examined the chlorine concentrations of the aqueous solutions from which the catalyst samples were prepared. It can be found that the catalytic activity of Pd/Fe_2O_3 in nitrobenzene hydrogenation can be related to the chlorine concentration reasonably. The catalyst had the best catalytic performance when the chlorine concentration in the aqueous solution was ~2.2 ppm. The conversion of nitrobenzene increased with the increasing of chlorine concentrations until that was up to ~2.2 ppm. When the chlorine concentration exceeded ~2.2 ppm, the catalytic activity of Pd/Fe_2O_3 decreased with the increasing of chlorine concentration. This observation was in agreement with our former results about nano-Au catalyst preparation for CO oxidation [18,19]. In order to verify the generality of the above rule, the catalytic activity of the Pd/Fe_2O_3 catalysts were further investigated in the hydrogenation of styrene and aldehyde and almost the same observations were got.

Typically, in order to gain high activity, the supported palladium catalysts should be pre-treated by hydrogen especially when they were used in hydrogenation reactions. So the Pd/Fe_2O_3 catalysts were reduced under hydrogen flow to see if the hydrogen