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Bimetallic Pt–Pd/silica–alumina hydrotreating catalysts – Part I: Physicochemical characterization

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ABSTRACT

Supported Pt–Pd catalysts were synthesized using the respective tetrammonium complexes as precursor salts. The materials used as carriers were silica and amorphous silica–alumina (ASA) with Al_2O_3/SiO_2 wt.% ratio of 55/45, 20/80, and 5/95. The concentration of Lewis acid sites increased with the alumina content of support, whereas the concentration of Brønsted acid sites reached a maximum at 20 wt.% of alumina. According to the chemical analysis, the content of Pt and Pd was close to 0.3 and 0.5 wt.%, respectively, keeping the Pd/Pt molar ratio of 3. The average particle size slightly varied from 1.4 to 1.8 nm (TEM). The analysis of the EXAFS and CO adsorption IR characterization revealed that the general morphology of the bimetallic clusters was Pt-rich core and Pd-enriched surface. The Pt atoms in the bimetallic clusters were electron deficient due to electron transfer to Pd (XANES). Furthermore, monometallic Pd clusters coexist with those Pt–Pd particles. The proportion of surface Pt increased (from 13.9% to 16.9%) with increasing alumina content in the support. The catalyst supported on ASA(55/45) exhibited the highest coverage of Pt. The varying surface metal composition is attributed to different interaction strengths between the metal precursors and the supports during the preparation steps.

1. Introduction

Bimetallic Pt–Pd catalysts have received considerable attention, because they show high activity in a variety of catalytic applications [1]. The interest in studying Pt–Pd catalysts originates from its superior activity, selectivity, and stability compared with monometallic Pt or Pd catalysts. For instance, the bimetallic Pt–Pd catalysts have been shown to have higher resistance toward poisons compared to Pt catalysts [2–4]. From a fundamental point of view, exploring bimetallic catalysts also allows a better understanding of mechanisms and variables involved in the catalytic reactions. Therefore, extensive efforts have been undertaken to elucidate the morphology of metallic clusters and to draw structure–activity relationships [5–7].

For supported bimetallic clusters, the surface and bulk composition strongly depend on a series of parameters, for example, preparation procedures, metal–metal and metal–support interactions. Thus, it is not surprising that diverse and apparently contradictory studies on the genesis and structure of Pt–Pd catalyst are found in the literature. The formation of homogenous Pt–Pd particles on silica and NaY zeolite has been reported [8,9]. However, experimental and theoretical evidence for the segregation of Pd to the surface of bimetallic Pt–Pd clusters is more abundant [10–15]. Pd is claimed to segregate to the surface during thermal treatment, probably because of the different surface energy of Pt and Pd [16]. Many other factors, however, may also affect Pd migration. For example, studies of alumina- and carbon-supported Pt–Pd catalysts show that the migration of Pd atoms to the surface is enhanced by thermal treatment in H_2 or O_2, but suppressed by high metal dispersion [17]. Furthermore, the variables involved in the reduction step can also influence the characteristics of Pt–Pd catalysts. For instance, the particle size and composition of bimetallic clusters on alumina are notably affected by replacing nitrate precursors with acetylacetonate during the preparation procedure [18]. The thermal treatment applied to the catalyst precursor may also affect the oxidation state of the metal before the reduction step as shown in Ref. [8].

The large number of variables determining the nature of supported bimetallic particles makes it difficult to deduce general models for the metal phase in the Pt–Pd catalysts without characterizing a sizable number of different bimetallic catalysts to deduce structure–activity correlations. In this study, we aim to investigate the characteristics of Pt–Pd clusters supported on amorphous silica–alumina (ASA) as a function of the silica to alumina ratio,

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which induces a change in the concentration of Brønsted and Lewis acid sites of the support. Nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy using CO and pyridine as probe molecules, transmission electron microscopy (TEM), and X-ray absorption spectroscopy using EXAFS analysis are utilized to derive a structural model for the Pt–Pd catalysts. XANES provides information concerning the electronic state of Pt and Pd in the catalysts.

The features of the catalysts here studied are going to be correlated with their catalytic performance in the hydrogenation of tetralin in the absence and presence of dibenzothiophene and quinoline in the second part of this work [19]. The final goal is to propose a mechanistic model of the tetralin hydrogenation on the Pt–Pd/ASA catalysts that includes the metal phase and Brønsted acid sites in the support. To better address the effect of acidity, a monometallic Pt catalyst and its Cs-exchanged form were also prepared and characterized.

2. Experimental

2.1. Preparation of supported Pt–Pd catalysts

A series of Pt–Pd-based catalysts (with a molar ratio of Pd/Pt = 3) supported on amorphous silica–alumina (ASA) with Al_2O_3/SiO_2 weight ratios of 5/95, 20/80, and 55/45 and pure silica were prepared by incipient wetness impregnation. The ASA supports were synthesized by mixing aqueous solutions of $AlCl_3·6H_2O$ in acetic acid (pH = 1.5) and sodium silicate in aqueous ammonia (pH = 12). The pH of the mixture was 7.5. The resulting gel was washed with a diluted solution of ammonium acetate to eliminate sodium cations. Subsequently, the gel was dried at 400 K and treated in air at 783 K for 2 h and at 949 K for 2 h. The pure silica support was provided by Shell and thermally treated in air at 783 K for 2 h and at 949 K for 2 h.

The catalysts were prepared following the incipient wetness impregnation technique using aqueous solutions containing both $[Pt(NH_3)_4](NO_3)_2$ and $[Pd(NH_3)_4](NO_3)_2$. The pH of the solution was 7.7. Subsequently, the catalysts were equilibrated for 0.5 h on a mini rolling road, dried (453 K, 10 min), and calcined (563 K, 10 min) in a rotating-tube oven. Finally, the catalysts were reduced at 623 K in hydrogen for 2 h.

Two additional monometallic Pt catalysts were synthesized to study the role of the Brønsted acidity in tetralin hydrogenation in the absence and presence of poisons. One of the catalysts was 0.8 wt.% Pt supported on ASA with an alumina to silica mass ratio of 38/62 (Pt/ASA(38/62)). In the other catalyst (Cs–Pt/ASA(38/62)), the Brønsted acid sites were ion-exchanged by cesium ions, to suppress the support acidity. The parent Pt/ASA(38/62) catalyst was prepared by the same method as described for Pt/ASA samples in Ref [20]. In order to exchange this catalyst with Cs, the sample was first reduced in flowing H_2 at 623 K and then cooled to room temperature in He. After passivation at room temperature (1 vol.% O_2 in He), the sample was impregnated with an aqueous solution of $CsNO_3$ in excess (30 mg Cs per gram of catalyst) followed by equilibration on a mini rolling road for 1 h. Subsequently, the catalyst was dried for 2 h at 393 K, treated in synthetic air for 2 h at 573 K, and finally reduced in H_2 for 2 h at 623 K.

2.2. Elemental analysis, specific surface area and porosity

The chemical compositions of the supported catalysts were determined by atomic absorption spectroscopy (AAS) using an UNICAM 939 spectrometer. The specific surface area and average pore diameter of the catalysts were derived from N_2 adsorption–desorption measurements carried out at liquid nitrogen temperature using a PMI automated BET sorptometer. Prior to the measurements, all samples were outgassed at 523 K for 20 h. The specific surface areas and the micropore and mesopore distributions were calculated applying the BET and BJH models, respectively.

2.3. MAS-NMR spectroscopy

The catalyst samples were packed at ambient conditions into 4-mm ZrO_2 rotors for the ^{27}Al NMR experiments. The spectra were obtained with a Bruker Avance AMX 400 NMR spectrometer operating at 104.263 MHz for aluminum. Solid $(NH_4)Al(SO_4)_2$ ($\delta_{Al} = -0.59$ ppm) was used as standard for the chemical shifts [20].

2.4. IR spectroscopy

IR spectra of adsorbed pyridine were used to characterize acid sites, while the spectra of adsorbed CO were used to characterize the properties of the metal surface. The adsorption of pyridine was studied with a Perkin Elmer 2000 spectrometer using a resolution of 4 cm^{-1}. Prior to the sorption experiments, the catalyst samples were activated in vacuum ($p = 10^{-6}$ mbar) at 673 K for 1 h. The samples were exposed to pyridine ($p_{(Pyd)} = 10^{-2}$ mbar) at 423 K for 0.5 h and outgassed in vacuum for 1 h. The spectra recorded after this treatment correspond to pyridine adsorbed on weak and strong acid sites. Subsequently, the samples were heated at 673 K in vacuum for 1 h and a second series of spectra was collected, which correspond to pyridine adsorbed on strong acid sites. The concentration of weak acid sites was determined by subtracting the spectra taken after high-temperature treatment from the corresponding spectra taken at 423 K. The concentration of Lewis (LAS) and Brønsted (BAS) acid sites was quantified using the molar extinction coefficients of 0.965 cm μmol^{-1} for LAS and 0.726 cm μmol^{-1} for BAS.

The CO adsorption experiments were performed with a Bruker ISF88 spectrometer using a resolution of 4 cm^{-1}. Samples of the catalysts were reduced in H_2 at 623 K for 1 h at a pressure 1 bar followed by outgassing in vacuum ($p = 10^{-6}$ mbar) for 1 h to remove the adsorbed hydrogen. The samples were cooled to 313 K, and CO was adsorbed at 0.5 mbar. Subsequently, the sample was evacuated for 15 min at 10^{-6} mbar, and an additional spectrum was recorded.

2.5. Transmission electron microscopy

The catalyst samples treated in H_2 (623 K for 2 h) were ground, suspended in ethanol, and ultrasonically dispersed. Drops of the dispersions were applied on a copper grid-supported carbon film. A JEM-2010 JEOL transmission electron microscope operating at 120 kV was used to perform the measurements.

2.6. X-ray absorption spectroscopy

X-ray absorption spectra were collected at the beamlines X1 and C at HASYLAB, DESY, Hamburg, Germany. The storage ring was operated at 4.5 GeV at an average current of 100 mA. The Si (3 1 1) double-crystal monochromator was detuned to 60% of the maximum intensity to minimize the intensity of higher harmonics in the X-ray beam. The samples were prepared as self-supporting wafers and reduced in situ with H_2 at 588 K for 1 h and then flushed with He at 588 K for 0.5 h to remove adsorbed H_2. The X-ray absorption spectra were collected at the Pt L_{III} edge (11,564 eV) and the Pd K edge (24,365 eV) at 77 K. The position of the edge was calibrated using the spectra of a simultaneously measured Pt or Pd foil. For the EXAFS and XANES analysis, the scattering background was subtracted using a polynomial function and all spectra were normalized to unity. The VIPER and XANDA programs were used for analyzing the datasets [21].