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Applied Catalysis A: General 320 (2007) 144–151

APPLIED CATALYSIS A: GENERAL

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The effects of iron addition to Pd/C and Pd + Pt/C catalysts on the selective hydrogenation of nitric acid in the presence of GeO_2

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Received 5 September 2006; received in revised form 10 January 2007; accepted 15 January 2007
Available online 18 January 2007

Abstract

Upon the selective catalytic hydrogenation of nitric acid to hydroxylamine, the promotion effect of one or more additional metals on Pd/C or Pd + Pt/C system in the presence of GeO_2 has been investigated. Among various metal elements used here, iron was found to be particularly effective for improving the catalytic activity on both the Pd/C and Pd + Pt/C systems as well as the selectivity on the Pd + Pt/C system. The new iron-doped multimetallic catalyst system is a promising alternative to the currently used catalyst system due to its excellent ability to convert the nitric acid into hydroxylamine.
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Keywords: Nitric acid; Selective hydrogenation; Hydroxylamine; Pd/C; Fe-doping

1. Introduction

Hydroxylamine has been used as an important chemical product in the field of polymers, rubber chemicals, electrochemistry, agriculture products, food chemistry, and drugs. It is frequently used as a starting material for manufacturing ε-caprolactam [1–3], which is one of the most widely used chemical intermediates. Nylon-6 polymers are by far the largest outcome from ε-caprolactam [3,4]. The global demand for ε-caprolactam continuously increased from ca. 3.5 million metric tonnes in 2001, and then reached roughly 4.0 million metric tonnes in 2005. Today, due to such a growing demand of ε-caprolactam particularly in Asia [1,3], more efficient methods for producing ε-caprolactam are significantly required in order to increase the productivity and reduce the cost. For the ε-caprolactam production, at least nine manufacturing processes have been industrially used in the world [1,3]. This intermediate is derived from the reaction of cyclohexanone with hydroxylamine to give cyclohexanone oxime, which undergoes a Beckmann rearrangement to yield ε-caprolactam. There are also new processes that do not use hydroxylamine [3,5–13], although they are not utilized as much as the hydroxylamine's one. The hydroxylamine required for this process is usually produced by the selective hydrogenation of nitric oxide or nitric acid with precious metal powder catalysts, for instance, by BASF and DSM technologies [3,14,15].

In the past, the precious metal sources as well as the promoters added in the catalytic system were extensively studied and reported [14–21]. In the course of this study, the Pd/C system promoted with GeO_2 was found to be one of the most effective systems and it has been successfully employed on an industrial scale [15,22]. Nevertheless, industry still requires more effective techniques for the manufacturing of hydroxylamine, though there have been very few studies in the literature for this process. Furthermore, most of these studies were not focused on the catalyst system, but rather on the lifetime, the filtration system, and storage condition of the catalyst [23–26].

Therefore, we were prompted to improve the catalyst system. We have examined the effects of additional promoters with the most common Pd/C + GeO_2 and Pd + Pt/C + GeO_2 systems [15,16]. As a result of this investigation, we have found

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doi:10.1016/j.apcata.2007.01.028

that iron was particularly effective for the enhancement of catalytic activity on both Pd/C and Pd + Pt/C systems as well as the selectivity of the Pd + Pt/C system. This paper deals with the results of these hydrogenation experiments with the new multimetallic catalysts and the plausible reaction mechanism.

2. Experimental

2.1. Preparation of catalysts

Multimetallic catalysts for the investigation on effects of various promoters were prepared from a general 10% palladium on carbon catalyst (commercially available from Degussa Japan Co., Ltd. [27], E 1533 R/W 10%Pd) with various metal promoters such as manganese, cerium, iron, copper, ruthenium, rhodium, and platinum. These promoters were fixed onto the palladium on carbon catalyst in aqueous media by sequential precipitation. For instance, a promoter metal chloride was added to the catalyst slurry in aqueous media, and then most of the metal cation was converted into the corresponding neutral metal form on the surface of catalyst in the presence of reductants such as formaldehyde or hydrazine. The total amount of promoters loaded was adjusted in the range of 0.5–7 wt% based on the catalyst.

2.2. Characterization of catalysts

2.2.1. CO chemisorption

In order to compare the accessible precious metal sites on each catalyst, CO chemisorption measurements were carried out at room temperature using a general pulse gas flow technique with Quantachrome ChemBET-3000 [28]. Each catalyst was pre-treated by exposing it to flowing hydrogen at 473 K for 30 min, followed by a helium purge at 473 K for 10 min prior to the measurement. A detail description regarding the measured CO chemisorption is given in Section 3.3.

2.2.2. TEM/EDX analysis

High resolution TEM analysis was performed on a JEOL 2010-F instrument equipped with an EDX system of NORAN SYSTEM 6.

The operation of TEM analysis was done by operating at emission of 200 kV field, downing resolution to 0.12 nm units.

The EDX spectra were obtained by focusing the electron beam on the selected area and accumulating the spectra, downing to nano scale structures. The detection limit of EDX-analysis is about ca. 0.2 at% related to the analyzed volume. The Cu-peaks in the EDX-Spectra result from the TEM-sample holder.

A detail description regarding the analyzed TEM/EDX is reported in Section 3.4.

2.3. Catalytic hydrogenation of nitric acid to hydroxylamine

The main reaction and possible side reactions are shown in Scheme 1. The catalytic hydrogenation of nitric acid was performed as follows:

Main reaction

$$NO_3^- + 3H_2 + 2H^+ \rightarrow NH_3OH^+ + 2H_2O$$

Examples of possible side reactions

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$$

$$2NO_3^- + 4H_2 + 2H^+ \rightarrow N_2O + 5H_2O$$

$$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$$

Scheme 1. Hydrogenation of nitric acid to hydroxylamine.

In a 1-L three-necked flask, the catalyst (750 ± 1 mg) was suspended in a buffered solution (1 L) composed of 85% H_3PO_4 (331 g), $NaNO_3$ (198 g), NaOH (84 g), and GeO_2 (2.625 mg which corresponds to 0.24 wt%-Ge doping) dissolved in ion-exchange water. The suspension was stirred under a hydrogen flow of 150 L/h at 30 ± 0.2 °C for 30–120 min.

In order to determine the hydroxylamine yield and selectivity in the hydrogenation of nitric acid, the aliquots were taken from the flask in a 30 min interval (usually 4 times during 90 min of reaction time including the point at 0 min for the blank analysis), and then the amounts of hydroxylamine produced and total H^+ consumption were analyzed by titrating the obtained sample with 0.1 M aqueous potassium hexacyanoferrate (III) solution and 0.1 M aqueous NaOH solution, respectively. The hydroxylamine yield, defined as ‘‘(g of hydroxylamine produced/g of Pd metal)/h’’, was determined from the production of hydroxylamine, and the selectivity, defined as ‘‘(mmol of hydroxylamine produced/mmol of total H^+ consumption) × 100’’, was determined from the total H^+ consumption.

3. Results and discussion

3.1. Promoter effect on Pd/C system combined with GeO_2 in hydrogenation of nitric acid to hydroxylamine

In order to investigate the third promoter effect on the selective hydrogenation of nitric acid to hydroxylamine on the Pd/C system combined with GeO_2, various metal elements were employed as promoters. Table 1 summarizes the hydroxylamine yield, selectivity, and catalytic activity in each case, which are defined as ‘‘(g of hydroxylamine produced/g of Pd metal)/h’’, ‘‘(mmol of hydroxylamine produced/mmol of total H^+ consumption) × 100’’, and ‘‘(mol of nitric acid consumed/g of Pd metal)/h’’, respectively. As the definition suggests, the catalytic activity includes the conversion into by-products as well as the desired hydroxylamine.

Most of the metal-doped Pd/C systems combined with GeO_2 showed comparable or low hydroxylamine yield compared to that in non-doped Pd/C system combined with GeO_2 (Entry 1). In the cases of ruthenium, rhodium, and sulfur, the

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