Tetrahedron 70 (2014) 6050–6054

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Active Pd/Fe(OH)$_x$ catalyst preparation for nitrobenzene hydrogenation by tracing aqueous phase chlorine concentrations in the washing step of catalyst precursors

Chengming Zhang[a,b], Xinjiang Cui[a], Youquan Deng[a], Feng Shi[a,*]

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No. 18, Tianshui Middle Road, Lanzhou 730000, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 18 November 2013
Received in revised form 13 February 2014
Accepted 20 February 2014
Available online 28 February 2014

Keywords:
Chlorine
Heterogeneous catalysis
Catalyst preparation
Nitrobenzene
Hydrogenation

ABSTRACT

By tracing the chlorine concentrations in the aqueous solutions containing the catalyst precursors, Pd/Fe(OH)$_x$ catalysts with different activities can be controllably prepared. For the hydrogenation of nitrobenzene, the active Pd/Fe(OH)$_x$ catalysts were obtained from aqueous solutions with chlorine concentrations below 18 ppm and above 8 ppm.

1. Introduction

It is widely accepted that the presence of chlorine in noble metal catalysts, especially nano-gold catalysts, normally results in aggregation of nano-scale particles, and the chlorine is also possibly adsorbed on the active sites of the catalysts and then leads to dramatic loss of catalytic activity or complete deactivation.[1–4] Therefore, in order to gain highly active catalysts, the operation of total removal of chlorine from the catalyst is often preferentially considered.[2–6] However, the presence of chlorine in the catalysts is not always detrimental to obtain active catalyst. As an example, if the chlorine was maintained in the catalyst precursor without washing in the preparation of Au/FeO$_x$ with co-precipitation method, the catalyst can also be active in CO oxidation reaction if it was dried at low temperature (<200 °C) and no further calcination at relatively high temperature.[7] Furthermore, it was also reported that for some reactions, the presence of chlorine in the catalysts was favorable to improve the activity. For instance, the powdered Fe_2O_3 treated with chloride ion exhibits appreciable high activity for the photo-adsorption of NO, whereas the pure iron oxide does not.[8] Based on the silver catalyzed partial oxidation of ethylene to ethylene epoxide (EO), periodic density functional theory calculations proved that chlorine was the best promoter in halogen group.[9] For the styrene epoxidation on Au(111), the introduction of chlorine significantly enhanced the selectivity of styrene oxide, and the rate of styrene oxide formation was increased, too.[10] During the exploration of Au/Fe_2O_3 catalyst preparation with co-precipitation method, we have found that the activity of Au/Fe_2O_3 catalyst for CO oxidation varied with the chlorine concentration of the aqueous solution containing the catalyst precursors.[11] By tracing the chlorine concentration, we found that the catalytic activity for CO oxidation reached the maximum at an appropriate chlorine concentration. Consequently, we conjecture that this experience may also be applicable to other catalyst systems.

As an important intermediate in chemical industry, the syntheses of aromatic amines have been studied for long time. Except the traditional route using iron as reducing agent,[12] a series of heterogeneous catalysts, such as supported Pd and Pt have been developed and nice results were obtained in the catalytic hydrogenation of nitrobenzene in the presence of molecular hydrogen.[13–19] The catalytic hydrogenation of nitrobenzene using polymer anchored Pd(II) complexes as catalyst was also reported.[20] Moreover, other supported nano-Pd catalysts stabilized by surfactants,[21] dendrimers,[22] ionic liquids,[23,24] and polyvinylpyridine[25] were used in various fields and exhibits excellent performance, too.

In this work, the catalytic hydrogenation of nitrobenzene was used as a model reaction to study whether the activity of supported

---

* Corresponding author. E-mail address: fshi@licp.cas.cn (F. Shi).

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.02.057

nano-Pd catalyst can be varied by tracing the chlorine concentrations of the aqueous solutions during the washing of the catalyst precursors without any other stabilizer. A series of Pd/Fe(OH)$_x$ catalysts were prepared by tracing the chlorine concentrations of the aqueous solutions containing the catalyst precursors with reduction-precipitation method. To our delight, active Pd/Fe(OH)$_x$ catalysts for nitrobenzene hydrogenation can be obtained when the chlorine concentrations are below 18 ppm and above 8 ppm while less active catalysts will be produced when it deviates from this range.

2. Results and discussion

2.1. Catalytic activity measurement

38 samples of Pd/Fe(OH)$_x$ catalyst were prepared from aqueous solutions with chlorine concentrations in the range of 0–250 ppm with several batches. The activity of the catalyst samples were tested by the hydrogenation reaction of nitrobenzene and the results were shown in Fig. 1. Clearly, there is a peak area in the catalytic hydrogenation activity, i.e., catalyst samples prepared from 8 to 18 ppm chlorine concentrations possessed the best catalytic performance, which normally generated >90% yields to aniline. Furthermore, there are two boundaries related to the decrease of catalytic activity. One side which slope is more sharply is 6–8 ppm, and the other side which slope is more gently is 18–50 ppm. Also, when the chlorine concentration is higher than 80 ppm, the hydrogenation activity of Pd/Fe(OH)$_x$ remains stable. In this range, the effect of chlorine or washing operation might reach the maximum and therefore the catalytic activity didn't vary.

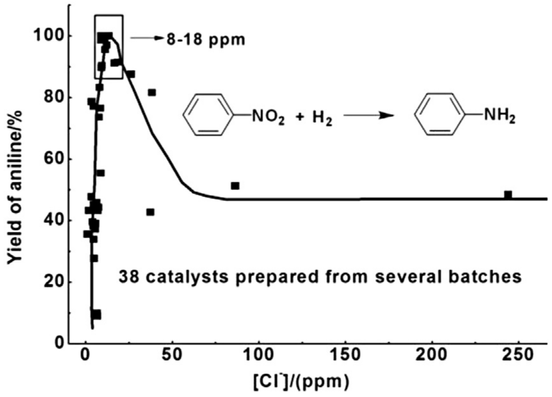

Fig. 1. The yield to aniline versus the chlorine concentration of the aqueous solution during catalyst preparation.

It is easy to understand the decrease of catalytic activity when the chlorine concentration is in the range of 18–50 ppm because it is a common sense that the presence of chlorine might poison the active site. The remarkable dropping in catalytic activity is uncommon if further remove the chlorine when its concentration in aqueous solution is <8 ppm. As it was shown in the experimental section, the only difference in these samples was that they were prepared from different amount of aqueous solutions with different chlorine concentrations. So the different activity of these catalysts might be derived from the different chlorine concentrations or the washing operation.

2.2. Characterization of the catalysts

In order to explore the influence of washing step on catalyst structure, three catalyst samples including Pd/Fe(OH)$_x$-4.2, Pd/Fe(OH)$_x$-9, and Pd/Fe(OH)$_x$-48, with which the yields to aniline were 39%, 99%, and 50%, were characterized by ICP-AES, XPS, and BET. The results were given in Table 1. The Pd loadings of these samples are 1.4%, 1.5%, and 1.6%, respectively. Fe(OH)$_x$-0 has the highest BET surface area, i.e., 263 m^2/g. When Pd was loaded and chlorine was introduced, the BET surface area decreased slightly. The BET surface areas of Pd/Fe(OH)$_x$-4.2, Pd/Fe(OH)$_x$-9, and Pd/Fe(OH)$_x$-48 are 258, 246, and 239 m^2/g, respectively. These results are in agreement with the reports by Liu and co-eworkers.[26] Furthermore, a remarkable difference was observed from the chemical state of Pd species according to the XPS spectra as shown in Fig. 2. The Pd species of Pd/Fe(OH)$_x$-4.2 were a mixture of Pd^0 and Pd^{2+} with a ratio of about 1.2:1. Whereas, the amount of Pd^0 decreased in samples Pd/Fe(OH)$_x$-9 and Pd/Fe(OH)$_x$-48 and the corresponding ratios were about 0.9:1 and 0.7:1. After reaction, the ratio of Pd^0 and Pd^{2+} of Pd/Fe(OH)$_x$-4.2 and Pd/Fe(OH)$_x$-48 increased to 3.7:1 and 4.9:1. But the ratio of Pd^0 and Pd^{2+} in Pd/Fe(OH)$_x$-9 only increased to 1.6:1. These results suggested that chlorine concentration of the aqueous solution or the different washing operation can mediate the properties of the catalysts and then obtain the active catalyst with specific palladium species. If considering the results of catalytic reaction together with the characterization results, we can conclude partially that suitable BET surface area and suitable Pd^0/Pd^{2+} ratio might be important for the high activity and the active catalyst can be obtained by controlling the chlorine concentrations of the aqueous solutions in the range of 8–18 ppm.

Table 1
Physicochemical properties of catalyst samples

Entry	Catalysts	Pd/wt %[a]	Pd^0/Pd^{2+} [b]	S_{BET}/m^2/g	[Cl$^-$]/%[b]
1	Fe(OH)$_x$-0	0	—	263	0
2	Pd/Fe(OH)$_x$-4.2	1.4	1.2(3.7)	258	0.94
3	Pd/Fe(OH)$_x$-9	1.5	0.9(1.6)	246	1.08
4	Pd/Fe(OH)$_x$-48	1.6	0.7(4.9)	239	1.48

[a] Determined by ICP-AES.
[b] Determined by XPS. The numbers in the brackets are obtained from the used catalysts.

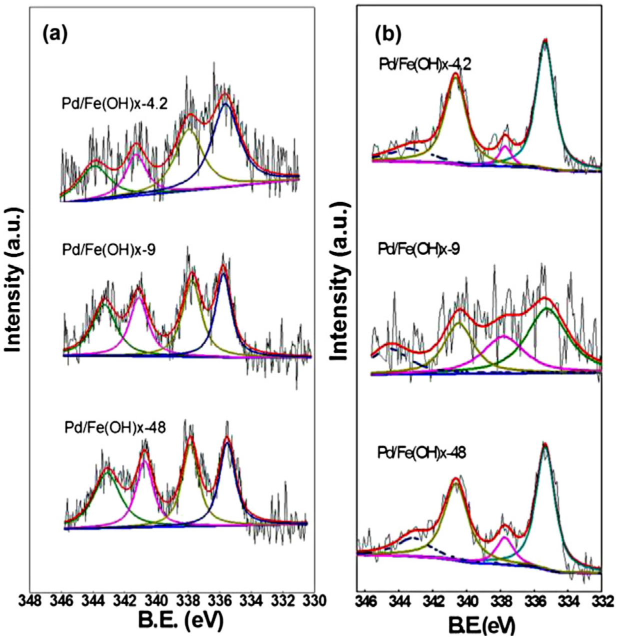

Fig. 2. XPS spectra of Pd/Fe(OH)$_x$-Y before (a) and after (b) reaction.

Following, the detailed results of nitrogen adsorption-desorption study of Pd/Fe(OH)$_x$-4.2, Pd/Fe(OH)$_x$-9, and Pd/Fe(OH)$_x$-48 were given in Fig. 3. All samples showed well-pronounced H_1 type hysteresis loops above P/P_0=0.8. The hysteresis loop of Pd/Fe(OH)$_x$-9 is distinctly different from the other