

Green Chemistry Route for Selective Oxidation of Cyclohexane to Adipic Acid Using Bimetallic Gold Catalysts

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Introduction

The selective oxidation of cyclohexane (CH) is an industrial important reaction due to the fact that its oxidation products cyclohexanol and cyclohexanone (KA-oil) are adipic acid (AA) precursors. AA has a large industrial application in the Nylon-6 and Nylon-66 manufacture. AA is commercially obtained in a two-step oxidation of CH by i) oxidation of CH to produce KA oil, and ii) further oxidation to AA by nitric acid [1]. However, this process is environmentally unfriendly since a large amount of nitrogen oxides (N_2O and NO_x) are obtained. Therefore, it is indeed very advantageous to explore different possibilities to develop one-step process for the direct synthesis of AA from CH without producing NO_x . Such approach is also an important issue from the green chemistry point of view. In this communication, we made attempts to provide a direct method for producing AA in a single step with acceptable selectivity using different gold-containing bimetallic catalysts.

Experimental

Catalyst preparation involves two steps. In the first step, $HAuCl_4$ was dissolved in 60 mL distilled water. In the second step, required amount of $PdCl_2$ solution (M) was dissolved in 10 mL of distilled water. This solution was heated to 50 °C for 10 min and few drops of HCl were added to completely dissolve the $PdCl_2$ precursor. The solution was then added to the gold chloride solution that prepared in the first step followed by the reduction of bimetallic solution using a mixture of 1% tannic acid and 1% of sodium citrate under stirring at 60 °C. After that, the resulting materials from step-1 and -2 were deposited onto a suitable oxidic support (e.g. TiO_2). Afterwards, the resulting slurry was stirred for 2 h at r.t. and then the excess solvent was removed on rotavapor. The obtained solid was oven dried at 120 °C for 16 h and then calcined at 350 °C for 5 h in air. The catalysts were characterized by different methods such as BET surface area, XRD, TEM etc. Catalytic tests were carried out using Parr autoclave (100 mL), which was loaded with 0.3 g catalyst, 2 g of CH, 10 g of CH_3CN (as solvent), and 0.1 g of tert-butyl hydroperoxide (TBHP) under 10 bar of O_2 , in general. Products were collected at different intervals and analyzed by gas chromatograph (Agilent 6890 N).

Results and Discussion

TEM image of Au-Pd catalyst indicates that the particles supported on TiO_2 are nearly spherical and the average size ranges between 1 nm to 4 nm. The (111) lattice spacing is also determined to be 0.234 ± 0.01 nm. Bulk Au and Pd have lattice spacing of 0.236 and 0.225 nm, respectively.

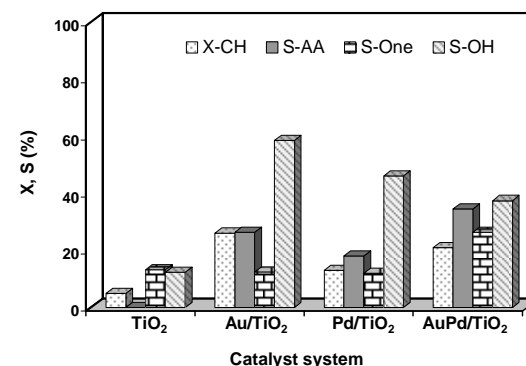


Figure 1. Comparison on the catalytic activity of the mono-metallic (Au or Pd) and bi-metallic (Au-Pd) catalysts in the oxidation of CH (X = Conversion; Y = Yield; S = Selectivity).

To investigate the influence of second-metallic element (i.e. bimetallic system) in the catalytic performance for the oxidation reaction of CH, a set of experiments were also performed under identical reaction conditions. For these tests, different catalysts such as pure TiO_2 support, monometallic systems (e.g. 1% Au/TiO_2 and 1% Pd/TiO_2) and bimetallic system (1% Au-1% Pd/TiO_2) were used. The results of these investigations are portrayed in Figure 1. As expected, the pure TiO_2 is found to show the poorest performance, while the Au/TiO_2 displayed improved catalytic activity as mentioned above (i.e. X-CH = ca. 25%, and S-AA = 26%) [2]. In addition, the monometallic Pd catalyst (i.e. Pd/TiO_2) exhibit somewhat inferior performance (X-CH = 16%, S-AA = 18%) compared to Au/TiO_2 solid. Interestingly, the combination of Au and Pd ($Pd-Au/TiO_2$) markedly improved the selectivity of AA from 26 to ca. 34 %, which is almost double to the S-AA obtained on Pd/TiO_2 and also remarkably higher even when compared to monometallic Au/TiO_2 catalyst. However, the conversion of CH (X = 21 %) obtained on bimetallic $Pd-Au/TiO_2$ is significantly higher than monometallic Pd/TiO_2 but slightly lesser than monometallic Au/TiO_2 sample. In summary, it can be stated that the product distribution depends on the type of noble metal used. Furthermore, bimetallic catalysts display improved selectivity of AA compared to its mono-metallic parent sample.

References.

1. P.V. Saji, C. Ratnasamy, S. Gopinathan, U.S. Patent No. 6,392,093, B1, (2002).
2. A. Alshammari, A. Köckritz, V. N. Kalevaru, A. Martin, EU Patent filed (2010).