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Highly selective formation of imines catalyzed by silver nanoparticles supported on alumina

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ABSTRACT

The oxidative dehydrogenation of alcohols to aldehydes catalyzed by Ag nanoparticles supported on Al_2O_3 was studied. The catalyst promoted the direct formation of imines by tandem oxidative dehydrogenation and condensation of alcohols and amines. The reactions were performed under mild conditions and afforded the imines in high yield (up to 99%) without any byproducts other than H_2O. The highest activity was obtained over 5 wt% Ag/Al_2O_3 in toluene with air as oxidant. The reactions were also performed under oxidant-free conditions where the reaction was driven to the product side by the production of H_2 in the gas phase. The use of an efficient and selective Ag catalyst for the oxidative dehydrogenation of alcohol in the presence of amines gives a new green reaction protocol for imine synthesis.

1. Introduction

In recent years there has been rising demand for efficient solid catalyzed processes for the oxidation of alcohols for the production of fine and bulk chemicals [1]. Much effort has been devoted to the development of aerobic oxidation methods using molecular oxygen or air as the oxidant. Compared to the use of high valence inorganic metal oxides, such as chromate or permanganate, these methods are very attractive because oxygen is a cheap and abundant oxidant that produces water as the only byproduct [2].

Another attractive alternative is the oxidant-free dehydrogenation of alcohols to carbonyl compounds and molecular hydrogen [3]. Although tremendous advances have been achieved in the dehydrogenation of alcohols with homogeneous platinum-group metals [4–7], only a limited number of similar solid catalysts that are effective under mild reaction conditions, have appeared to date. Recently, Kaneda et al. [8] used Ag supported on hydrotalcite (Ag/HT) for the dehydrogenation of alcohols under oxidant-free conditions. The reaction afforded high yields of the corresponding carbonyl compounds at 130 °C with the co-production of H_2. Shimizu et al. [9] reported that Ag/Al_2O_3 showed higher catalytic activity than the conventional catalysts based on platinum group metals (such as Rh/Al_2O_3 and Pd/Al_2O_3), and suggested that the high activity was due to the presence of sub-nanometer sized Ag particles and the acidic and basic surface sites on γ-Al_2O_3. Furthermore, Shimizu et al. [10,11] showed that Ag/Al_2O_3 could be used for amide synthesis and also for the direct synthesis of secondary amines via intermediate imine formation by the borrowing hydrogen mechanism when it is used together with a strong Lewis acid co-catalyst. Liu et al. [12] showed that with Ag nanoparticles, secondary amines could be formed from alcohols and amines via intermediate imine formation by

the borrowing hydrogen mechanism. Similar reactions have also been shown possible with metals other than Ag [13,14]. Although reports on Ag catalyzed reactions is increasing, the application of supported Ag catalysts is still limited in liquid phase organic chemistry. Furthermore, the addition of additives such as a base is usually required to give high yields.

In this work, we showed that Ag supported on Al_2O_3 was an active and highly selective catalyst for the formation of aldehydes from alcohols without the use of additives. Furthermore, we showed that Ag/Al_2O_3 catalyzed the direct formation of imines by consecutive oxidative dehydrogenation and condensation of alcohols and amines as shown in Scheme 1.

The reactions were performed under mild reaction conditions with a number of different alcohols and amines, which demonstrated that the method was versatile and applicable to a broad range of substrates. Although the highest catalytic activity was obtained with 5 wt% Ag/Al_2O_3 in toluene using air as oxidant, the reaction also occurred under oxidant-free conditions where the reaction was driven to the product side by the production of H_2 in the gas phase [9].

2. Experimental

2.1. Catalyst preparation

A series of supported Ag catalysts were prepared by incipient wetness impregnation of the solid supports with an aqueous solution of $AgNO_3$ to give 1, 5, and 10 wt% Ag on the support. Before each reaction, the impregnated and dried catalysts were reduced with 10%H_2/N_2 in a tube oven for 2 h at 300 °C and a heating ramp of 5 °C/min.

The support materials investigated were various combinations of magnesium and aluminum oxides, including metal oxides (Al_2O_3 and $MgAl_2O_4$) and layered double hydroxides ($Mg_6Al_2(CO_3)(OH)_{16}$, hydrotalcite, HT). All supports were purchased from commercial sources (Saint-Gobain and Sigma Aldrich) and used without further purification or pretreatment. For comparison, 5 wt% Au/Al_2O_3 catalyst was prepared by the standard impregnation procedure. In addition, a HT-like catalyst was prepared by the co-precipitation of $AgNO_3$, $Mg(NO_3)_2$, and $Al(NO_3)_3$ in an aqueous alkaline solution of Na_2CO_3 and NaOH using a modified literature procedure [15]. The amounts of metal nitrates used were calculated to give a final composition of 5 wt% Ag. The metal nitrates were dissolved in water and added dropwise to the alkaline solution under vigorous stirring. After ageing for 24 h, the catalyst was collected by filtration, washed in water, and dried at 90 °C overnight. Finally, the catalyst was reduced using the standard procedure.

2.2. Characterization

N_2 physisorption was performed on a Micromeritics ASAP 2020 surface area and porosimetry analyzer. The samples were outgassed in vacuum at 200 °C prior to measurement. The specific surface area (S_{BET}) was calculated by the BET method. X-ray diffraction (XRD) analysis was carried out on a Huber G670 diffractometer operated in transmission mode with Cu
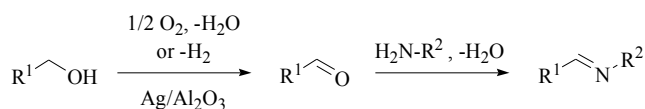
Scheme 1. Formation of imines by consecutive oxidative dehydrogenation and condensation of alcohols and amines using Ag/Al_2O_3 as catalyst.

$K_{\alpha1}$ irradiation from a focusing quartz monochromator. The sample was fixed on a piece of tape. Transmission electron microscopy (TEM) was performed on a FEI Tecnai T20 G2 microscope operated at 200 kV. All specimens were dispersed in ethanol and left to dry on the TEM grids at room temperature before the analysis. The diameter of the nanoparticles was estimated from the measurements of about 100 particles.

2.3. Standard oxidation procedure

In a typical experiment, alcohol (2.0 mmol), amine (2.0 mmol), anisole (internal standard, 0.2 mmol), and toluene (6.0 ml) was charged into a reaction tube and connected to the reaction station (Radley Carrousel 12 Plus). The reaction station provided stirring, heating and an atmosphere of Ar, O_2 or atmospheric air at ambient pressure. The reaction tube was flushed with gas, heated to the desired temperature and then 100 mg catalyst was added. Unless otherwise noted, the reactions were performed at 100 °C for 24 h.

During the reaction, samples of 0.1 ml were periodically collected, filtered and analyzed by GC-FID and GC-MS using a HP-5 column from Agilent Technologies Inc. The amounts of substrates and products were quantified using anisole as an internal standard. The conversions were calculated from the conversion of alcohol. The reported values were consistent with the corresponding values calculated from the conversion of amine within ±5%. The selectivity and yield were determined from the area of the product peak relative to the total area of all product peaks.

3. Results and discussion

3.1. Characterization

Table 1 shows the overview of the prepared catalysts. As expected, S_{BET} of all the catalysts were similar to those of the parent support, that is, the Ag loading only has a relatively small effect on the surface area.

The catalysts were also characterized by XRD. The results were as expected, but the co-precipitated HT-like catalyst displayed poor crystallinity. The diffraction peaks assigned to Ag on both the co-precipitated and impregnated catalysts were distinct. Figures 1–4 show TEM images and the size distribution of the nanoparticles of the 5 wt% Ag catalysts together with the XRD patterns.

The TEM results showed that the nanoparticle size distribution was relatively broad. As expected, the average size of the nanoparticles increased with the Ag loading. In general, the nanoparticles were evenly dispersed over the support and