Supported nano-gold a recyclable catalyst for aerobic oxidative dehydrogenation of amines to imines

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ABSTRACT: The aim of present work is to determine the catalytic activity of supported gold using ceria as main constituent of all supports used. The model catalysts $Au/CeO_2:TiO_2$ $Au/CeO_2:SiO2$, $Au/CeO_2:ZrO_2$ and $Au/CeO_2:Al_2O_3$ were prepared by deposition co-precipitation method and deposition of gold was determined by EDEX analysis. The supported nano-gold catalyzes the dehydrogenation of secondary amines to imines without loss of activity. On recycling good amount of product yield is obtained. Oxidation of secondary amines to imines is carried at 100˚C and almost 90 % conversion was obtained with >99% selectivity.

Introduction

Gold based catalysts attracted wide attention ever since Haruta et al., found that supported gold catalysts are highly active for the oxidation of CO at temperatures as low as -73˚C especially when deposited as nanoparticles on metal oxides [1-2].The catalytic activity of a gold catalyst does not depend on the size of the gold particles only, but also on the nature of the support material, the preparation method, and the activation procedure [3–6]. Support materials like transition metals and rare earth elements and their oxides provide high reactive surface area, thermal stability, higher dispersion of nano-metallic particles and longer catalyst life etc [7].

Imines are one of the basic building blocks of modern synthetic organic chemistry which can be prepared by using gold as catalyst as gold is used as strong oxidant in many oxidation reactions. Though the synthesis of aldimines is quite easy by using aldehyde and primary amines but the synthesis of many classes of imines is problematic e.g. ketimines (especially aryl ketimines) [8-10]. Its synthesis is difficult and it requires metal chloride, which is used as dehydrating agent to overcome the competing reverse reaction, but metal chloride generates HCl which leads to unwanted side reactions in many systems even in the presence of excess amine [11-12]. Stoichiometric methods utilizing strong oxidants such as Swern oxidation have the disadvantage of forming major amounts of side products [13-14]. So the oxidative dehydrogenation of secondary amines has been explored as an alternate route for the preparation of imines.

EXPERIMENTAL:

Catalyst prepration:

The first step is co-precipitation of metal oxide from metal nitrate solutions. A solution containing $Ce(NO_3)_3.6H_2O$(9.314 g) and $SiO(NO_3)_2$ (3.6052 g) is treated with a solution of NH_4OH at constant pH 9.0 and room temperature with constant stirring using mechanical stirrer. The resulting precipitates were aged at the same temperature for 12h, then filtered and washed until the removal of nitrate ions. The washed precipitate is dried at 100^0C and calcined under air at 500^0C for 5h. The support prepared in this way is denoted as CS. Similarly we prepared Ceria-titania (CT) using solution containing 8.6112 g Ce $(NO_3)_3.6H_2O$ and 3.7276 g $TiO (NO_3)_2$: Ceria-Zirconia (CZ) by using 7.3004 g Ce $(NO_3)_3.6H_2O$ and 3.915 g $ZrO (NO_3)_2$ and Ceria-alumina (CA) by using 7.9169 g Ce $(NO_3)_3.6H_2O$ and 6.8432 g Al $(NO_3)_3.9H_2O$. All solid supports are in the 1:1 molar ratio for $Ce_2O_3:M_2O_3$.

To prepare the catalysts Au/ CS, Au/ CZ, Au/ CT and Au/ CA, aqueous solution of $HAuCl_4.3H_2O$ was precipitated by adding 1N aqueous NaOH at constant pH and temperature upon mixed metal oxide preliminary suspended in water by mechanical stirring. The resulting precipitate was aged at room temperature for 12h, then filtered and washed carefully until complete elimination of Cl⁻ ions as detected by using silver nitrate as precipitating agent. The sample was dried at 80^0C and then calcined at 200^0C.The samples contain Au/ CS=1.01, Au/ CZ=1.15, Au/ CT=1.79 and Au/ CA=1.34 Wt% gold as determined by SEM EDEX method using instrument SEM Hitachi- S520, Japan; Oxford Link ISIS-300 UK with instrument operated at

98 eV resolution. The results were further confirmed by fluorescence X-ray crystallography using D8 – Advance, Bruker, Germany Multi Res-Vac34 method. Same method was used to determine Ce and the other metals which were found to be Ce=41.43 %and Si=20.32 % in Au/ CS, Ce=42.27 % and Zr=18.87 % in Au/ CZ, Ce=29.56 %and Ti=27.31% in Au/ CT, Ce=37.48 %and Al=24.20% in Au/ CA. The other constituents found were oxygen and minor impurities of Na, Ca, V, Rb and Th etc. The N2 BET surface areas of the powders were determined by N2 adsorption at liquid nitrogen temperature using a Micromeritics Gemini 2360 instrument. Prior to analysis, samples were oven dried at 393 K for 12 h and flushed with Argon gas for 2 h. The surface area thus found was 107 m^2/g for Au/CS, 101 m^2/g for Au/CA, 98 m^2/g for Au/CT and 87 m^2/g for Au/CZ

Catalytic tests:

The reactants used for the present work were of Analytical grade obtained from Fluka chemicals. The reactions were carried out in two neck glass reactor fitted with a condenser in one neck and other neck was closed by a rubber septum through which a syringe needle was passed to supply oxygen (O_2) from oxygen balloon. Reactant (0.1mmol) was dissolved in toluene (2 ml) in the reactor to which 50 mg of catalyst was added. Molecular oxygen was passed through syringe needle and the mixture was kept stirring using magnetic stirrer for 35h at 100° C. the reaction mass was filtered to remove the catalyst powder. Products of these reactions were identified by comparing their mass spectra and GC retention times with those of authentic samples. Yields were determined by GC using authentic samples of the products as calibrants.
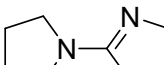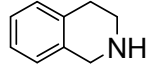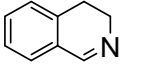
Scheme 1:
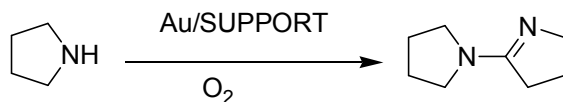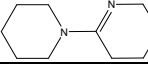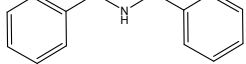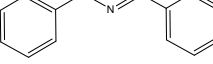
SUPPORT = 1.CeO_2:TiO_2, 2.CeO_2:SiO2, 3. CeO_2:ZrO_2, 4. CeO_2:Al_2O_3

Result and Discussion:

In this work, we selected conversion of secondary amines to imines as our model reaction to study the activity of ceria based mixed oxide supported nano-gold catalyst for selective oxidative dehydrogenation using molecular oxygen. The optimised catalyst i.e. Au/CT was tested up to four reaction cycles (fig. 1) with negligible loss in catalytic activity as well as selectivity which was regained by washing the catalyst by piranha [15] (3:1 concentrated sulfuric acid to 30% hydrogen peroxide solution). Almost 90 % conversion is achieved by using Au/CT which makes it clear that the catalyst Au/CT is most efficient catalyst among all the catalysts prepared in this study. On correlating the catalytic activity with the characterization of the catalysts it was observed that the surface area and the gold content are not in agreement with catalytic activity. On SEM EDEX and BET surface analysis it is observed Au/CS has highest and Au/CT has the lowest surface area among the as prepared catalysts, the metal deposition is maximum in

Au/CA and minimum in Au/CS. Au/CA although has higher gold content as well as surfaces area than Au/CT but has lesser commotion than latter. Making a look at CeO_2:MO_2 ratio it is clear that among all the four supports (or catalysts as a whole) the ratio is lowest for CT (Au/CT) and highest for CZ (Au/CZ), thus the catalytic activity is inversely proportional to the CeO_2:MO_2 ratio. Ceria-titania combination shows higher catalytic activity among all the four catalysts, which may be due to the lower CeO_2:MO_2 ratio, the best fit of Ti^{4+} into the CeO2 lattice (Ti=1.3 ^{o}A and Ce=1.1 ^{o}A) and high dispersion capacity of titania [15]. From the above discussion it can be proposed that the catalytic activity of supported gold is affected by CeO_2:MO_2 ratio of the catalyst support and its composition. Apart from the affect of the catalyst support, substrate also has an immense effect on the yield of the reaction as can be seen from table 1. that irrespective of the catalyst substrate 1 gives highest yield and that of 4 gives lowest yield.

Table 1: Gold-catalyzed oxidation of secondary amines to imines

S.NO	SUBSTRATE	PRODUCT	YIELD IN % Au/CT	YIELD IN % Au/CA	YIELD IN % Au/CS	YIELD IN % Au/CZ
1.			89	88	86	80
2.			85	83	82	80
3			78	75	72	72
4			71	66	64	59

Reaction conditions: amine, 2 mL of solvent, catalyst powder (50 mg), O_2 (1.0 L at 1 atm.) at 100°C for 35 h in toluene

It can be concluded that nano-gold supported on CeO_2-M_2O_3 is a suitable, efficient, and selective catalyst for the oxidative dehydrogenation of secondary amines to imines in aerobic conditions. It is also observed that support effects the deposition of metal and also the activity of the catalyst. This process is very selective, productive and the catalyst though is costly but it is recyclable which compensates the cost so we can propose that the process is economically beneficial.
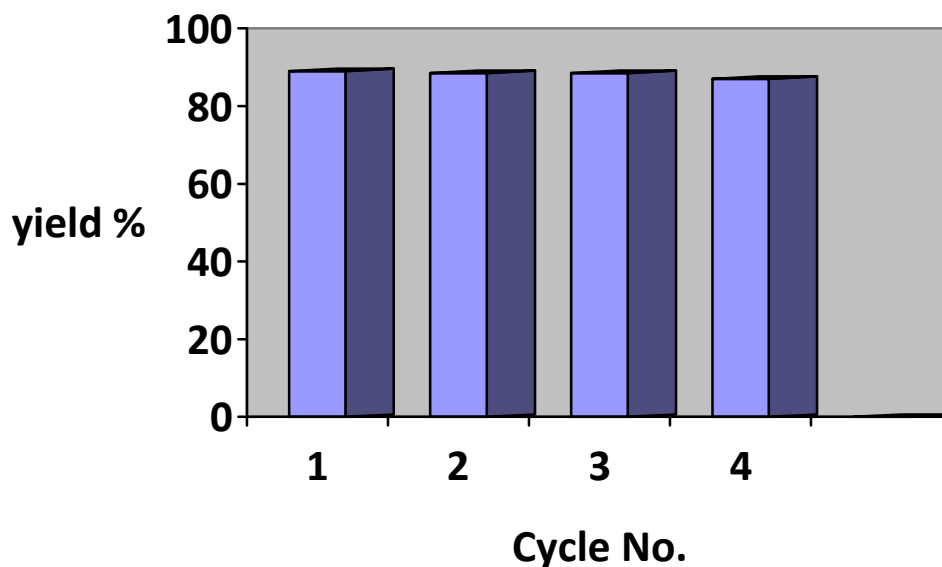
Figure 1. Reaction cycle of AU/CT catalyst

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