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Highly efficient transfer hydrogenation of 4-Methoxybenzaldehyde over supported silver nanoparticles

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ABSTRACT

Silver nanoparticles were simply synthesized via the reduction of silver salt using ascorbic acid as reducing agents. These silver nanoparticles were then embedded on the supports X (X = Bent, C, ZnO, Zeolit, and Al_2O_3) in high yield. The optical property of these catalysts was characterized by UV-Vis spectroscopy, the structure of Ag-X was studied by Powder X Ray Diffraction (PXRD), the distribution of Ag particles in X was studied by Transmission Electron Microscopy (TEM), the specific surface area of catalysts was evaluated by N_2 adsorption isotherms analysis at 77K. All results consisted to the loading method, indeed, TEM image indicated that the silver nanoparticles size is in range of 10÷15 nm and fully loaded into X. The efficiency of these catalysts was performed on the transfer hydrogenation of 4-methoxybenzaldehyde in the presence of potassium hydroxide as base at atmosphere pressure. The results showed that Ag-X exhibited high activities of up to 89.8% conversion within 60 min at 60 °C in the case of Ag-C catalyst.

Introduction

Transfer hydrogenation has been studied since 1897 [1,2], it is still attracting the attention of many researchers by its convenient and powerful method to access a variety of industrial applications from organic synthesis to fine chemicals [3,4]. Recently, a number of researches have been reported with high efficiency, excellent selectivity, long-term stability, and easy recovery when palladium [5–8] and nickel [9–11] catalysts were used.

However, not many publications have been found in the uses of silver nanoparticles, most of the researches focused on the hydrogenation of anthracenes [12], nitroarenes [13] and unsaturated substrates [14]. In an attempt to explore more the scope of catalytic processes available from embedded silver nanoparticles, we have tried to test the activity of silver catalyst in variety of organic synthesis reactions [15]. In which, transfer hydrogenation is one of the reactions of high industrial relevance, and silver is typically less active metal which required high hydrogen pressure and its limited ability to activate hydrogen compared to other metals [16]. Despite this, activating silver toward hydrogen splitting could help reduce the high temperature and pressure for this reaction.

Besides, immobilization of the metallic nanoparticles on solid materials has received a great interest because of their use in industrial application, especially hydrogenation of carbonyl compounds. Though nanomaterials serve as an excellent heterogeneous catalyst, often they need an additional support to

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acquire thermal stability. Therefore, varieties of materials like zeolites, aluminum oxides, aluminosilicates, silica gel, chitosan, activated carbon, zinc oxides, etc., have been used as supports for nanocatalysts [17–19]. Among these materials, activated carbon, bentonites, aluminum oxide, zeolites, and zinc oxide are widely used as catalyst and support for number of reactions as well.

This study focused on the preparation of silver nanoparticles embedded on the supports such as bentonites, zeolites, activated carbon, zinc oxide, and aluminum oxide. Catalytic activity was evaluated via the transfer hydrogenation of 4-methoxybenzaldehyde. The results will be presented in this report.

Experimental

Materials

Unless otherwise noted, all experiments were carried out in air. Reagent grade silver nitrate 99.8% ($AgNO_3$), aluminum oxide 99% (Al_2O_3), zinc oxide 99% (ZnO), 4-methoxybenzaldehyde 98%, and ascorbic acid 99% were purchased from Merck. Potassium hydroxide 98%, zeolite (white amorphous powder, Zeolit) was supplied by Himedia Laboratories. Polyvinyl pyrrolidone K-30 (PVP) were purchased from various Chinese suppliers. Bình Thuận bentonite (Bent) and activated carbon were purchased from the local suppliers. Absolute ethanol and isopropanol were supplied by Chemsol and used as received.

Characterization

The morphology of catalysts was examined by scanning electron microscope (SEM, JEOL series JSM-7401F). The X-ray diffraction (XRD) data of all samples was collected in a Bruker D8 powder X-Ray with Cu Kα radiation running at 35 kV/30 mA in the 2θ range $5^o \div 75^o$ with a step size of 0.2^o/min. Nitrogen adsorption–desorption isotherms were collected at 77K using Brunauer–Emmett–Teller calculation (BET, AUTOSORB-1C Quantachrome, for specific surface area), all the samples were degassed at 100 ^oC and 10^{-6} Pa. GC-MS were obtained by using an Agilent 7890A series model with an electron energy of 20 or 70 eV. UV-vis spectras were recorded on Agilent Cary 60 UV-Vis. All the catalytic tests were performed in Multireactors Carousel 12 plus.

Catalyst preparation

To the 250 mL two-necked round bottom flask, 0.4 g of PVP and 70 mL of deionized water (DI) were added. After stirring for 15 min, 0.34 g of $AgNO_3$ (2.0 mmol) was dissolved in the mixture at 80 ^oC. In another flask, 0.40 g of ascorbic acid in 50 mL of DI water were prepared. Then, the solution of reducing agent was dropwise added to the mixture of silver salt. The mixture was stirred for 6h until the black solution appeared.

The silver nanoparticles were then loaded into the supports X (X = Bent, C, Zeolit, and Al_2O_3 which were calcinated at 120 ^oC in 8h) in suitable amount by low pressure method at room temperature. This process was repeated several times to make sure all the metal nanoparticles were fully loaded into the supports. The obtained powders were dried at 80 ^oC under vacuum in 4h.

Catalyst evaluation

In this work, the catalytic activity of silver nanocatalysts was investigated via the hydrogenation of 4-methoxybenzaldehyde under liquid phase in the presence of potassium hydroxide. The catalytic evaluation of Ag-X was carried out in 20 mL multireactors with stirring at 60 ^oC under reflux condensation. In this process, 5.0 mol% of Ag-X was used in the hydrogenation of 4-methoxybenzaldehyde (5.0 mmol), isopropanol (IPA, 5.0 mL) and 1.0 mL of potassium hydroxide solution 5% in isopropanol. Hydrogen was directly connected through Schlenk line to the reaction at atmosphere pressure within 60 min. The conversion of substrate and selectivity of products were analyzed by GC and GC-MS (HP5 column 30 m x 0.25 mm, FID detector). Reproducibility was checked by repeating the measurement several times and was found to be within acceptable limits.

Results and discussion

Silver nanoparticles were simply synthesized by the reduction of $AgNO_3$ using ascorbic acid as reduction agents. In reality, there are many methods to reduce silver ion to metallic silver, for example A. Pyatenko and coworkers used weak acid like citric acid to reduce silver salt to silver nanoparticles within 1h at boiling temperature [20]. Thus, in this study, ascorbic acid was employed to easily reduce silver nitrate to silver nanoparticles as a green chemistry method. Furthermore, the obtained mixture is stable for a long time because silver nanoparticles were distributed in the PVP solution which is a well-known polymer with large molecular size and free electron couple on nitrogen site that is able to bond with silver nanoparticles, hence PVP acts as a protecting agent to avoid the agglutination and deposition of silver nanoparticles.

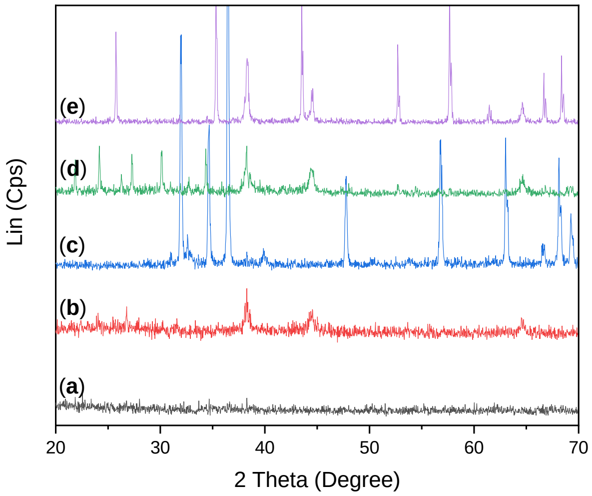


Figure 1: XRD patterns of a) Ag-Bent; b) Ag-C; c) Ag-ZnO; d) Ag-Zeolit; e) Ag-Al_2O_3

Figure 1 shows XRD pattern of the synthesized Ag-X. In which, Ag could be detected with diffraction peaks located at 2θ° = 38.27° and 44.41° correspond to the reflections of the (111) and (200) crystalline planes, which confirm the reduction of Ag^+ to Ag^0 [21]. Even though the peaks are quite weak because of the low concentration of metal particles in the samples (Figure 1a and 1c). Besides, the corresponding diffraction peaks of ZnO, Zeolit and Al_2O_3 located at the position of 2θ = 29.95°; 34.62°; 36.49°; 47.75°; 56.72°; 63.01°, 21.90°; 24.21°; 27.43°; 30.25°; 33.21°; 34.53°; 36.17°; 45.50°; and 25.90°; 35.43°; 38.04°; 43.61°; 52.92°; 57.77°; 66.80°; 68.42°, respectively. Meanwhile, C and Bent are amorphous lattice structure leading to the XRD patterns as noise at the baseline.

Table 1: Specific surface area and AAS analysis of catalysts

Catalysts	S_{BET} ($m^2.g^{-1}$)				
	Bent	C	Zeolit	ZnO	Al_2O_3
Blank	54	318	65	49	17
Ag	13	269	26	11	10
AAS (%Ag)	2.32	7.58	2.12	8.60	7.12

Besides, TEM images of Ag nanoparticles in Figure 2a show that these nanoparticles had a spherical morphology with an average particle size in the range of 10÷15 nm. On the other hand, X supported Ag in Figure 2b, 2c, and 2d described that almost the silver nanoparticles were well dispersed on the supports Al_2O_3, C, and ZnO, respectively. Furthermore, the morphology surface of catalysts was defined by SEM, in fact in Figure 3a, the surface of Ag-Bent was occupied by slit-shaped pores. Meanwhile, in Figure 3b-3e the spherical shapes of Ag were attached on the surface and inside the pores of supports. Especially, in Table 1, Ag-ZnO and Ag-Al_2O_3 have a low specific surface area about 11 and 10 m^2g^{-1}, respectively, which can be ascribed to that the large amount of Ag nanoparticles occupy inside of the supports (Figure 2c and 2e).

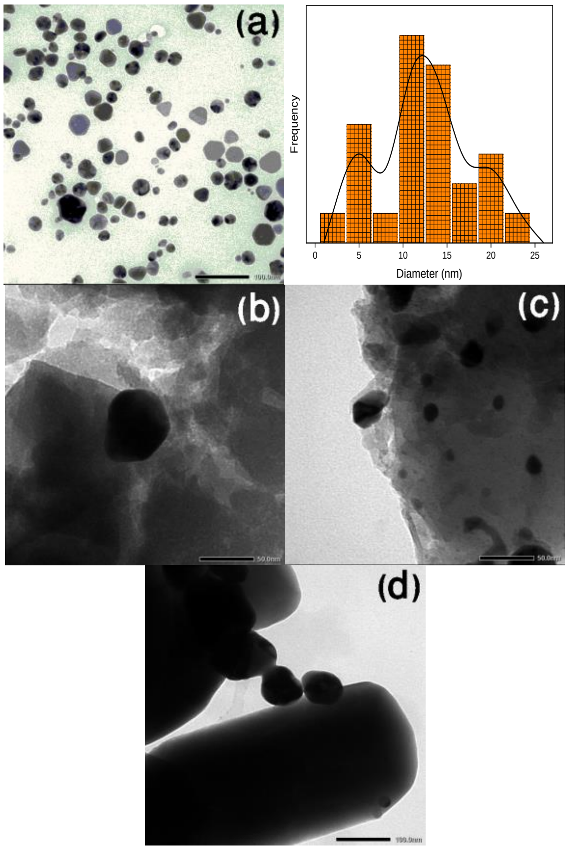
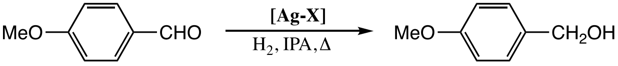


Figure 2: TEM image of a) Ag nanoparticles; b) Ag-Al_2O_3; c) Ag-C; d) Ag-ZnO

In order to evaluate the transfer hydrogenation efficiency of the catalysts, 5.0 mol% of Ag-X catalysts were used to hydrogenate the solution of 4-methoxybenzaldehyde in the presence of potassium hydroxide. The previous report indicated that the hydrogenation possessed the best activity in isopropanol at 60 °C within 1 hour [8]. Hence in this study, the transfer hydrogenation of 4-methoxybenzaldehyde was performed under similar condition. It is worth noting that all the catalysts give 100% selectivity of 4-methoxybenzyl alcohol as shown in Scheme 1, therefore this study did not mention the selectivity of the product.



Scheme 1: Transfer hydrogenation of 4-methoxybenzaldehyde

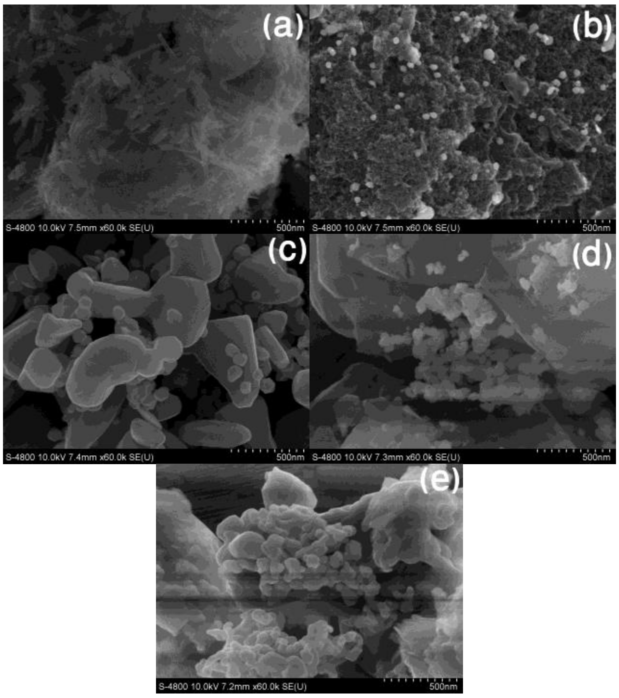


Figure 3: SEM image of a) Ag-Bent; b) Ag-C; c) Ag-ZnO; d) Ag-Zeolit; e) Ag-Al_2O_3

As far as we know, the silver catalyst is often effective in the hydrogenation reaction of levulinic acid [2], anthracenes [12], nitroarenes [13] as mentioned above. In this study, we report the transfer hydrogenation of 4-methoxybenzaldehyde as an probe activity of supported silver nanoparticles.

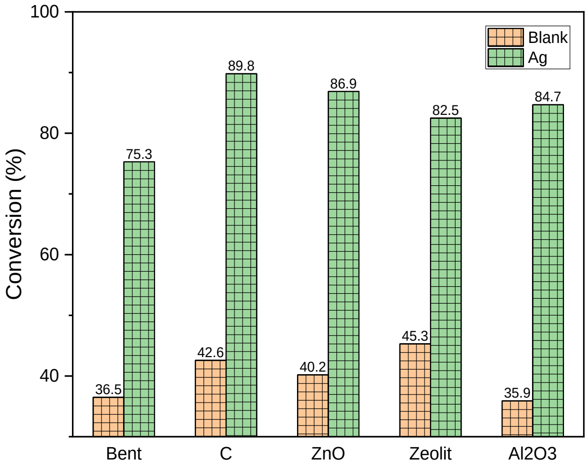


Figure 4: Conversion of 4-methoxybenzaldehyde over Ag-X catalysts

Furthermore, the support alone yielded low activity obtained the moderate conversion in a range of 35.9÷45.3%. Literally, as shown in Figure 4, carbon supported silver nanoparticles gave the highest efficiency reaching up to 89.8% conversion in the case of Ag-C catalyst. Likewise, 86.9, 82.5, and 84.7% conversion were observed in the cases of Ag-ZnO, Ag-Zeolit, and Ag-Al_2O_3, respectively. Except of Ag-Bent catalyst, it gave low activity, only 75.3% conversion was obtained. These could be explained in terms of the specific surface area of the catalysts as well as the concentration of the silver loaded on the supports as shown in Table 1. We could see that a higher Ag concentration increases the conversion of carbonyl substrate. On the other hand, in the reference [8], the same substrate was hydrogenated over palladium catalyst, 98% conversion and 99% selectivity was obtained within 1h at 60 °C. Whereas, Hengne and coworkers hydrogenated levulinic acid and formic acid to γ-valerolactone at 220 °C within 7h under Ag-Ni/ZrO_2 as catalyst, 99% conversion and 99% selectivity were observed [21].

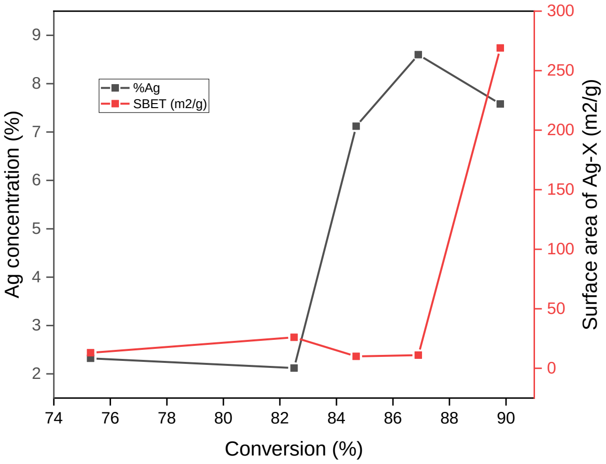


Figure 5: Influence of %Ag and surface area of catalysts on the conversion of 4-methoxybenzaldehyde

As illustrated in Figure 5, the silver concentration based on AAS analysis effected to the conversion of 4-methoxybenzaldehyde in the transfer hydrogenation in liquid phase. In reality, in the case of Ag-Bent, the lowest conversion was obtained when the %Ag and surface area were lowest 2.32% and 13 $m^2.g^{-1}$, respectively. The conversion was increased when the %Ag and surface area increased. Espectially, when the %Ag was rised up to 8.60%, the conversion was up to 86.9% while the surface area of catalyst was only 11 $m^2.g^{-1}$. That result revealed that the conversion was mostly effected by %Ag. Besides, the dispersion of silver nanoparticles on the support was effected to the activity of the catalyst as well, for example, the conversion was rising up to 89.8% in the case of Ag-C, as shown in the TEM image (Figure 2c), the silver nanoparticles were well dispersed on activated carbon. In sum, it is worth noting that silver catalytic hydrogenation exhibited an excellent conversion of carbonyl substrate in the presence of potassium hydroxide.

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Conclusion

We have demonstrated that ascorbic acid is one of the efficient reduction agents to converse all silver salt to metallic silver. Besides, silver nanoparticles were successful loaded into X in high yield (X = Bent, C, ZnO, Zeolit, and Al_2O_3). All the results were presented in detail. The catalytic activity of transfer hydrogenation of 4-methoxybenzaldehyde was performed in the presence of potassium hydroxide, in which 89.8% conversion was obtained in the case of activated carbon supported silver nanoparticles.

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