Catalysis Communications 117 (2018) 53–56

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Highly active and stable spinel-oxide supported gold catalyst for gas-phase selective aerobic oxidation of cyclohexanol to cyclohexanone

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ARTICLE INFO

Keywords:
Cyclohexanol
Cyclohexanone
Gold nanoparticles
Spinel oxides
Gas phase oxidation

ABSTRACT

Highly dispersed gold nanoparticles supported on Cu-doped spinel oxides were prepared by a simple deposition-precipitation method. The results indicate that Au/$MgCuCr_2O_4$ catalyst is very efficient for gas-phase oxidation of cyclohexanol to cyclohexanone, giving 69.5% and 86.4% yield of cyclohexanone at 260 °C and 300 °C, respectively. Deactivation was not observed in a 100 h stability test. This excellent performance can be correlated with the highly stable gold nanoparticles in the reaction deriving from the strong gold-support interaction and efficient Au—Cu synergy.

1. Introduction

Dehydrogenation of cyclohexanol (CH-ol) to cyclohexanone (CH-one) is an important industrial process as CH-one is a raw material for the production of nylon [1–5]. In current industrial practice, CH-one is produced through direct dehydrogenation of CH-ol over Cu- or Zn-based catalysts in the gas phase. However, direct dehydrogenation of CH-ol is limited by thermodynamic equilibrium under practical conditions. Typically, the catalysts used for this process suffer from deactivation due to deposition of heavy products [6–8], requiring frequent regeneration. These drawbacks can in principle be overcome if a suitable catalyst for the oxidative dehydrogenation of CH-ol to CH-one would be available. The oxidative dehydrogenation of CH-ol is not limited by thermodynamics and the use of an oxidant such as O_2 inhibits deposition of carbonaceous products on the catalytic surface.

There are only few reports in the open literature that discuss catalysts for gas-phase oxidative dehydrogenation of CH-ol. CuO-ZnO has been studied by Lin et al., but this catalyst deactivated rapidly because of the deposition of high-molecular-weight products on active sites [9]. Valente and co-workers encountered similar problems with ETS-10, likely due to the strong adsorption of heavy products in its micropores [10]. Mn-modified MCM-41 has also been evaluated for the title reaction by Santhanaraj et al. [11]. High reaction temperatures were needed to achieve a reasonable yield, which led to deactivation of the mesoporous silica catalyst due to steaming by co-produced water. To the best of our knowledge, there is no report of a highly active, selective and stable catalyst for the gas-phase oxidative dehydrogenation of CH-ol to CH-one.

The interest in supported gold nanoparticle catalysts for selective alcohol oxidation has increased remarkably in the past two decades [12–19]. Gold is effective in activating C—H bonds. As its activity in O—H bond activation is limited, often solid or soluble bases are used as co-catalysts [12,17,19]. Besides providing basic sites, the support may also play a role in oxygen activation, which is important as gold cannot strongly activate molecular oxygen [20]. Oxygen activation is often associated with redox properties of oxide supports, because oxygen vacancies can strongly adsorb molecular oxygen [21]. Another role of oxide supports is to stabilize small gold nanoparticles. Therefore, it is desirable to select a proper support to achieve a suitable gold-support synergy for selective oxidation reactions.

Among the various oxide materials used as supports for gold catalysis (e.g., titania, ceria, hydrotalcites) [12,16,17,22], spinel oxides have only been scarcely explored [20]. Spinel oxides with the general structure AB_2O_4 form an important class of inorganic materials in catalysis [23–27]. They usually exhibit excellent thermal stability and they can be made basic by using Mg^{2+} as an A cation, while surface redox properties can be introduced by doping with other transition metal cations. These redox properties can be beneficial for oxidation reactions [28]. Recently, Liu et al. have demonstrated that Au/$MgCuCr_2O_4$ is an efficient catalyst for the oxidation of ethanol to acetaldehyde [20]. This motivated us to explore the use of spinel-oxide-supported Au catalysts for the conversion of CH-ol.

2. Experimental

The spinel oxide supports, i.e., $MgCr_2O_4$, $(Mg_{0.75}Cu_{0.25})Cr_2O_4$,

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https://doi.org/10.1016/j.catcom.2018.07.019
Received 23 June 2018; Received in revised form 26 July 2018; Accepted 30 July 2018

$MgFe_2O_4$, $(Mg_{0.75}Cu_{0.25})Fe_2O_4$ and MgO and CuO were prepared by a coprecipitation-calcination method using metal nitrates as precursors. $(Mg_{0.75}Cu_{0.25})Cr_2O_4$ and $(Mg_{0.75}Cu_{0.25})Fe_2O_4$ were denoted as $MgCuCr_2O_4$ and $MgCuFe_2O_4$, respectively. Gold was deposited on the oxide supports via a deposition-precipitation method using urea as the precipitation agent. For the detailed information on materials preparation, catalysts test, as well as characterizations, see Suppporting Information (SI).

3. Results and discussion

Herein, we report our efforts to develop a catalyst for the oxidative dehydrogenation of CH-ol to CH-one using supported gold catalysts. $MgFe_2O_4$, $MgCr_2O_4$ and Cu-doped variations (Cu replaces partially Mg) were synthesized by a co-precipitation method. Although Au/$MgCuCr_2O_4$ displays the best performance in the selective oxidation of ethanol, we choose to study Cr replacement by Fe given the environmental safety concerns associated with Cr. Earlier work has already shown that $MgCuAl_2O_4$ can also be used for selective oxidation with gold, although it displays a lower performance, likely because of the weaker retention of Cu ions in the spinel structure [20]. CuO and MgO served as reference materials in the present study. Gold nanoparticles were loaded on these supports by a deposition-precipitation method targeting a loading of 1 wt%. The specific surface areas of the fresh catalysts were 26 m^2/g (Au/$MgFe_2O_4$), 29 m^2/g (Au/$MgCr_2O_4$), 25 m^2/g (Au/$MgCuFe_2O_4$), 10 m^2/g (Au/$MgCuCr_2O_4$), 30 m^2/g (Au/MgO), and 5.5 m^2/g (Au/CuO). Loading the supports with gold did not change the textural properties nor the crystal structure of the spinel oxide supports and no gold diffraction peaks were observed in the XRD patterns indicative of a high metal dispersion (Fig. S1).

Fig. 1 shows the catalytic performance of the different supported gold catalysts in the oxidative dehydrogenation of CH-ol at 260 °C. The evolution of the CH-ol conversion against time on stream is plotted in Fig. 1a. The two Cu-free spinel-based gold catalysts (Au/$MgCr_2O_4$ and Au/$MgFe_2O_4$) show stable but low conversion. Au/CuO can reach a conversion of ca. 40% and does not show any sign of deactivation after 24 h. Au/MgO presents the highest initial CH-ol conversion, which is however followed by a rapid deactivation. This rapid deactivation can probably be linked to the strong basicity of the support (Fig. S7). Au/$MgCuFe_2O_4$ and Au/$MgCuCr_2O_4$ show a different time-on-stream behavior. The CH-ol conversion increased slowly during the reaction and stabilized at ~50% and ~70%, respectively. These data demonstrate that the presence of Cu is essential to achieve a high and stable CH-ol conversion.

The stable CH-ol conversion and the product distribution are given in Fig. 1b. Minor by-products of the reaction are 2-cyclohexen-1-one, which is the dehydrogenation product of CH-one, and COx (mainly CO_2). In all cases, the selectivity to the desired CH-one product is higher than 96%. The CH-one selectivity for the most active Au/$MgCuCr_2O_4$ catalyst is 97.4% at a conversion of 71.4% (yield 69.5%). A very small amount of 2-cyclohexen-1-one is observed for this catalyst, while the COx selectivity is lower than 1%. Although the conversion for Au/$MgCuFe_2O_4$ is lower, its CH-one selectivity is slightly higher (98.4%), mainly because of the lower selectivity to the unsaturated by-product. Notably, Au/$MgCr_2O_4$ and Au/$MgFe_2O_4$ did not produce full combustion products, which may be due to the lower conversion. The highest selectivity to CH-one was observed for Au/MgO. It is also seen that the COx selectivity is the highest for the Au/CuO catalyst. Thus, the supported gold catalysts show good selectivity in activating the –CHOH moiety over the C—C bonds in CH-ol. The role of Cu is crucial to achieve a high CH-ol conversion.

In order to study the role of gold and O_2, we investigated the catalytic performance of $MgCuCr_2O_4$ with O_2 and Au/$MgCuCr_2O_4$ without O_2 (Fig. S3 and Fig. S4). These data show that the $MgCuCr_2O_4$ itself does not catalyze the reaction. This is indicative of a synergy between gold and Cu surface species. Without O_2 in the feed, the Au/$MgCuCr_2O_4$ catalyst shows a low activity and there is also a pronounced deactivation as the reaction proceeds. This result shows that O_2 or species derived from O_2 dissociation are involved in the catalytic cycle.

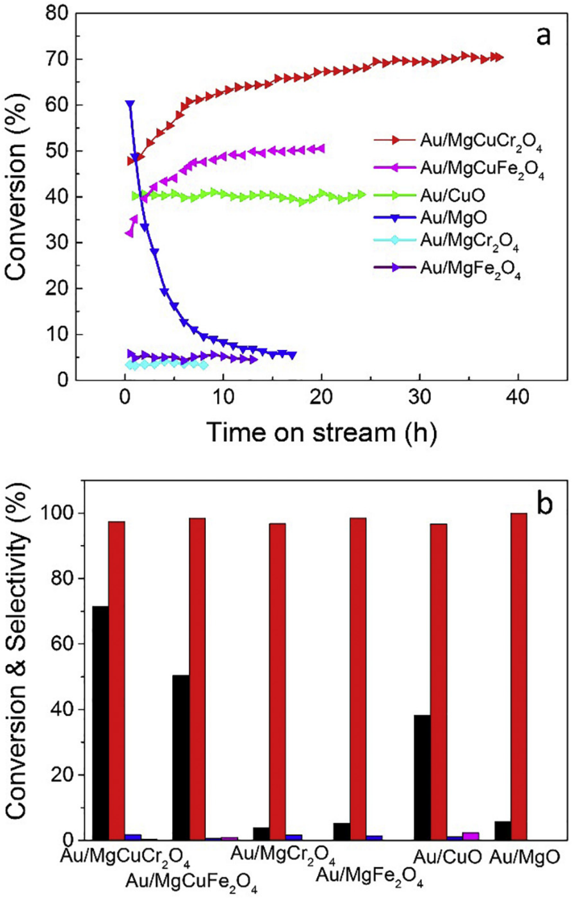

Fig. 1. Catalytic performance of various supported gold catalysts in gas-phase oxidative dehydrogenation of CH-ol at 260 °C. (a) CH-ol conversion evolution as a function of time on stream. (b) CH-ol conversion (black bar) and selectivity to CH-one (red bar), 2-cyclohexen-1-one (blue bar) and COx (pink bar) of various gold catalysts at stable state. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

TEM images of fresh and used Au/$MgCuCr_2O_4$ catalysts are shown in Fig. 2 (a complete set of TEM images is given in Fig. S5). It can be seen that the gold nanoparticles are uniformly distributed over the $MgCuCr_2O_4$ surface. The average particle size is about 3 nm. During the reaction, the particles did not sinter appreciably (Fig. 2). On contrary, the initially ~3 nm gold particles sintered substantially to ~6 nm in Au/CuO (Fig. S5). These differences indicate that the gold-support interaction is much stronger for $MgCuCr_2O_4$ than for CuO. Au/$MgCuFe_2O_4$ contained already relatively large particles in the fresh catalyst (d_{Au} = 6.9 nm), and these particles only grew slightly to 7.5 nm during the reaction (Fig. S5). We expect that the lower activity of this catalyst in comparison to Au/$MgCuCr_2O_4$ can be explained by the lower dispersion.

In order to determine the oxidation state of the different catalyst components, X-ray photoelectron spectroscopy (XPS) analysis was carried out. The binding energy (BE) was corrected for surface charging by taking the C 1 s peak of contaminant carbon as a reference at 284.6 eV. As the Mg 2 s signal overlaps with the Au $4f_{5/2}$ component (Fig. S8), we used the $4f_{7/2}$ peak for analysis. Its position at 84 eV for the spinel-oxide-based catalysts confirms that gold is in the metallic state in the fresh and the used sample [29,30]. Due to the high Mg content, we cannot ascertain the presence of metallic gold in Au/MgO. The Cu $2p_{3/2}$ XP spectra of Au/$MgCuCr_2O_4$ before and after the reaction