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# Influence of nanoparticles oxidation state in gold based catalysts on the product selectivity in liquid phase oxidation of cyclohexene

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ABSTRACT

Supported gold catalysts $Au/TiO_2$ and $Au/ZrO_2$ were prepared and used for oxidation of cyclohexene with TBHP. These catalysts were characterized by ICP, TEM and diffuse-reflectance UV–vis. The catalytic tests were carried out in liquid phase, at 80 °C and at atmospheric pressure.

The effects of support and thermal treatment (oxidation state of Au nanoparticles) on catalytic performance were studied. Gold in the catalysts that have been dried is deposited as $Au^{\delta+}$. These catalysts have a high selectivity towards alkene oxides, 81% of 2-cyclohexene-1-ol for $Au/TiO_2$ and 85% of 2-cyclohexene-1-one for $Au/ZrO_2$.



## 1. Introduction

Catalytic oxidation of olefins into value added oxygenated derivative is very important in chemical industry [1]. The oxidation of cyclohexene can give rise to a number of products (Scheme 1) depending on the catalysts and reaction conditions. The 2-cyclohexene-1-ol and 2-cyclohexene-1-one are used in the manufacture of high value pharmaceutical chemicals [2]

In the past decades, an increasing interest has been directed to the catalytic potential of gold catalysts. Gold-based catalysts are used in different reactions of carbone oxidation, such as oxidation of CO [3–14], oxidation of sugar [15], oxidation of benzylacohol [17–20], oxidation of aliphatic alcohols [21–23], oxidation of polyols [16,24,25], oxidation of glycerol [26,27] epoxidation of trans-stilbene [28,29], epoxidation of styrene [30,31] oxidation of cyclohexane [32–34,37].

However, the literature reports few studies on the use of gold catalysts for the oxidation of cyclohexene, except those of Zhen-Cai et al. about Au/OMS-2(La-OMS-2) [38] and Au/HNTs [39]. They report that conversion does not exceed 50% and selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-2-one is between 30 and 49%.

In addition, supported gold nanoparticles on C [1] and CNTs [40] showed a remarkable catalytic activity for this reaction.

The objective of this work is to study the influence of gold nanoparticles oxidation state, on the oxidation of cyclohexene by TBHP. $TiO_2$ and $ZrO_2$ oxides are used as supports because they have comparable acidities but different reducibility features.

## 2. Experimental

### 2.1. Catalysts preparation

A suspension of support ($TiO_2$ or $ZrO_2$) in distilled water is introduced into a three-necked flask and heated to 80 °C. Then, a solution of gold salt, $HAuCl_4{\cdot}3H_2O$, (10 g/L) is mixed with urea (0.9 g). All is closed and stirred for 16 h at the same temperature in the dark. At the end, the solid is separated by centrifugation and washed with distilled water many times.

After each washing, a test with ($AgNO_3$) is carried out to verify the presence of chlorides. Generally, after the first wash, no trace of chloride is found. A second qualitative test was also carried out on the wash solution by $NaBH_4$. No changes in the wash solution color indicate that the total amount of the introduced gold is deposited on oxides. The resulting solids are dried at 120 °C overnight (dried catalyst). A part of the dried samples are then reduced by hydrogen at 300 °C (reduced catalyst), and are stored in a vacuum desiccator, protected from light [34,38,41,42].

### 2.2. Catalysts characterization

The effective contents of Au and Cl in the catalysts were determined by ICP chemical analysis. TEM photographs were obtained

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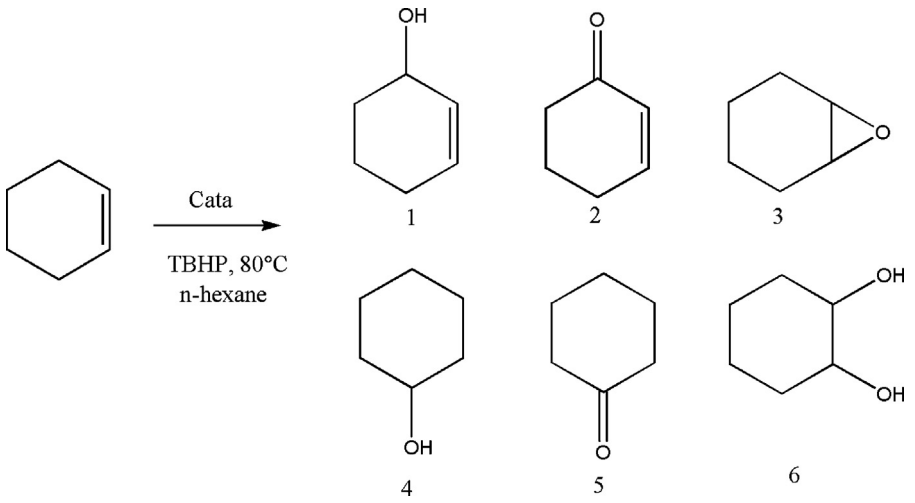


**Scheme 1.** Products resulting from the cyclohexene oxidation.

**Table 1**
Analysis of the catalysts.

| Sample | Nominal content (wt%) | | *d* (nm) |
|---|---|---|---|
| | Au | Cl | |
| $Au/TiO_2$ | 0.9 | 0.02 | 3.4 |
| $Au/ZrO_2$ | 0.8 | <0.02 | 6.0 |

from a JOEL JEM-100CXII instrument, operating at 120 KV with a resolution of 0.35 nm. Diffuse reflectance UV–vis spectroscopy measurements were carried out at room temperature with Lambda 800 UV/Vis spectrometer in the range of 200–800 nm. This setup was equipped with a diffuse reflectance accessory set to collect the diffuse reflected light only.

### 2.3. Catalytic tests

Catalytic tests were performed using 0.1 g of catalyst, 4 mL of cyclohexene and 5.5 mL of *tert*-butyl hydroperoxide [TBHP (70%) in water]. The oxidation of cyclohexene was carried out at 70 °C for 6 h under atmospheric pressure.

The consumption of TBHP was determinate by iodometric titration, and the products were analyzed by gas chromatography (GC SCHIMADZU 14-B) with a capillary column "HP-FFAP" and an FID detector.

The oxidation activity is expressed in TON (turnover number), calculated at the end of the reaction (6 h) as follows:

$$\mathrm{TON} = \frac{n_0.C\%}{m_{\mathrm{cat}}.\%\mathrm{Au}D}$$

$n_0$: initial mole number of cyclohexene, $C\%$: cyclohexene conversion, $m_{\mathrm{cat}}$: amount of catalyst, %Au: gold loading, $D$: gold accessibility is calculated considering the hypothesis according to which the particles are regarded as cubes with one face in contact with the support and the five others are accessible [43].

## 3. Results and discussion

### 3.1. Catalysts characterization

The catalysts metal loading analysis shows that the majority of the dissolved gold is deposited onto the oxides (Table 1).

The characterization by TEM of reduced $Au/TiO_2$ (Fig. 1a) reveals the presence of gold nanoparticles, uniformly distributed on the

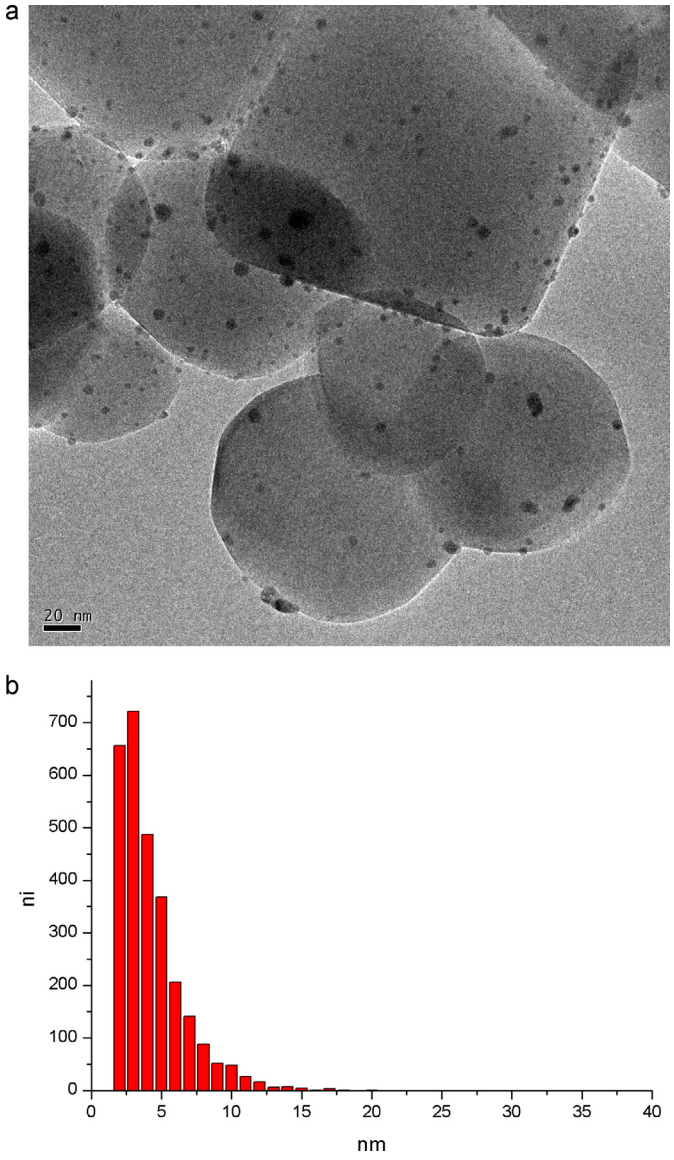


**Fig. 1.** TEM characterization of reduced $Au/TiO_2$ (a) TEM image (b) size distribution histogram.