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Journal of Catalysis 223 (2004) 236–239

JOURNAL OF CATALYSIS

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Priority Communication

# Epoxidation of styrene by anhydrous t-butyl hydroperoxide over reusable gold supported on MgO and other alkaline earth oxides

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Received 21 November 2003; revised 15 January 2004; accepted 15 January 2004

## Abstract

Gold nanoparticles deposited on MgO, CaO, SrO, and BaO by homogeneous deposition–precipitation using urea are, for the first time, reported to be novel highly active/selective and reusable catalysts in the epoxidation of styrene to styrene oxide (SO) by anhydrous t-butyl hydroperoxide. Au/MgO prepared by deposition–precipitation using NaOH is also studied in styrene epoxidation. The slightly poorer performance of Au/MgO prepared by deposition–precipitation in epoxidation of styrene (conversion: 44.6%, SO selectivity: 36.1%), as compared with to the gold catalysts prepared on alkaline earth oxides by homogeneous deposition–precipitation (styrene conversion: $\geqslant 53\%$, SO selectivity: 45–60%), is attributed to the lower loading (4.1 wt%), larger particle size ($D_{\mathrm{Au}} = 17.9$ nm), and possible presence of trace impurities ($Na^+$ and $Cl^-$) in the former. Higher gold loading (4.7–7.5 wt%) and smaller gold particles ($D_{\mathrm{Au}} \cong 8.0$ nm) were observed in the alkaline earth-supported Au catalysts prepared by homogeneous deposition–precipitation.

*Keywords:* Epoxidation of styrene; Styrene oxide; Au/MgO catalyst; Au/alkaline earth oxides

## 1. Introduction

Epoxidation of olefinic compounds to corresponding epoxides is an important and first step in the production of large number of bulk, fine and pharmaceutical grade chemicals [1]. Tradionally, stoichiometric amounts of peracids (e.g., peracetic acid and percarboxylic acid) are used in the epoxidation reaction [2]. However, the use of peracid is unsafe and, moreover, it is corrosive and also generates voluminous amounts of waste. Hence, the synthesis of epoxides using a safer and cleaner oxidizing agent and a more active/selective, easily separable and reusable catalyst is of great practical importance. In general, the epoxidation of terminal alkenes, such as styrene and 1-octene, is difficult and hence requires prolonged reaction times [3]. Use of easily separable solid catalysts, such as TS–1 [4], Ti–$SiO_2$ [5], and TBS–2 and TS–2 [6], has been reported for the epoxidation of styrene. However, these catalysts showed poor selectivity when $H_2O_2$ was used as the oxidizing agent. High styrene oxide selectivity (> 80%) was achieved using organic hydroperoxide [7] or urea–$H_2O_2$ adduct [8] instead of aqueous $H_2O_2$ but at low styrene conversion (9.8 and 17.7%, respectively). Sharpless and co-workers [9] have reported pyridine ligand-accelerated methyl trioxorhenium (MTO)-catalyzed olefin epoxidations with excellent yields (> 90%) to epoxides. However, catalyst reusability was not reported and the MTO is very expensive. Hence, there is a great practical need to develop a novel reusable solid catalyst showing both high activity and high selectivity in the epoxidation.

Since discovery, by Haruta and co-workers, of the highly active supported nanometer-sized gold catalysts for low-temperature CO oxidation ($\leqslant 0\,^{\circ}\mathrm{C}$), interest in gold chemistry has grown dramatically throughout the world [10]. An important discovery using supported gold catalysts is the single-step gas-phase epoxidation of propylene by mixed $H_2$ and $O_2$ [11]. Recently, Galvagno and co-workers [12] and Biella and Rossi [13] reported liquid-phase oxidation of alcohols to aldehydes or ketones over Au/$Fe_2O_3$ and Au/$SiO_2$ catalysts prepared by coprecipitation and impregnation techniques, respectively. So far, the use of supported gold catalysts in the liquid-phase epoxidation of olefins has not been reported. We report here, for the first time, the liquid-phase epoxidation of styrene by anhydrous t-butyl hydroper-

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0021-9517/$ – see front matter © 2004 Published by Elsevier Inc.
doi:10.1016/j.jcat.2004.01.014

Table 1
Epoxidation of styrene by anhydrous TBHP over the alkaline earth metal oxide-supported Au catalysts (prepared by the DP and/or HDP methods)

| Catalyst (preparation method) | Au loading (wt%) | Styrene conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | Styrene oxide | Phenyl acetaldehyde | Benzaldehyde | Other products |
| Au/MgO (DP) | 4.1 | 44.6 | 36.1 | 11.7 | 22.8 | 29.4 |
| Au/MgO (HDP) | 7.5 | 62.6 | 54.3 | 16.8 | 10.8 | 18.1 |
| Au/MgO (HDP)[a] | 7.5 | 67.0 | 66.1 | 2.8 | 0.1 | 31.0 |
| Au/CaO (HDP) | 4.7 | 53.6 | 60.2 | 19.2 | 6.3 | 14.4 |
| Au/BaO (HDP) | 5.3 | 55.9 | 53.5 | 17.6 | 10.2 | 18.7 |
| Au/SrO (HDP) | 5.1 | 53.0 | 44.8 | 26.0 | 11.7 | 17.4 |

[a] Styrene epoxidation on the used catalyst.

oxide (TBHP), using reusable, highly active and selective nanometer-sized gold particles supported on MgO or other alkaline earth oxides (which are basic in nature) as the catalyst. Our new approach involves bringing the catalyst into contact with styrene and anhydrous TBHP (in benzene) under reflux, while continuously removing the reaction water, using the Dean–Stark assembly.

## 2. Experimental

Gold was deposited on MgO and other alkaline earth oxides by homogeneous deposition–precipitation (HDP) using urea as the precursor for precipitating agent (ammonium hydroxide) [14,15], similar to that used recently by Zanella et al. [16] for the deposition of gold on $TiO_2$. In a typical procedure, a known amount of $HAuCl_4 \cdot 3H_2O$ is dissolved in 300 mL distilled water. A known quantity of urea (normally 50 times more than that required for hydrolysis of gold chloride) is then added to the solution. To this clear solution, alkaline earth metal oxide support is added and the temperature of the resulting slurry is increased gradually to 95 °C, while monitoring the pH of the slurry continuously. The temperature is maintained for 6 h. The final pH of the slurry is $8.3 \pm 1.1$, depending on the support used. The solid mass is filtered, washed several times with distilled water, dried, and then calcined at 400 °C for 2 h in static air. Au/MgO catalyst is prepared by the deposition–precipitation (DP) method, described elsewhere [17]; the catalyst is calcined in air at 400 °C for 2 h. All catalysts were characterized with respect to Au loading by ICP-OES (using a Perkin–Elmer Analyser) and XRD (using a Phillips Diffractometer, 1730, Cu-$K_\alpha$, 40 kV, 40 mA) and with respect to Au particle size by TEM (using JEOL Model No. JEM 1200 EX).

The styrene epoxidation reaction over the catalysts was carried at atmospheric pressure by bringing 0.1 g supported Au catalyst into contact with 1.2 mL (10 mmol) styrene and 5.7 mL (15 mmol) anhydrous TBHP (26% TBHP in benzene) in a stirred batch reactor (capacity: 10 $cm^3$), under reflux (at 80 °C) and vigorous stirring for 3 h. The catalyst was separated from the reaction mixture by filtration. The reaction products and unconverted reactants were analyzed in a gas chromatography with flame ionization dector using an SE-30 column and $N_2$ as carrier gas. The used catalyst was washed with benzene, dried, and then reused for the epoxidation.

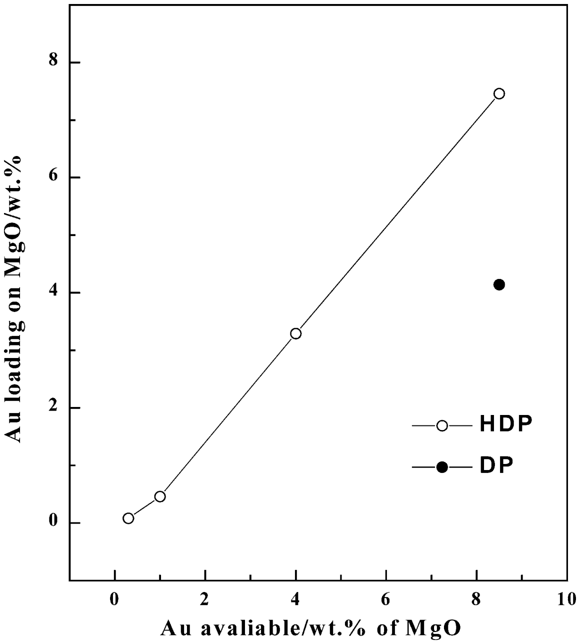

Fig. 1. Influence of catalyst preparation methods (HDP and DP) on the deposition of Au on MgO.

## 3. Results and discussion

Results for the epoxidation over the catalysts, prepared by HDP of gold on different alkaline earth oxide supports (viz. MgO, CaO, BaO, and SrO), are listed in Table 1. Gold loadings in the Au/MgO catalysts, prepared by HDP and DP methods, are compared in Table 1 and Fig. 1, and TEM images are shown in Fig. 2. Homogeneously dispersed and dense nanometer-sized gold particles were observed in the Au (7.5 wt%)/MgO [$D_{Au} = 7.9 \pm 0.3$ nm (by TEM), 8.9 nm (by XRD)] and Au (4.7 wt%)/CaO [$D_{Au} = 5.7 \pm 2.6$ nm (by TEM)] catalysts prepared by HDP as shown in Figs. 2b and c, respectively. XRD (results not shown) confirmed the partial transformation of MgO to $Mg(OH)_2$ due to hydration [17]. The higher Au loading when Au/MgO catalysts are

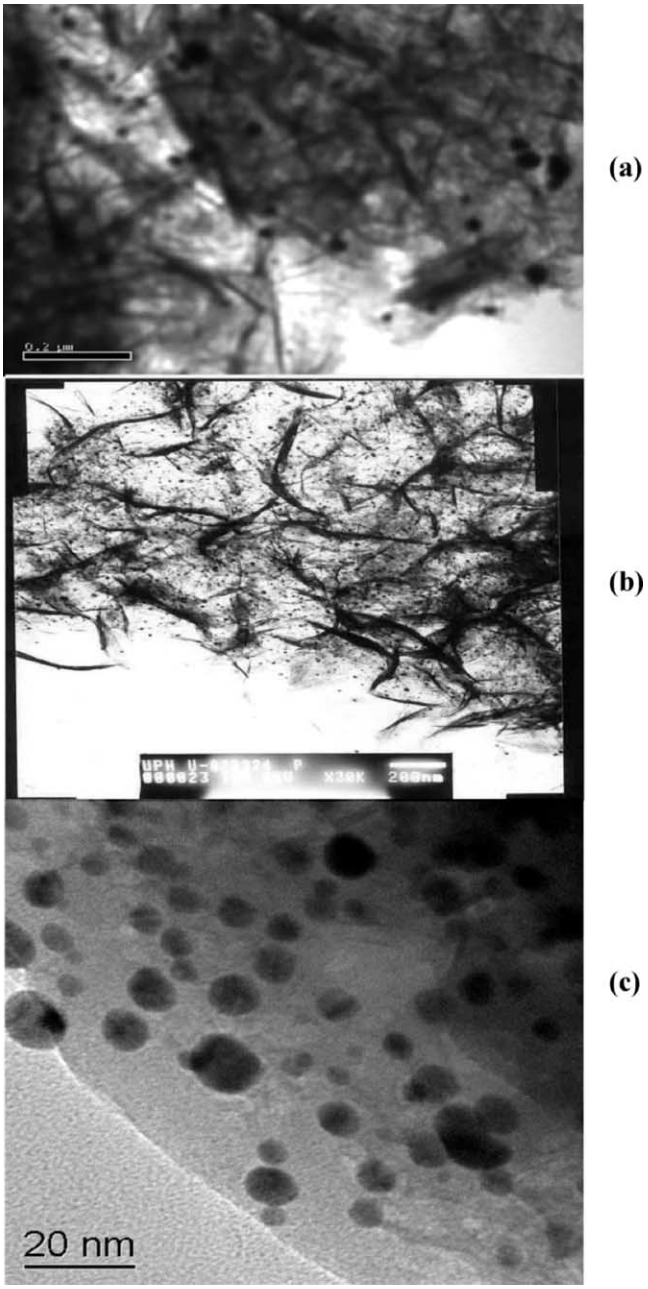

Fig. 2. TEM photographs of (a) Au (4.1 wt%)/MgO (DP), (b) Au (7.5 wt%)/MgO (HDP), and (c) Au (4.7 wt%)/CaO (HDP) catalysts.

prepared by HDP can be explained as follows. Continuous monitoring of pH during preparation showed that, in the case of the Au/MgO catalyst prepared by DP, the initial pH of the gold solution–MgO slurry (9.4) increases to 9.7 at the end of the deposition. When the HDP method was used, the initial pH (9.9), however, decreased to 7.7. The isoelectric point (IEP), which is also called the point of zero charge (PZC), of MgO and $Mg(OH)_2$ is close to 12.2 ± 0.2 [18,19]. As the final pH in case of the HDP method is much lower than the IEP of MgO and $Mg(OH)_2$, most of the $AuCl_4^-$ anions from the solution are adsorbed on the positively charged surface of MgO and $Mg(OH)_2$, where the anions are hydrolyzed and precipitated on the surface, leading to a high gold loading. This is consistent with the observation by Haruta and coworkers [20] that the gold loading on the support is higher if the pH is set in the range 6 to 8.0. In the case of gold deposition on MgO by the DP method, the final pH was much higher than that observed for the HDP method (7.7), leading to a smaller adsorption of $AuCl_4^-$ anions and, consequently, lower gold deposition.

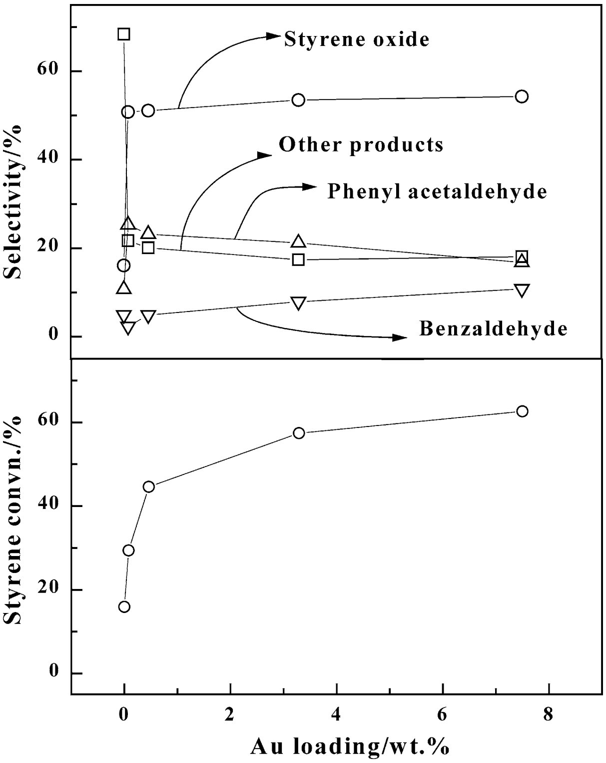

Fig. 3. Influence of gold loading of the Au/MgO catalyst on styrene conversion and selectivity for styrene oxide (○), phenylacetaldehyde (△), benzaldehyde (▽), and other products (□) in the epoxidation of styrene by anhydrous TBHP [reaction conditions: styrene = 1.2 mL (10 mmol), anhydrous TBHP (26% in benzene) = 5.7 mL (15 mmol), catalyst = 0.1 g, temperature = 80 °C, time = 3 h].

Results on the epoxidation of styrene by anhydrous TBHP over the nanometer-sized gold supported on different alkaline earth oxides are given in Table 1 and Fig. 3. Both styrene conversion and styrene oxide selectivity are high irrespective of the alkaline earth oxide support used for the catalyst prepared by the HDP method. However, the best results were obtained using Au/MgO prepared by HDP, particularly when the Au loading was high (7.5 wt%). The much lower activity and styrene oxide selectivity of the Au (4.1 wt%)/MgO prepared by DP are expected due to its lower Au loading, larger Au particle size ($D_{Au}$ = 17.9 ± 3.4 nm) as shown in Fig. 2a, and possible traces amounts of $Na^+$ and $Cl^-$ ions. The results showing the influence of gold loading of the Au/MgO catalyst (prepared by the HDP method) on styrene conversion and styrene oxide selectivity are presented in Fig. 3. The support MgO alone also showed appreciable styrene conversion activity (styrene conversion of 15.9%) but with very poor selectivity for styrene oxide (16.1%); in this case, benzoic acid (52.5%) was found to be the major product. The deposition of Au on MgO resulted in an increase in both styrene conversion activity and styrene oxide selectivity of the catalyst, depending on the gold loading. This indicates the important role played by the nanometer-size gold of the catalyst in styrene epoxidation. The Au (7.5 wt%)/MgO (prepared by HDP) showed excellent reusability with a significant improvement in both catalytic activity and selectivity in the epoxidation (Table 1).

The results of this investigation lead to the conclusion that nanometer sized gold deposited on a basic support, such as MgO or CaO, is a promising catalyst for the epoxidation of styrene by anhydrous TBHP. This catalyst combines high activity with high selectivity in the epoxidation of styrene. Further detailed studies are, however, necessary to understand nanometer size gold–alkaline earth oxide support interactions and the reaction mechanism.

## Acknowledgment

N.S.P. and B.S.U. are grateful to RMIT, Melbourne, Australia, and CSIR, New Delhi, India, respectively, for the award of fellowships. The authors are grateful to Mrs. R. Pasricha for her help in TEM of the catalysts.

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