Epoxidation of Styrene by *t*-Butyl Hydroperoxide over Gold Supported on Yb_2O_3 and Other Rare Earth Oxides

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(Received December 8, 2003; CL-031194)

Gold nanoparticles deposited [by homogeneous deposition-precipitation (HDP) using urea] on Yb_2O_3 and other rare-earth oxides (viz. Sm_2O_3, Eu_2O_3, and Tb_2O_3) are novel highly active/selective and reusable catalysts for the selective epoxidation of styrene to styrene oxide by anhydrous or aqueous *t*-butyl hydroperoxide and no problems are foreseen for a large scale operation of this green process.

Epoxidation of styrene is a practically important reaction for producing styrene oxide, an industrially important organic intermediate. It is conventionally carried out using organic peracids as an oxidizing agent,[1] which is very expensive, hazardous to handle and non-selective for the styrene oxide formation, and also leads to a number of undesirable products, creating a lot of waste. To avoid the waste production, recently a few solid catalysts, such as TS-1,[2] Ti/SiO_2,[3] TS-2, and TBS-2[4] and γ-alumina,[5] using H_2O_2,[2–5] H_2O_2-urea adduct[6] or TBHP[7] as the oxidizing agent for the epoxidation of styrene have been reported. However, the catalysts show low activity[2–4,6,7] and/or poor selectivity for styrene oxide[2–4] or deactivation by the reaction water.[5] It is, therefore, of both scientific and practical interest to develop a better solid catalyst having both high activity and high selectivity in the epoxidation.

Recently, supported nano-gold, particularly Au/TiO_2[8] and Au deposited on Ti-containing micro- and mesoporous silica,[9,10] has attracted a lot of attention for the direct vapour phase oxidation to propylene to propylene oxide by mixed H_2 and O_2. We report here that gold nanoparticles supported on Yb_2O_3 and other rare earth oxides (viz. Sm_2O_3, Eu_2O_3, and Tb_2O_3), prepared by homogeneous deposition precipitation (HDP), shows both high activity and high selectivity in the liquid phase epoxidation of styrene to styrene oxide by anhydrous or aqueous TBHP, requiring much shorter reaction time for achieving styrene conversion of practical interest ($>50\%$).

The rare earth oxide supported nano-gold catalysts were prepared by homogeneous deposition precipitation (HDP) by contacting a rare earth oxide under stirring with aqueous urea solution containing $HAuCl_4$, increasing the temperature of the mixture up to 95 °C, maintaining the temperature at 95 °C for 6 h, aging at 30 °C for 12 h, filtering, thoroughly washing the solid, drying and then calcining the solid in air at 400 °C for 2 h. Au/Yb_2O_3 catalyst was also prepared by deposition precipitation (DP), using aqueous NaOH or Na_2CO_3 as precipitating agents, described earlier.[11] The catalysts were characterized for their Au loading (by ICP–OES) and also for their Au particle size (by TEM). The epoxidation reaction over the catalysts was carried at atmospheric pressure by contacting 0.1 g supported Au catalyst with 1.2 mL (10 mmol) styrene and 5.7 mL (15 mmol) anhydrous *t*-butyl hydroperoxide (TBHP) (26% TBHP in benzene) in a stirred batch reactor (capacity: $10\,cm^3$) under reflux (at 82 °C) and vigorous stirring for a period of 3 h, while removing continuously the reaction water using the Dean–Stark trap.[5]

Results in Figure 1 indicate that, among the rare-earth oxide supported gold catalysts (prepared by HDP), Au/Yb_2O_3 shows the best performance (64% conversion and 55% styrene oxide selectivity). The Au/Tb_2O_3, Au/Eu_2O_3, and Au/Sm_2O_3 catalysts also showed a comparable performance. The order of the catalysts for their performance in the epoxidation is as follows: $Au/Yb_2O_3 > Au/Tb_2O_3 \geq Au/Eu_2O_3 \approx Au/Sm_2O_3 > Au/CeO_2 > Au/La_2O_3 \gg Au/Er_2O_3 > Au/Nd_2O_3 \gg Au/Gd_2O_3$. The Au/Gd_2O_3 showed very high TBHP decomposition activity and hence it is not useful for the epoxidation. The gold loading in all the catalysts was more or less the same (6.5 ± 0.3 wt %).

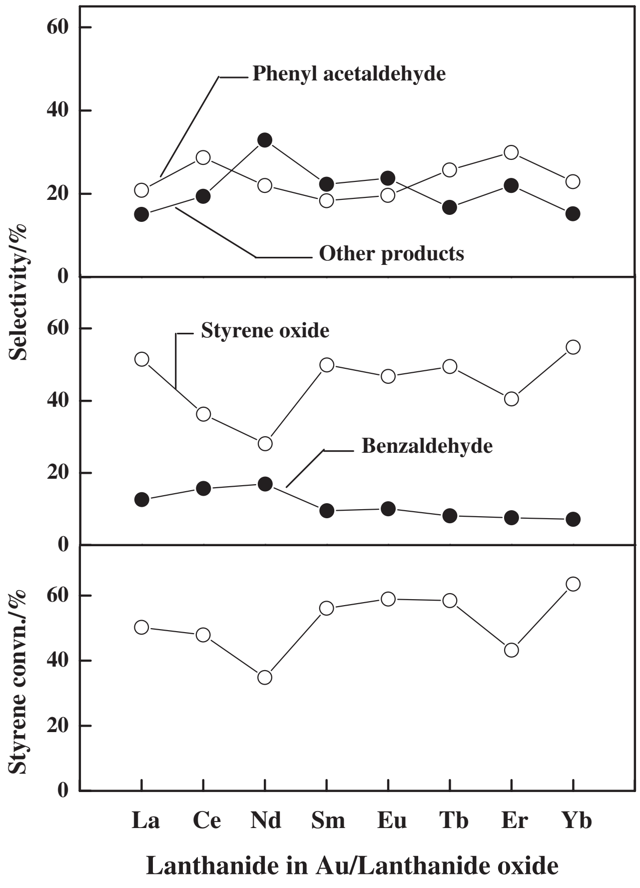

Figure 1.

Table 1. Results of the styrene epoxidation by anhydrous or aqueousTBHP over Au/Yb_2O_3 prepared by the different methods (DP and HDP)

Catalyst	Method of preparation	Au loading /wt %	Au particle size /nm[e]	Styrene conversion /%	Selectivity/%				Styrene oxide yield /%
					Styrene oxide	Phenyl acetaldehyde	Benzaldehyde	Other products	
Yb_2O_3[a]	—	—	—	10.9	4.2	2.8	8.7	84.3	0.08
Au/Yb_2O_3[a]	DP (using NaOH)	4.7	11.9 ± 1.3	42.0	45.1	30.0	7.1	17.8	18.9
Au/Yb_2O_3[a]	DP (using Na_2CO_3)	3.6	6.3 ± 0.3	52.2	36.8	24.5	6.6	32.1	19.2
Au/Yb_2O_3[a]	HDP (using urea)	6.6	10.8 ± 0.5	63.5	54.8	22.9	7.1	15.2	34.8
Au/Yb_2O_3[a,b]	HDP (using urea)	6.6	10.8 ± 0.5	64.4	57.6	23.4	7.9	11.1	37.1
Au/Yb_2O_3[c]	HDP (using urea)	6.6	10.8 ± 0.5	65.3	59.5	8.6	1.4	30.5	38.9
Au/Yb_2O_3[d]	HDP (using urea)	6.6	10.8 ± 0.5	74.0	72.8	2.9	3.3	21.0	53.9
Au/Yb_2O_3[d,b]	HDP (using urea)	6.6	10.8 ± 0.5	73.7	73.0	2.8	3.6	20.6	53.8

[a] Using anhydrous TBHP (26% in benzene). [b] Reuse of the catalyst, [c] Using anhydrous TBHP (26% in benzene) and 0.5 mL water in the reaction mixture without continuous removal of the water. [d] Using aqueous TBHP (70% in water) without continuous removal of the water. [e] Determined by TEM.

Results in Table 1 reveal that the Au/Yb_2O_3 prepared by the DP method is less active and selective in the epoxidation as compared to the one prepared by the HDP method, most probably because of the lower Au loading in the former case. In case of Au/TiO_2 catalyst prepared by DP and HDP methods, the gold loading was 0.48 and 6.0 wt %, respectively, and the styrene oxide yield in the epoxidation was 19.5 and 31.6%, respectively. The Au/Yb_2O_3 (HDP) showed a better performance than the Au/TiO_2 (HDP) in the epoxidation. The styrene oxide selectivity and yield in the epoxidation by anhydrous TBHP over the Au/Yb_2O_3 (HDP) increased with the reaction period (the selectivity was 38.2, 54.8, and 67.5% and the yield was 13.0, 34.8, and 49.3%, respectively, for the reaction period of 1, 3, and 5 h). It is interesting to note that the Au/Yb_2O_3 (HDP) catalyst shows even better performance in the presence of water; when aqueous TBHP was used instead of the anhydrous TBHP, both the conversion and styrene oxide selectivity were higher and consequently the styrene oxide yield (53.9%) was much higher. The Au/Yb_2O_3 (prepared by the HDP method) also showed excellent reusability without a significant loss in its activity or selectivity in the epoxidation (Table 1). The styrene oxide yield (percentage conversion of styrene to styrene oxide) obtained in this study is much higher than those obtained earlier in the styrene epoxidation over TS-1[2,6] using aqueous H_2O_2 (1.2% in 6 h)[2] and H_2O_2-urea (15.4% in 12 h),[6] γ-Al_2O_3 using anhydrous H_2O_2 (25.6% in 5 h)[5] and over the surface modified Ti/HMS using TBHP (15.8% in 3 h).[7] The beneficial effect of water (Table 1) on the epoxidation is consistent with that observed earlier in case of the oxidation of CO over Au/TiO_2.[12] Further studies are, however, necessary to understand the beneficial effect of water and also the epoxidation reaction mechanism.

In summary, the rare-earth oxide (viz. Yb_2O_3, Tb_2O_3, Eu_2O_3, and Er_2O_3) supported nanosize gold catalyst (prepared by HDP method), particularly the Au/Yb_2O_3, is highly active, selective and reusable and hence highly promising catalyst for the selective epoxidation of styrene by TBHP.

N.S.P. is grateful to RMIT, Melbourne, Australia for the award of fellowship. Dr. B.S. Uphade and P. Jana are grateful to CSIR, New Delhi, India, for the award of Senior Research Associateship and Sernior Research Fellowship, respectively.

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