Epoxidation of styrene by anhydrous *t*-butyl hydroperoxide over Au/TiO_2 catalysts

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Nanosize gold deposited on TiO_2, by homogeneous deposition-precipitation (HDP) using urea as the precipitation agent is an active/selective and reusable catalyst for the epoxidation of styrene (at 82 °C) by anhydrous *t*-butyl hydroperoxide (TBHP). The activity and epoxide selectivity of the Au/TiO_2 catalyst in the epoxidation is increased with increasing the Au loading on the TiO_2 support. The Au/TiO_2 catalyst prepared by the deposition precipitation using sodium hydroxide as the precipitation agent (DP method) has much lower gold loading and also lower Au dispersion and consequently possesses lower epoxidation activity as compared to that prepared by the HDP method. The styrene oxide selectivity is not influenced very significantly by the catalyst preparation method or by the Au loading (except at the very low Au loading). In the Au/TiO_2 catalysts prepared by both the methods, Au is found to exist in both the metallic (Au°) and cationic (Au^{3+}) forms.

KEY WORDS: epoxidation of styrene; styrene oxide; Au/TiO_2 catalysts; *t*-butyl hydroperoxide.

1. Introduction

Epoxides are versatile and an important intermediates in the organic synthesis of fine chemicals and pharmaceuticals. Epoxidation of olefinic compounds has traditionally been carried out using organic peracids (e.g. peracetic acid and percarboxylic acid). However, the use of peracids is unsafe, corrosive, and costly and also produces huge amounts of waste. It is highly desirable to replace the conventional process with a safer and cleaner oxidizing agents and more active/selective, easily separable catalysts. Sharpless and co-workers [1] have reported pyridine ligand-accelerated methyltrioxorhenium (MTO) – catalysed epoxidation of various olefinic compounds with excellent yields (>90%) to epoxides. However, the catalyst reusability is not reported and also the MTO is very expensive. Earlier, easily separable solid catalysts, such as TS-1 [2–4], Ti–SiO_2 [5] and TS-2 [6] have been reported for the epoxidation of styrene. However, these catalysts showed poor styrene oxide selectivity when H_2O_2 was used as the oxidizing agent. When alkyl hydroperoxide [7] and urea–H_2O_2 adduct [4] were used in place of aqueous H_2O_2 as an oxidizing agents, very high styrene oxide selectivity (>80%) was achieved but the styrene conversion was very low, 9.8% and 17.7%, respectively. Recently, we reported better styrene oxide yield (25.6%) in the styrene epoxidation by anhydrous H_2O_2 over γ-Al_2O_3 catalyst [8] but the presence of water in the reaction mixture drastically decreased the catalyst performance. It is, therefore, highly desirable to develop a novel reusable solid catalyst, which shows both high styrene conversion and also high styrene oxide selectivity in the styrene epoxidation.

Until 1985 gold was considered to be catalytically inactive when Haruta *et al.* [9] developed highly active supported gold catalysts, Au/Fe_2O_3, for the low-temperature CO oxidation ($\leq$0 °C). Since then dramatic growth of interest in the catalysis of gold has occurred throughout the world [10]. The most important discovery using gold catalysts is the vapor-phase epoxidation of propylene using H_2 and O_2 [11–13]. It is interesting to know whether gold catalyst could be used for liquid-phase selective epoxidation of terminal olefin, like styrene, which is difficult to be accomplished [1]. In this paper, we report that Au/TiO_2, prepared by homogeneous deposition-precipitation (HDP) (using urea as the precipitation agent) method is an active and selective catalyst for the liquid-phase epoxidation of styrene to styrene oxide by an anhydrous *t*-butyl hydroperoxide (TBHP). The Au/TiO_2 catalyst prepared by the deposition precipitation (DP) method (using sodium hydroxide as precipitation agent), however shows lower epoxidation activity and selectivity and also has much lower gold loading.

2. Experimental

2.1. Catalyst preparation and characterization

Gold with different loadings was deposited on TiO_2 (Loba-chemie, 99.5% purity, surface area = 19 m^2 min

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g^{-1}) by two different methods, one DP, using NaOH [14], and second, HDP, using urea as the precursor for precipitating agent (ammonium hydroxide) [15–17]. The preparation of the Au/TiO_2 catalysts by the two methods is described below.

2.1.1. DP using NaOH

The catalyst Au/TiO_2 with different gold loadings was prepared by contacting the support TiO_2 under stirring with aqueous NaOH solution containing HAuCl4 · 3H2O (Thomas Baker Chem. Ltd., Mumbai, India) at a pH of 7.0 and 70 °C for 1 h, aging the mixture at 30 °C for 1 h, filtering and thoroughly washing the solid with deionized water, drying and calcining the dried solid in air at 400 °C for 2 h.

2.1.2. HDP using urea

Gold with different loadings was deposited on the TiO_2 support by the HDP method described elsewhere [17]. In a typical procedure, the metal oxide support, TiO_2, was contacted under stirring with aqueous urea solution containing $HAuCl_4 \cdot 3H_2O$. The temperature of the reaction mixture was gradually increased up to 95 °C and maintained for 6 h. Thereafter, the mixture was aged at 30 °C for 12 h and then the solid was filtered, thoroughly washed with deionized water, dried at 90 °C for 12 h and finally calcined in air at 400 °C for 2 h.

The catalysts were characterized for their Au content by ICP-OES (using Perkin-Elmer Analyser), by XPS (taking C1s electron binding energy 285.0 eV as the reference), and also for their Au particle size by TEM (at 200 kV in a JEOL 1200 EX using CCD camera). The surface area of the support (TiO_2) and the catalysts was measured by the single point N_2 adsorption method (using a surface area analyzer; Quanta Chrome, USA).

2.2. Catalytic activity

The styrene epoxidation reaction over the catalysts was carried out at atmospheric pressure by contacting 0.1 g Au/TiO_2 catalyst 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 82–83 °C) and vigorously stirring for a period of 3 h. The catalyst was separated from the reaction mixture by filtration. The reaction products and unconverted reactants were analysed by GC with FID using SE-30 column and N_2 as carrier gas. The used catalyst was washed with benzene, dried and then it was reused for the epoxidation.

3. Results and discussion

3.1. Characterization of the catalysts

Results showing the influence of the method of gold deposition (the DP and HDP methods) on the gold loading in the Au/TiO_2 catalysts are presented in figure 1. Very high gold loading on the support (TiO_2) close to the theoretically expected one was achieved for the Au/TiO_2 catalysts prepared by the HDP method. Whereas, the observed gold loadings on the TiO_2 support when using the DP method was very much lower than that the theoretical one. These results are consistent with those observed earlier [17]. The observed much higher gold loading for the catalysts prepared by the HDP method than those prepared by the DP method is expected due to the large difference in the pH of the solution containing gold in the two cases. It is well known fact that the gold chloride is converted mostly into colloidal gold, >95%, and Au(III) species, 1–5%, during its precipitation [18] and that the colloidal gold is negatively charged [18,19]. The TiO_2 support is negatively charged during the gold deposition by the DP method. This is because of the higher solution pH (7.0 ± 0.1) than the point of zero charge (PZC) of TiO_2 (6.0–6.4) [20,21]. Since the gold species (colloidal gold or $AuCl_4^-$ ionic species) are negatively charged, the negative charge on both the TiO_2 and the gold species will lead to a repulsion between the two, thus leading to the observed lower gold loading. Whereas in case of the gold deposition by the HDP method, the initial pH of the mixture containing TiO_2, aqueous urea and gold species is very low, 2.5 ± 0.8, and it increases with an increase in the reaction temperature. Hence, at the pH lower than the PZC of the support, the TiO_2 surface is positively charged and therefore the adsorption of negatively charged gold species on the support is favoured, resulting into a much larger gold loading on the support. A further increase in the pH of the mixture

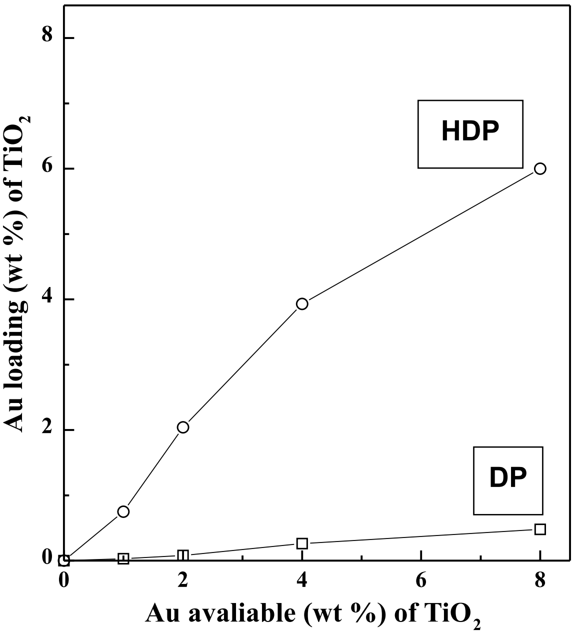

Figure 1. Influence of the method of Au deposition on TiO_2 on the gold loading in Au/TiO_2 catalysts.

with increasing the temperature led to a decrease in the gold particle size, as shown earlier by Zanela *et al.* [17].

TEM images of the Au/TiO$_2$ catalysts prepared by the DP (figure 2a) and HDP (figure 2b and c) methods are shown in figure 2. The catalysts prepared by the HDP method shows the presence of homogeneously dispersed smaller gold particles (figure 2b and c) on the TiO$_2$ support. However, the TEM image of Au/TiO$_2$ prepared by the DP method shows the presence of larger size gold particles (figure 2a). The TEM picture in figure 2b shows that the Au on the TiO$_2$ is in the form of hemispherical particles in contact with the support, similar to that observed earlier [22].

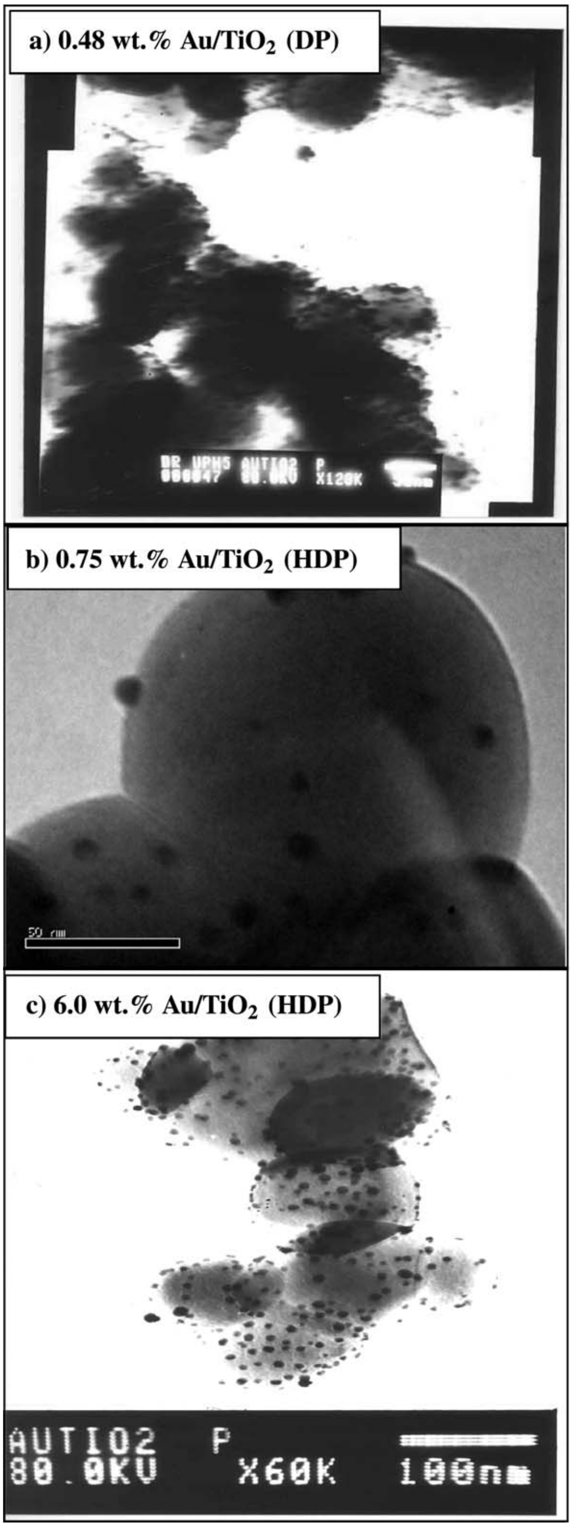

Figure 2. TEM of Au/TiO$_2$ catalysts, prepared by the (a) DP and (b, c) HDP methods.

From the XPS analysis of the catalyst (with the highest Au loading) the binding energies for Au4f5 and Au4f7 electrons have been found to be 89.05 and 86.75 eV, and 85.01 and 83.0 eV, respectively, for the Au/TiO$_2$ (HDP) and 89.04 and 86.38 eV and 84.82 and 82.68 eV, respectively, for the Au/TiO$_2$ (DP). These results clearly indicate the presence of Au in both the catalysts in both the metallic (Au°) and cationic (Au^{3+}) forms, similar to that observed in the case of the Au/CeO$_2$ catalyst [23].

3.2. Epoxidation of styrene

Results on the epoxidation of styrene over the Au/TiO$_2$ catalysts (with the different gold loadings), prepared by the DP and HDP methods, are presented in figure 3.

The conversion of styrene for the Au/TiO$_2$ catalyst prepared by the DP method is appreciably lower than that for the catalyst prepared by the HDP method and it is increased with increasing the Au loading on the support. However, no much difference in the styrene oxide selectivity is observed irrespective of the catalyst preparation method and the Au loading on TiO$_2$, except at very low Au loading. The lower epoxidation activity of the Au/TiO$_2$ catalysts prepared by the DP method is expected due to much lower Au loading on the TiO$_2$ support and also probably due to somewhat lower dispersion of gold on the support. The TiO$_2$ support alone showed a styrene conversion of 5.8% but without any selectivity for styrene oxide; the main product in this case was benzoic acid with 80% selectivity. Thus, the deposition of gold on the TiO$_2$ resulted in a large increase in both the styrene conversion and the styrene oxide selectivity in the epoxidation, depending upon the gold loading on the support. This clearly indicates the important role played by the gold nanoparticles of the catalyst in the styrene epoxidation. The Au/TiO$_2$ (HDP) also showed excellent reusability without a significant loss in both the catalytic activity and selectivity in the epoxidation (figure 3).

The high epoxidation activity of the Au/TiO$_2$ catalysts is most probably attributed to both the metallic nanosize gold (Au°) particles, particularly the low coordinated gold atoms at corners and edges [24–26] and the cationic gold species (Au^{3+}) located at the interface between the gold nanoparticles and the TiO$_2$ support. The cationic gold species are likely to be formed by the oxidation of gold at the interface by the

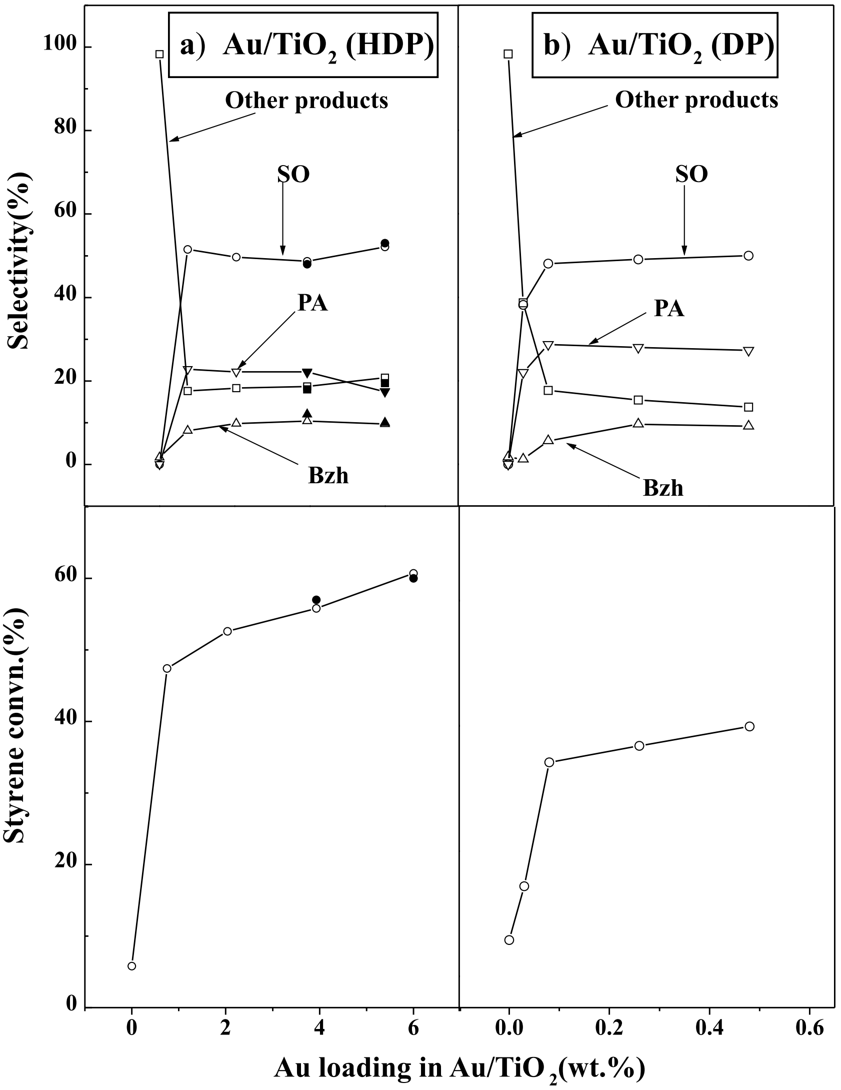

Figure 3. Epoxidation of styrene by anhydrous TBHP over (a) Au/TiO_2 (HDP), and (b) Au/TiO_2 (DP) catalysts [reaction mixture = 1.2 mL (10 mmol) styrene + 5.7 mL (15 mmol) anhydrous TBHP (26% in benzene) + 0.1 g catalyst, temperature = 82 °C, reaction time = 3 h]. SO = styrene oxide, PA = phenyl acetaldehyde, Bzh = benzaldehyde (●, data for reuse of the catalyst).

TiO_2 (which is reducible) during the high temperature calcination of the catalysts. Further studies are, however, necessary for knowing the interactions of gold nanoparticles with TiO_2 support and that of the reactants with the surface gold species for understanding the epoxidation reaction mechanism.

4. Conclusions

The present studies on the Au/TiO_2 catalysts, prepared by the DP (using NaOH) and HDP (using urea) methods, for the epoxidation of styrene by anhydrous TBHP lead to the following important conclusions:

1. Much higher gold loading, close to the theoretical one, and better dispersion of gold nanoparticles on TiO_2 are obtained when gold is deposited on TiO_2 by the HDP method instead of the DP method.
2. Gold supported on TiO_2 is a promising catalyst having high activity, selectivity and excellent reusability in the epoxidation of styrene to styrene oxide by TBHP.
3. The better performance of the Au/TiO_2 catalysts prepared by the HDP method is attributed to its higher Au loading and better dispersion of gold on the TiO_2 support.
4. In the Au/TiO_2 catalysts, prepared by both the DP and HDP methods, the gold exists in both the metallic (Au°) and cationic (Au^{3+}) forms.

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References

[1] J. Rudolph, K.L. Reddy, J.P. chiang and K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189.
[2] S.B. Kumar, S.P. Mirajkar, G.C.G. Pais, P. Kumar and R. Kumar, J. Catal. 156 (1995) 163.
[3] Q. Yang, C. Li, J.L. Wang, P. Ying, Q. Xin and W. Shi, Stud. Surf. Sci. Catal. 130 (2000) 221.
[4] S.C. Laha and R. Kumar, J. Catal. 204 (2001) 64.
[5] Q Yang, S. Wang, J. Lu, G. Xiong, Z. Feng, X. Xin and C. Li, Appl. Catal. A: Gen. 194 (2000) 507.
[6] J. Fu, D. Yin, Q. Li, L. Zhang and Y. Zhang, Micro. Mesopor. Mater. 29 (1999) 351.
[7] V.R. Grieken, J.L. Sotelo, C. Martos, J.L.G. Fierro, M. Lopez-Granados and R. Mariscal, Catal. Today 61 (2000) 49.
[8] V.R. Choudhary, N.S. Patil and S.K. Bhargava, Catal. Lett. 89 (2003) 55.
[9] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Catal. 115 (1989) 301.
[10] M. Haruta, Cattech 6 (2002) 102 and references therein.
[11] T. Hayashi, K. Tanaka and M. Haruta, J. Catal. 178 (1998) 566.
[12] T.A. Nijhuis, B.J. Huizinga, M. Makkee and J.A. Moulijn, Ind. Eng. Chem. Res. 38 (1999) 884.
[13] B.S. Uphade, T. Akita, T. Nakamura and M. Haruta, J. Catal. 209 (2002) 331.
[14] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, Stud. Surf. Sci. Catal. 72 (1991) 695.
[15] H.H. Willard and N.K. Tang, Ind. Eng. Chem. Anal. Ed. 9 (1937) 357.
[16] K. Tanabe, M. Itoh, K. Morishige and H. Hattori, in: *Preparation of Catalysts I,* eds. B. Delmon, P.A. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1969) p. 65.
[17] R. Zanela, S. Giorgio, C.R. Henry and C. Louis, J. Phys. Chem. B 106 (2002) 7634.
[18] C. Greffié, M.F. Benedetti, C. Parron and M. Amouric, Geochem. Cosmochim. Acta 60 (1996) 1531.
[19] J. Enzweiler and I. Joekes, Geochem. Explor. 40 (1991) 133.
[20] H. van Olphen, *An Introduction to Clay Colloid Chemistry* (Interscience Publishers, John Wiley, New York, 1977).
[21] T. Blasco and J.M.L. Nieto, Appl. Catal. A: Gen. 157 (1997) 117.
[22] T. Akita, K. Tanaka, S. Tsubota and M. Haruta, J. Electron Micros. 49 (2000) 657.
[23] Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, Science 301 (2003) 935.
[24] N. Lopez and J.K. Nørskov, J. Am. Chem. Soc. 124 (2002) 11262.
[25] L.M. Molina and B. Hammer, Phys. Rev. Lett. 90 (2003) 206102.
[26] J.A. Rodriguez, M. Pérez, T. Jirsak, J. Evans, J. Hrbek and L. González, Chem. Phys. Lett. 378 (2003) 526.