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Oxidation of Benzyl Alcohol to Benzaldehyde by *tert*-Butyl Hydroperoxide over Nanogold Supported on TiO₂ and other Transition and Rare-Earth Metal Oxides

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Liquid-phase oxidation of benzyl alcohol to benzaldehyde by tertiary butyl hydroperoxide (at 95 °C) over nanogold supported on TiO₂ and other transition-metal oxides (viz, MnO₂, Fe₂O₃, CoO_x, NiO, CuO, ZnO, and ZrO₂) or rare-earth oxides (viz, La₂O₃, Sm₂O₃, Eu₂O₃, and Yb₂O₃) by the homogeneous deposition—precipitation (HDP) method has been investigated. The Au/TiO₂ catalyst, prepared using the HDP method, showed high activity and selectivity in the reaction. The ZrO₂-supported nanogold catalyst (HDP) also showed very good performance. The Au/TiO₂ catalyst that was prepared using the deposition—precipitation (DP) method, however, showed poor catalytic activity, mostly because of its much-lower gold loading and/or lower Au³⁺/Au⁰ ratio. Irrespective of the catalyst preparation method, the catalytic activity increased as the gold loading increased. The gold deposition method strongly influenced the amount of gold that was deposited on TiO₂, the gold particle size distribution, and also the surface Au³⁺/Au⁰ ratio; using the HDP method, the gold deposition was much larger, the gold particle size was smaller, the gold particle size distribution was much narrower, and the Au³⁺/Au⁰ ratio was higher. Both the metallic and ionic gold species (Au⁰ and Au³⁺) are present in the Au/TiO₂ catalyst. However, the Au³⁺ species are mostly responsible for the high catalytic activity in the oxidation process.

Introduction

Benzaldehyde, which is an important intermediate for the production of perfumery, pharmaceutical, dyestuff, and agrochemicals, is commercially produced via the hydrolysis of benzyl chloride and as a byproduct during the oxidation of toluene to benzoic acid. However, the traces of chlorine in the product from the former process and poor benzaldehyde selectivity in the latter process are limiting factors of these two processes. To overcome these limitations, since the last two decades, many studies have been reported on the catalytic vaporphase oxidation of benzyl alcohol to benzaldehyde. 2-7 However, in the vapor-phase oxidation process, a very significant carbon loss, resulting from the formation of carbon oxides, is a major problem. A few studies have been reported earlier on the liquidphase oxidation of benzyl alcohol by O2, H2O2, or t-butyl hydroperoxide (TBHP) using palladium, ^{8,9} Ni-Al hydrotalcite, ¹⁰ and heteropolyacid¹¹ catalysts in the presence and/or absence of the solvent. We have also recently reported the MnO₄-exchanged Mg-Al hydrotalcite¹² and other transition-metal-containing hydrotalcite-like solids^{13,14} as active/selective catalysts for the liquid-phase oxidation of benzyl alcohol to benzaldehyde using TBHP and O2 as an oxidizing agents, respectively.

After the discovery of supported nanosized gold as a highly active low-temperature (<273 K) CO oxidation catalyst, greater attention has been given to exploring various organic/inorganic reactions using gold catalysts. Recently, Galvagno and co-workers and also Rossi and co-workers reported the oxidation of benzylic alcohols to aldehydes using Au/Fe₂O₃ (prepared by coprecipitation and impregnation) and Au/SiO₂

(prepared by impregnation followed by reduction) catalysts, respectively. Very recently, Choudhary et al. 20,21 and Hutching and co-workers²² reported the use of different supported nanogold catalysts (viz. Au/MgO, Au/Al₂O₃, Au/ZrO₂, and Au/ U₃O₈) and Au-Pd/TiO₂ catalyst, respectively, for the selective benzyl alcohol to benzaldehyde oxidation by oxygen without using a special solvent. Therefore, it is interesting to study the liquid-phase oxidation of different benzyl alcohols to corresponding benzaldehydes by TBHP, using different supported nanogold catalysts. In this paper, we report the high activity/ selectivity of TiO₂- or ZrO₂-supported nanogold catalysts, prepared via homogeneous deposition—precipitation (HDP), in the liquid-phase oxidation of benzyl alcohol to benzaldehyde by TBHP, as a model reaction. The influence of the method of gold deposition (HDP and deposition-precipitation (DP)) on the surface properties and performance of Au/TiO₂ in the oxidation of benzyl alcohol, and the effect of the gold loading of Au/TiO₂ on its performance, have been thoroughly investigated.

Experimental Section

Gold with different loadings was deposited on ${\rm TiO_2}$ (Lobachemie, 99.5% purity, surface area = 19 m²/g) by two different methods, viz, deposition—precipitation (DP), using NaOH,²³ and homogeneous deposition—precipitation (HDP), using urea as the precursor for precipitating agent (ammonium hydroxide),^{24–26} which are described as follows.

Au/TiO₂ (DP) catalysts with different gold loadings were prepared by contacting TiO₂, under stirring, with an aqueous NaOH solution containing HAuCl₄·3H₂O (Thomas Baker Chemicals, Ltd., Mumbai, India) at pH 7.0 and 70 °C for 1 h, aging the mixture at 30 °C for 1 h, and filtering and thoroughly washing the solid with deionized water, then drying and calcining the dried solid in air at 400 °C for 2 h.

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Table 1. Characterization of Au/TiO₂ Catalysts, Prepared by the DP and HDP Methods

Gold Concentra	ntion (mmol/g)			surface						
present in deposited solution on TiO ₂		surface area (m²/g)	gold particle size (nm)	Au ³⁺ /Au ⁰ ratio						
(a) Au/TiO ₂ Catalyst Prepared via the DP Method										
0.05	0.001	15.9								
0.10	0.004	9.0								
0.20	0.013	8.8								
0.40	0.024	8.0	$11.7 \pm 0.5 (12.1)^a$	0.06						
(b)	Au/TiO ₂ Catalys	st Prepared via	a the HDP Method							
0.05	0.04	9.6								
0.10	0.09	9.1								
0.20	0.17	8.0								
0.40	0.30	3.4	$4.9 \pm 0.5 (5.7)^a$	0.18						

^a Value given in parentheses is that measured using the XRD broadening peak ($2\theta = 44.38^{\circ}$).

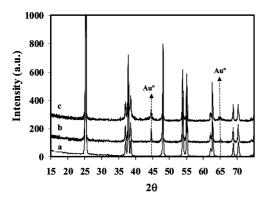


Figure 1. XRD spectra of TiO₂ (spectrum a), Au/TiO₂ (DP) (spectrum b), and Au/TiO₂ (HDP) (spectrum c).

Au/TiO $_2$ (HDP) catalysts with different gold loadings were prepared by contacting TiO $_2$ under stirring with aqueous urea solution containing HAuCl $_4$.3H $_2$ O, increasing the temperature of the reaction mixture up to 95 °C and maintaining it for 6 h. Thereafter, the mixture was aged at 30 °C for 12 h and then filtered, thoroughly washed with deionized water, dried at 90 °C for 12 h and finally calcined in air at 400 °C for 2 h.

Similarly, the other transition-metal oxides (viz, MnO_2 , Fe_2O_3 , CoO_3 , NiO, CuO, ZnO, and ZrO_2) and rare-earth oxide (viz, La_2O_3 , Sm_2O_3 , Eu_2O_3 , and Yb_2O_3) supported nanogold catalysts were prepared by the HDP method. ^{27,28} The calcined catalysts gave nanosized gold metallic particles over the supports.

The catalysts were characterized for their gold loading via inductively coupled plasma—optical emission spectroscopy (ICP—OES) (using a Perkin—Elmer analyzer), by X-ray dif-

fraction (XRD), using a Phillips 1730 series diffractometer and CuKα radiations, and for their gold particle size via transmission electron microscopy (TEM) (at 200 kV in a JEOL 1200 EX system, using a CCD camera). The surface area of the catalysts was measured using a single-point N₂ adsorption method (using a QuantaChrome surface area analyzer). The surface chemical analysis of the catalysts was conducted via X-ray phototelectron spectroscopy (XPS), using a Fisons VG 310F scanning Auger nanoprobe that was equipped with a 15 keV X-ray tube to measure binding energies up to 1487 eV. For the XPS studies, a thin layer of the sample powder was mounted using conducting carbon tape. A C 1s binding energy of 285.0 eV was taken as the reference.

The catalytic liquid-phase oxidation of benzyl alcohol over the catalysts, was conducted in a magnetically stirred roundbottom flask (with capacity of 25 cm³) that had been provided with a mercury thermometer (to measure the reaction temperature) and a reflux condenser. Unless mentioned otherwise, the oxidation was conducted under the following reaction conditions: reaction mixture, 52 mmol benzyl alcohol + 78 mmol TBHP (70% TBHP in water) + 0.5 g catalyst; temperature, under reflux (bath temperature = 94 ± 1 °C); and reaction time, 2 h. After the reaction, the catalyst was removed from the reaction mixture by filtration and the reaction products and unconverted reactants were analyzed using a gas chromatography (GC) system that was equipped for flame ionization detection (FID), using a Model SE-30 column and N₂ as a carrier gas. To measure the performance of the catalysts for the oxidation as function of time, liquid samples were removed occasionally from the reaction mixture via syringe and analyzed by GC.

Results and Discussion

Characterization of the Catalysts. The results showing the influence of the method of gold deposition (DP and HDP) preparation of the Au/TiO₂ catalyst on the gold loading and surface properties are given in Table 1. As compared to the DP method, the HDP method provided much higher gold loading on the TiO₂ support. The results are consistent with those observed earlier by Zanella et al.²⁵ The observed large difference in the gold loadings for the Au/TiO₂ catalysts prepared by the DP and HDP methods is attributed to the large difference in the pH value of the solution containing gold in the two cases, as explained earlier.^{25,26} The initial pH values of the solution for the DP and HDP were 7.0 and 2.5, respectively. Because the pH was higher than the point of zero charge of TiO₂ (6.0–6.4), the deposition of negatively charged Au species

Table 2. Performance of the Nanogold Supported on Transition-Metal Oxides and Rare-Earth-Metal Oxides by the HDP Method in the Oxidation of Benzyl Alcohol to Benzaldehyde by TBHP in the Absence of Any Solvent

gold loading		surface area			Selectivity (%)		turnover frequency,
catalyst	(mmol/g)	(m^2/g)	gold particle size (nm)	conversion of benzyl alcohol (%)	benzaldehyde	benzyl benzoate	$TOF^a (h^{-1})$
Au/TiO ₂	0.30	3.5	4.9	63.1	79.2	20.7	108.0
Au/MnO ₂	0.21	14.3	5.7	54.6	73.2	26.7	140.2
Au/Fe ₂ O ₃	0.31	12.4	6.1	29.6	88.7	11.2	50.6
Au/CoO_x	0.35	23.8	5.0	34.0	85.2	14.7	49.6
Au/NiO	0.31	4.0	19.5	37.5	82.5	17.4	61.9
Au/CuO	0.34	3.3	10.9	39.0	75.5	24.4	58.8
Au/ZnO	0.33	6.1	4.1	45.0	71.2	18.7	69.9
Au/ZrO ₂	0.17	36.5	4.5	59.5	81.5	18.5	206.1
Au/La ₂ O ₃	0.33	5.9	8.5	55.2	70.1	29.8	88.3
Au/Sm ₂ O ₃	0.21	3.2	7.1	50.4	63.2	36.7	83.1
Au/Eu ₂ O ₃	0.33	5.7	9.5	45.5	75.3	24.6	71.0
Au/Yb ₂ O ₃	0.33	2.7	10.1	47.5	80.6	19.3	73.7

^a Turnover frequency is defined as the number of moles of benzyl alcohol converted to all products per mole of gold in the catalyst per hour.

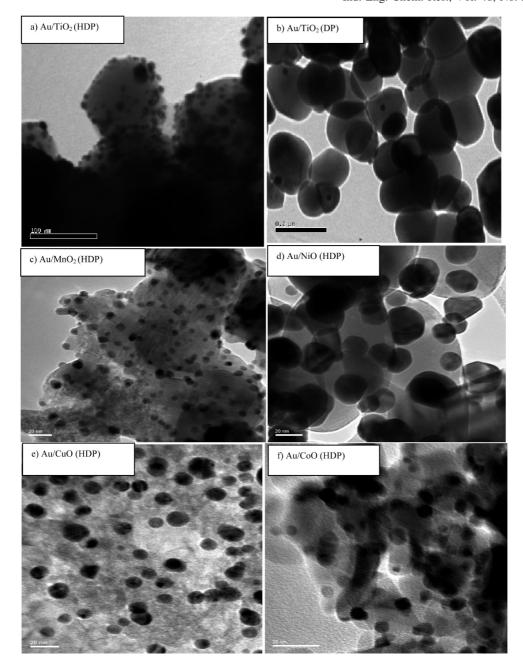


Figure 2. TEM photomicrographs of Au/TiO₂ (DP), Au/TiO₂ (HDP), and other transition-metal-oxide-supported gold catalysts (HDP).

[colloidal gold and Au(III) species] on the negatively charged TiO₂ support was much less during the DP.

Interestingly, note that the surface area of the TiO₂ support (19 m²/g) is decreased appreciably as the gold loading on the support for Au/TiO₂ catalysts prepared via both the DP and HDP methods increased (see Table 1).

The XRD spectra of the TiO2 and Au/TiO2 (DP) and Au/ TiO₂ (HDP) are compared in Figure 1. The XRD spectra of the TiO_2 (XRD major peak at $2\theta = 25.3^{\circ}$) indicate the presence of a pure anatase phase. The XRD spectra of both the Au/TiO₂ (DP and HDP) catalysts also show the presence of a pure anatase phase for TiO₂ and gold in the metallic (Au⁰) form.

Representative TEM photomicrographs of Au/TiO₂ catalysts prepared via the DP and HDP methods, and their gold particle size distributions, are presented in Figures 2 and 3, respectively. Note that, for the measurement of particle size distribution, several TEM photomicrographs of the two catalysts were used. The catalyst prepared by the HDP method shows the presence of homogeneously dispersed smaller gold particles than those observed for the Au/TiO₂ catalyst prepared by the DP method. The density of gold particles for the Au/TiO₂ (DP) catalyst is also observed to be much smaller. For the Au/TiO2 catalysts prepared by both the methods, the HRTEM pictures (not given) also showed the presence of hemispherical gold particles strongly interacting with the TiO₂ support, similar to that observed earlier.²⁹ The TEM photomicrographs for nanogold supported (by the HDP method) on other transition-metal oxides are included in Figure 2. Whereas, that for nanogold supported (by the HDP method) on the rare-earth oxides are presented in Figure 4. The data for the gold loading obtained, the gold particle size, and the surface area of the supported nanogold catalysts are given in Table 2. A comparison of the TEM photomicrographs for the different catalysts indicates a strong influence of the support used in the catalysts on the gold particle size. This seems to be mostly due to the interaction of gold particles with the surface of the metal oxides. The strong influence of the

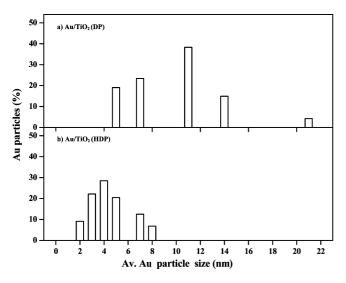


Figure 3. Gold particle size distribution for Au(0.024 mmol/g)/TiO₂ (DP) and Au(0.3 mmol/g)/TiO₂ (HDP) catalysts.

support used in the catalyst on its gold loading may be attributed to the point of zero charge (PZC) of the different supports. However, because the change of pH of the solution during the homogeneous deposition precipitation of gold on the different metal oxide supports was not monitored, no firm conclusion

can be made. Further detailed investigation is required to understand the influence of support on the gold loading.

The XPS spectrum of the Au/TiO $_2$ (DP) catalyst (see Figure 5a) shows that the binding energy values for Au $4f_{5/2}$ are 82.7 and 84.8 eV, and that for Au $4f_{7/2}$ are 86.4 and 89.0 eV. Whereas, for the Au/TiO $_2$ (HDP) catalyst, the binding energy values are determined to be 83.0 and 85.0 eV for Au $4f_{5/2}$, and 86.8 and 89.1 eV for Au $4f_{7/2}$ (Figure 5b). The observed binding energy shift in both cases is in the range of 2.0-2.7 eV. This suggests the presence of gold in both the metallic (Au 0) and cationic (Au $^{3+}$) forms in both of the Au/TiO $_2$ (DP and HDP) catalysts. However, note that the surface Au $^{3+}$ /Au 0 ratio is much higher in the case of the Au/TiO $_2$ (HDP) catalyst (see Table 1). The presence of Au 0 and Au $^{3+}$ species were also observed by Fu et al. 30 for Au/CeO $_2$ catalyst.

Oxidation of Benzyl Alcohol over Au/TiO₂ (DP and HDP) Catalysts. Results showing the performance of the Au/TiO₂ catalysts prepared by both the DP and HDP methods and having different gold loadings, in the solvent-free oxidation of benzyl alcohol to benzaldehyde by TBHP for reaction periods of 0.5 and 2 h, are presented in Figures 6 and 7. In the absence of any catalyst, the benzyl alcohol conversion was 14.3% after the time period of 2 h.

For both catalysts (see Figures 6 and 7), the conversion is increased and the selectivity for benzaldehyde is decreased as the gold loading increases, depending on the catalyst and the

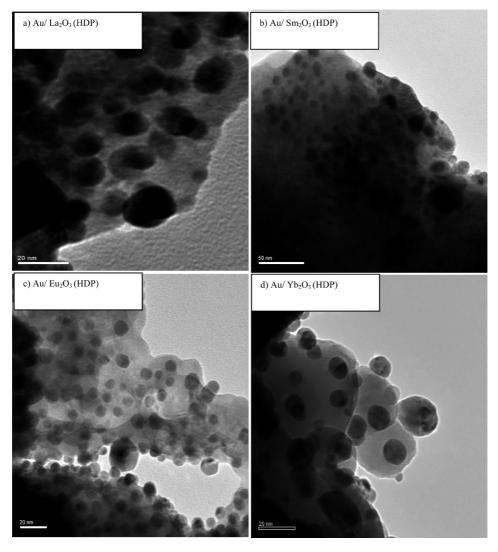
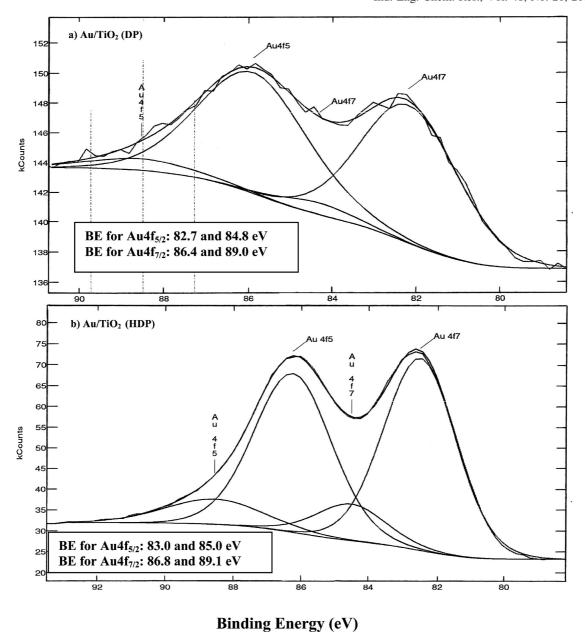


Figure 4. TEM photomicrographs of (a) Au/La₂O₃ (HDP), (b) Au/Sm₂O₃ (HDP), (c) Au/Eu₂O₃ (HDP), and (d) Au/Yb₂O₃ (HDP) catalysts.



 $\textbf{Figure 5.} \ \, \text{Au 4f}_{5/2} \ \, \text{and Au 4f}_{7/2} \ \, \text{XPS spectra of Au (0.024 mmol/g)/TiO}_2 \ \, \text{(DP) and Au (0.3 mmol/g)/TiO}_2 \ \, \text{(HDP) catalysts.}$

reaction period. The increase in the conversion of benzyl alcohol and TBHP is particularly sharp in the region of lower gold loadings (Figure 6). The benzoic acid in the reaction products was observed only for the very high gold loadings for the catalyst prepared by the HDP method.

The Au/TiO₂ catalyst prepared by the HDP method showed more catalytic activity in the benzyl alcohol oxidation, most probably because of their higher gold loading. It has a smaller gold particle size and higher Au³⁺/Au⁰ ratio, even at the muchhigher gold loading than that for the catalyst prepared via the DP method (see Table 1). However, the observed decrease in the benzaldehyde selectivity with increasing gold loading is expected, because of the increase in the benzyl alcohol conversion. Also, because the TBHP/benzyl alcohol molar ratio in the reaction mixture is >1.0, the results (see Figures 6 and 7) indicate appreciable decomposition of TBHP over the Au/TiO₂ catalysts simultaneously with the benzyl alcohol oxidation reaction, as follows:

$$2(CH3)3COOH \rightarrow 2(CH3)3COH + O2$$
 (1)

The formation and increase in the selectivity of benzyl benzoate, and the decrease in the selectivity of benzaldehyde, with increasing benzyl alcohol conversion indicates the occurrence of the following consecutive reactions in the benzyl alcohol oxidation:

$$C_6H_5CH_2OH + (CH_3)_3COOH \rightarrow C_6H_5CHO + (CH_3)_3C-OH + H_2O$$
 (2)

$$C_6H_5CHO + (CH_3)_3COOH \rightarrow C_6H_5COOH + (CH_3)_3C-OH$$
 (3)

$$C_6H_5COOH + C_6H_5CH_2OH \rightarrow C_6H_5COOCH_2C_6H_5 + H_2O$$
(4)

Because benzaldehyde is an intermediate product, its selectivity decreases as the reaction time or the benzyl alcohol conversion increases.

The benzyl alcohol oxidation over the catalyst seems to be initiated by the decomposition of TBHP, which leads to the

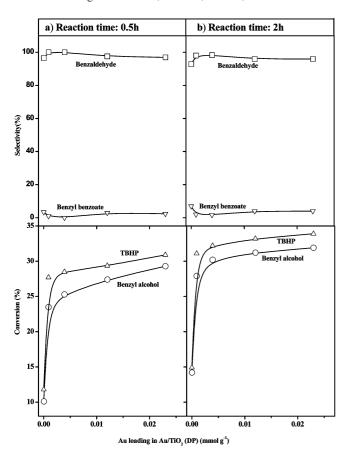


Figure 6. Influence of gold loading in Au/TiO₂ (DP) catalysts on its performance in the oxidation of benzyl alcohol.

formation of highly reactive atomic O species, which are responsible for the oxidation of benzyl alcohol to benzaldehyde and benzoic acid. These processes involve the following elementary reactions:

$$(CH3)3COOH \rightarrow (CH3)3COH + O$$
 (5)

$$C_6H_5CH_2OH + O \rightarrow C_6H_5CHO + H_2O$$
 (6)

$$C_6H_5CHO + O \rightarrow C_6H_5COOH$$
 (7)

As discussed later, because the reaction is structure-insensitive, the Au(III) species are expected to play an important role in the catalytic process. Because of the presence of easily reducible Au³⁺ species in both the Au/TiO₂ (DP and HDP) catalysts, a redox mechanism, similar to that described earlier for the oxidation of benzyl alcohol over MnO₄⁻-exchanged hydrotalcite catalysts¹² may also be operative simultaneously in the benzyl alcohol oxidation over the Au/TiO₂ catalysts. Furthermore, detailed investigation is required to understand the exact role played in the oxidation of benzyl alcohol by the metallic and cationic gold species present in the Au/TiO₂ catalysts.

Comparison of the Performance of Different Supported Nanogold Catalysts. Results showing the performance of the nanogold supported on the different transition-metal and rareearth oxides (all prepared by the HDP method) in the oxidation are included in Table 2. Because the gold loading for the catalyst is different, their catalytic performance is also expressed in terms of their turnover number (TOF), which is defined as the number of moles of benzyl alcohol converted to all products per mole

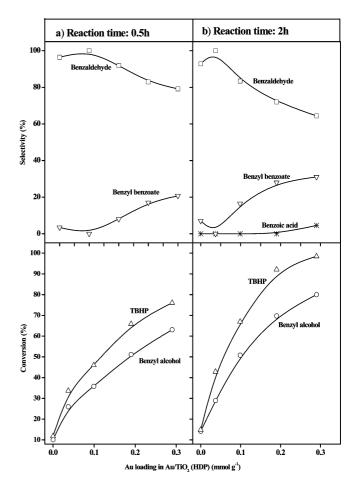


Figure 7. Influence of gold loading in Au/TiO₂ (HDP) catalysts on its performance in the oxidation of benzyl alcohol.

of gold per hour), for the purpose of comparing their performance in the oxidation.

The results show that the order of the catalysts for their performance is as follows:

Based on benzaldehyde yield:

$$\begin{aligned} \text{Au/TiO}_2 > \text{Au/ZrO}_2 > \text{Au/MnO}_2 > \text{Au/La}_2\text{O}_3 > \\ \text{Au/Yb}_2\text{O}_3 > \text{Au/Eu}_2\text{O}_3 > \text{Au/ZnO} > \text{Au/Sm}_2\text{O}_3 > \\ \text{Au/NiO} > \text{Au/CuO} > \text{Au/CoO}_x > \text{Au/Fe}_2\text{O}_3 \end{aligned}$$

Based on TOF (h^{-1}) :

$$\begin{aligned} &\text{Au/ZrO}_2 > \text{Au/MnO}_2 > \text{Au/TiO}_2 > \text{Au/La}_2\text{O}_3 > \\ &\text{Au/Sm}_2\text{O}_3 > \text{Au/Eu}_2\text{O}_3 > \text{Au/ZnO} > \text{Au/NiO} > \text{Au/CuO} > \\ &\text{Au/Fe}_2\text{O}_3 > \text{Au/CoO}_v \end{aligned}$$

To determine whether there is any correlation between the gold particle size and the TOF of the catalysts, a plot of TOF vs gold particle size for the catalyst having almost the same gold loading $(0.33 \pm 0.03 \text{ mmol/g})$ is presented in Figure 8. The plot does not show any trend; there is no direct dependence of the catalytic activity on the gold particle size of the different catalysts. This clearly reveals that the gold particles alone are not responsible for the catalytic activity. The reaction seems to be structure-insensitive. It seems that the gold particle—support interactions play a significant role in deciding the catalytic activity/selectivity in the process. These interactions may also be responsible for the presence of the cationic gold species Au^{3+} , which is observed on the Au/TiO_2 catalyst (see Table 1). Apart from the gold—support interactions, the support itself (which is a particularly easily

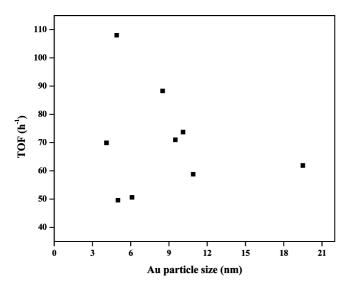


Figure 8. Turnover frequency (TOF) versus gold particle size plot for the supported nanogold catalysts (HDP) that have the same gold loading (0.33 \pm 0.03 mmol/g).

reducible metal oxide) may play a significant role, providing a redox reaction mechanism. Further detailed investigations are necessary to understand the gold—support interactions and the role of support of the supported nanogold catalysts in the catalytic process.

Conclusions

The present studies on the Au/TiO₂ (DP and HDP) and also on the other nanogold-supported transition and rare-earth oxide catalysts for the oxidation of benzyl alcohol to benzaldehyde by TBHP in the absence of any solvent lead to the following important conclusions:

- (1) The Au/TiO₂ and Au/ZrO₂ catalysts prepared by the HDP method are promising catalysts that show high activity and selectivity in the oxidation of benzyl alcohol to benzaldehyde.
- (2) For both of the Au/TiO₂ (DP and HDP) catalysts, their activity is increased but their selectivity for benzaldehyde is decreased as the gold loading in the catalyst increases.
- (3) The observed higher catalytic activity of the Au/TiO_2 (HDP) catalyst, compared to that of the Au/TiO_2 (DP) catalyst, is expected, most probably because of its higher Au^{3+}/Au^0 surface ratio. Even at the much higher gold loading, the Au/TiO_2 (HDP) catalyst has a smaller gold particle size and higher Au^{3+}/Au^0 ratio.
- (4) The catalytic activity and selectivity in the oxidation process are strongly influenced by the support used in the catalyst. For catalysts that have the same gold loading, the catalytic activity does not show any relationship with the gold particle size, indicating that strong interactions between the gold particles and the support, rather than the available gold surface, essentially control the catalytic activity. The reaction seems to be structure-insensitive.

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