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Selective Vapor-Phase Epoxidation of Propylene over Au/TiO_2 Catalysts in the Presence of Oxygen and Hydrogen

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Gold has long been thought to be chemically inert, however, it has recently been proven that its catalytic performance is dramatically tunable by control of the particle size and by careful selection of the support metal oxide. A typical example is the selective oxidation of propylene in a gas containing oxygen and hydrogen. When gold is deposited on TiO_2 by a deposition–precipitation technique as hemispherical particles with diameters smaller than 4.0 nm it produces propylene oxide with selectivities higher than 90% and conversions of 1–2% at temperatures of 303–393 K. The oxidation of hydrogen to form water is depressed by propylene, whereas propylene oxidation is not only enhanced but also restricted to partial oxidation by hydrogen. The depression of hydrogen combustion by the presence of propylene and a new peak due to gold deposition in TPD spectra have indicated that propylene is adsorbed on the surfaces of both gold particles and the TiO_2 support. The reaction rate is almost independent on the concentration of propylene and increases linearly with increasing concentrations of O_2 and H_2. The above results suggest that propylene adsorbed on a gold surface may react with oxygen species formed at the perimeter interface between the gold particles and the TiO_2 support through the reaction of oxygen with hydrogen. The effect of gold loading is surprising in that the reaction product switches from propylene oxide to propane when gold loading is decreased to 0.1 wt%. Careful TEM observation indicates that gold particles larger than 2.0 nm in diameter produce propylene oxide, whereas smaller gold particles produce propane.

INTRODUCTION

Propylene oxide (hereafter denoted as PO) is one of the most important chemical feedstocks for producing resins such as polyurethane. Major conventional manufacturing methods require two-stage processes, using chlorohydrin or hydroperoxides as an oxidant (1). The direct synthesis of PO, by the use of molecular oxygen, has long been desired and has been nominated one of the most important chemical reactions to remain unsolved by catalysis (2). Despite considerable effort, no economically viable route has yet been found. Most patents, featuring the vapor-phase oxidation of propylene to PO, show either low selectivity or low productivity (3). Since direct oxidation is difficult to achieve, a new process has been designed by Enichem to produce PO by oxidation with H_2O_2 over a titanium silicate catalyst (4, 5). For this process palladium supported on titanium silicate can be used to replace H_2O_2 with a mixture of molecular oxygen and hydrogen (6). The history of the epoxidation processes shows a shift of the oxidant from alkyl hydroperoxide with IV–VI elements toward hydrogen peroxide with Ti-silicate and, currently, toward hydrogen peroxide prepared *in situ* from dioxygen and hydrogen. Recently, a few new approaches have been attempted. Gas-phase partial oxidation of propylene in the copresence of propane (7), electrochemical oxidation on a Pt-black anode (8), and photochemical oxidation over SiO_2 based catalysts (9) can produce PO; however, selectivities are not sufficiently high, 50% at the highest.

Although gold was and still is regarded by many as being poorly active as a catalyst (10, 11), when gold is dispersed as fine particles over select metal oxides it has been found that the supported gold exhibits exceptionally high catalytic activity (12, 13). Examples include CO oxidation (14–22), hydrocarbon combustion (23, 24), hydrogenation of CO_2 and CO (25, 26), water gas shift reaction (27, 28), and also the reduction of NO to N_2 (29). Quite often reactions occur at low or subambient temperatures.

Results reported in the past for the partial oxidation of hydrocarbons over gold catalysts could not always be reproduced and may need for re-examination in view of chlorine contamination, dispersion of gold, support effect, and so forth. Gold catalysts investigated for C1 hydrocarbons are Au/$BaSO_4$ which can produce HCHO directly from CH_4 at 923K with a yield of 0.4% (30) and Au gauze which produces HCHO from CH_3OH at 723 K with a selectivity of 100% (31). It was reported that Au/SiO_2 catalyzed propylene oxidation to form PO with a yield below 1% and with 50% selectivity (32), whereas Cant and Hall reported that acrolein was produced with a yield of 5% and with

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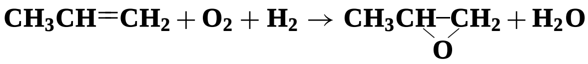
33% selectivity (33). Sinfelt described that the addition of gold to copper enhanced both activity and selectivity in the acrolein formation from proylene (34). Recently, Niiyama and his coworkers have reported that the deposition of Au onto $Bi_2Mo_3O_{12}$ is effective to improve the yield of acrolein from propylene maintaining its selectivity while Pd and Pt accelerate complete oxidation to CO_2 (35). Gold supported on Al_2O_3 and MgO was reported not to produce epoxide from ethylene and propylene because of two surface center adsorption per olefin molecule (36, 37).

In continuation with our recent work on highly dispersed gold catalysts, we present here the first evidence for the direct vapor-phase oxidation of propylene to PO in the presence of O_2 and H_2 using a catalyst comprising of gold deposited on TiO_2:



$$\mathbf{CH_3CH{=}CH_2 + O_2 + H_2 \rightarrow CH_3\underset{\diagdown O \diagup}{CH{-}CH_2} + H_2O} \quad [1]$$

propylene propylene oxide

EXPERIMENTAL

Catalyst Preparation

The TiO_2-supported gold catalysts were prepared by deposition–precipitation (DP) (38) of $Au(OH)_3$ onto TiO_2 (Nippon Aerosil, P-25, specific surface area; 50 m^2/g) in an aqueous solution of $HAuCl_4$ at pH = 7. The precursors were washed several times, dried, and calcined in air at 673 K for 3 h. By this method fine gold metal particles with diameters smaller than 4 nm could be deposited with almost uniform dispersion. They were mostly hemispherical in shape and were attached to the TiO_2 support at their flat planes (15). Actual gold loadings of Au/TiO_2 samples calcined were, of course, smaller than the gold contents in the starting solutions of $HAuCl_4$, usually by 40–80% (38). The gold loadings hereafter denoted are the gold contents in the finished catalysts measured by X-ray fluorescence analysis and are expressed as weight percentages to TiO_2 or TiO_2/SiO_2 support.

For comparison studies, the conventional impregnation method was also used; however, it produced spherical Au particles simply loaded on the TiO_2 support and with diameters larger than 10 nm. The $Au/TiO_2/SiO_2$ catalysts were also prepared by the same DP method by replacing TiO_2 with TiO_2/SiO_2 (TiO_2 loading, 3 wt% to SiO_2), which was prepared by impregnating the silica (Fuji Davison, ID gel, specific surface area; 310 m^2/g) with titanylacetylacetonate, followed by drying and calcination in air at 773 K for 2 h. The influence of metal oxide support was investigated by depositing gold on γ-Al_2O_3 (JRC-ALO-4, a reference sample of the Catalysis Society of Japan, with a specific surface area of 174 m^2/g), Fe_2O_3 (prepared from hydroxide precipitate, 37 m^2/g), Co_3O_4 (prepared from carbonate precipitate, 59 m^2/g), ZnO (prepared from hydroxide precipitate, 41 m^2/g), and ZrO_2 (Nippon Aerosil Co. Ltd., 40 m^2/g) in a similar manner. Because $Au(OH)_3$ could not be deposited on SiO_2, Au/SiO_2 was prepared by the impregnation method.

Pd/TiO_2 and Pt/TiO_2 catalysts were prepared by the usual impregnation method by using $(NH_4)_2PdCl_4$ and H_2PtCl_6, followed by drying, calcination in air at 673 K for 3 h, and H_2 treatment at 573 K for 2 h. These Pd and Pt metal particles obtained were confirmed to be smaller than 2 nm in diameter by TEM observation. In the case of Pd and Pt, deposition–precipitation did not lead to any appreciable difference in particle size nor in any catalytic activity for CO oxidation (39). Cu/TiO_2 and Ag/TiO_2 catalysts were also prepared by the impregnation method using nitrates as the starting material, followed by drying, calcination, and H_2 treatment, in a similar manner.

Catalyst Characterization

The particle size of gold was determined by a TEM (Hitachi H-9000NA). Except for Au loadings lower than 0.2 wt%, at least 200 particles were chosen to determine the mean diameter by using a computerized image analyzer (Nippon Avionics Co. Ltd., EXCEL). XPS measurements were conducted by using a spectrometer (Shimadzu ESCA-K1M) with a monochromatized Al focused X-ray beam and an analyzer energy of 50 eV. TPD measurements were carried out by using an apparatus equipped with TCD and FID detector after treating the samples in an O_2 or He stream at 673 K and then cooling to 273 K.

Catalytic Tests

Catalytic performance tests were made under atmospheric pressure in a quartz reactor using a continuous-flow system at a temperature range of 273 K and 623 K. A mixture of propylene, oxygen, hydrogen, and argon as diluent was passed through a fixed bed containing the catalyst samples. The concentration of C_3H_6, O_2, H_2 was varied from 2 to 20 vol%, 2 to 20 vol%, and 10 to 90 vol%, respectively. The feed gas compositions seem to be practical for an industrial process of the direct epoxidation of propylene; however, they need safety treatments because the explosion limit of H_2 is from 4.1 to 74.2 vol% in air and from 4.0 to 94.0 vol% in O_2.

Samples were sieved between 125 and 212μm of particle size for Au/TiO_2 and between 355 and 1000μm for $Au/TiO_2/SiO_2$ and in most cases weighed to 0.5 g. The temperature of the catalyst bed was measured by using a thermocouple in a glass tube which was fixed just above the catalyst bed. The flow rate was 2000 ml/h unless otherwise stated. All reaction products were identified by standard GC-Mass and NMR spectroscopic techniques and analyzed by two on-line gas chromatographs using four types of columns, Porapak Q (3m) for CO_2, C_3H_6, and C_3H_8, molecular sieve 5A (3m) for CO, and activated carbon (3m) for H_2 and O_2, as packed columns with a thermal conductivity detector (TCD), and HR-20M (0.53 mm × 50 m, Shinwa Chemical Industries, Co. Ltd.) capillary column for organic compounds with a flame ionization detector (FID). The detection limit of the FID was 0.001 vol% for organic compounds.

RESULTS

Catalyst Characterization

Figures 1 and 2 show typical TEM photopgraphs of Au/TiO_2 (Au loading 0.98 wt% (a) and 0.02 wt% (b)) and the distributions of the diameter of gold particles, respectively. Small gold particles with diameters of 1–4 nm and of hemispherical shape are homogeneously dispersed on TiO_2 particles. The mean particle diameter of Au was 2.4 nm with a standard deviation of 25% for 0.98 wt% Au loading and 1.7 nm with a standard deviation of 25% for 0.02 wt% loading. The Au 4d and 4f spectra of XPS for 0.98 wt% Au/TiO_2 showed no appreciable shift in binding energies from those of bulk gold, indicating that the gold particles were metallic in nature under high vacuum. Because of the very low loading (0.02 wt%), the XPS spectra for smaller gold particles could not be obtained.

Catalytic Properties

Table 1 shows the conditions and products for the reaction of C_3H_6 with O_2 and H_2 over Au, Pd, Pt, Cu, and Ag supported on TiO_2. The conversion tended to decrease sharply soon after the reaction and then after 10 to 20 min it gradually decreased with time on stream. The deactivation was caused mainly by oligomerization of PO and C_3H_6 and the catalysts used for reaction could be reactivated by air oxidation at 525 K. Only Au/TiO_2 prepared by the deposition–precipitation method could selectively catalyze the oxidation of C_3H_6 to PO. While C_3H_6 conversions are in general not large and the consumption of H_2 to form H_2O is much larger than that calculated from the stoichiometry of Eq. [1], the selectivities to PO are very high and exceed 90%. The other products detected were acetone and carbon dioxide. An increase in gold loading from 0.98 wt% to 3.2 wt% leads to an appreciable increase in the space time yield of PO but to a similar rate of PO formation per unit weight of Au.

When the TiO_2 support is replaced with TiO_2 deposited on SiO_2, the reaction temperature is shifted toward higher temperatures. The shift of reaction temperature can be correlated with a decrease in the catalytic activity for H_2 oxidation. It is also likely that the separation of active sites over the SiO_2 surface allows high temperature operation maintaining a good selectivity to PO. When the reaction temperature was raised to 373K with Au/TiO_2 catalysts, it was only the rate of H_2 combustion that was appreciably increased. The rate of PO formation was not increased but was decreased. It appears that there is an optimum temperature region for the epoxidation of C_3H_6 with each gold catalyst. On the other hand, H_2 combustion is monotonously enhanced with an increase in reaction temperature. The

TABLE 1

Reaction of Propylene with Oxygen and Hydrogen over Au, Pd, Pt, Cu, and Ag Supported on TiO_2 and over Au Supported on TiO_2/SiO_2

Catalyst	Metal loading,[a] wt%	Reaction temperature, K	Reaction[b] conditions	Conversion, %		Selectivity,[d] %				PO yield,[f] %	PO formation rate	
				C_3H_6[c]	H_2	PO[e]	Acetone	C_3H_8	CO_2		mmol/hr/g-cat	mmol/hr/g-Au
Au/TiO_2	0.98	323	A	1.1	3.2	>99	-	-	-	1.1	0.2	20.0
Au/TiO_2[g]	1.0	353	A	0.2	8.9	-	-	<10	>70	-	-	-
Au/TiO_2	3.2	303	B	0.3	2.5	93	7	-	-	0.3	0.27	8.4
		323	B	0.6	4.2	96	4	-	-	0.6	0.54	16.7
Au/TiO_2/SiO_2	0.20	393	C	2.5	2.6	93	-	-	7	2.3	0.21	102.7
Pd/TiO_2	1.0	298	A	57	98	-	0.4	98	1	-	-	-
Pt/TiO_2	1.0	298	A	12	87	-	2	92	6	-	-	-
Cu/TiO_2	1.0	393	A	<0.2	2.7	-	-	-	>99	-	-	-
Ag/TiO_2	1.0	393	A	<0.1	<0.1	-	-	-	-	-	-	-

[a] Actual metal loadings determined by X-ray fluorescence analysis.

[b] A: Feed gas, $C_3H_6/O_2/H_2/Ar = 10/10/10/70$; flow rate, 2000ml/hr; catalyst, 0.5g; B: Feed gas, $C_3H_6/O_2/H_2/Ar = 10/10/10/70$; flow rate, 2000ml/hr; catalyst, 0.1g; C: Feed gas, $C_3H_6/O_2/H_2/Ar = 5/10/40/45$: flow rate, 2000ml/hr; catalyst, 0.5g.

[c] Conversion of propylene = 100 (moles of all products detected by GC analysis)/(moles of propylene fed); moles of CO_2 formed divided by three.

[d] Selectivity = 100 (moles of each product detected directly by GC analysis)/(moles of all products detected directly by GC analysis); moles of CO_2 formed divided by three.

[e] PO = propylene oxide.

[f] PO Yield = 100 (moles of PO detected directly by GC analysis)/(moles of propylene fed).

[g] Prepared by impregnation method.

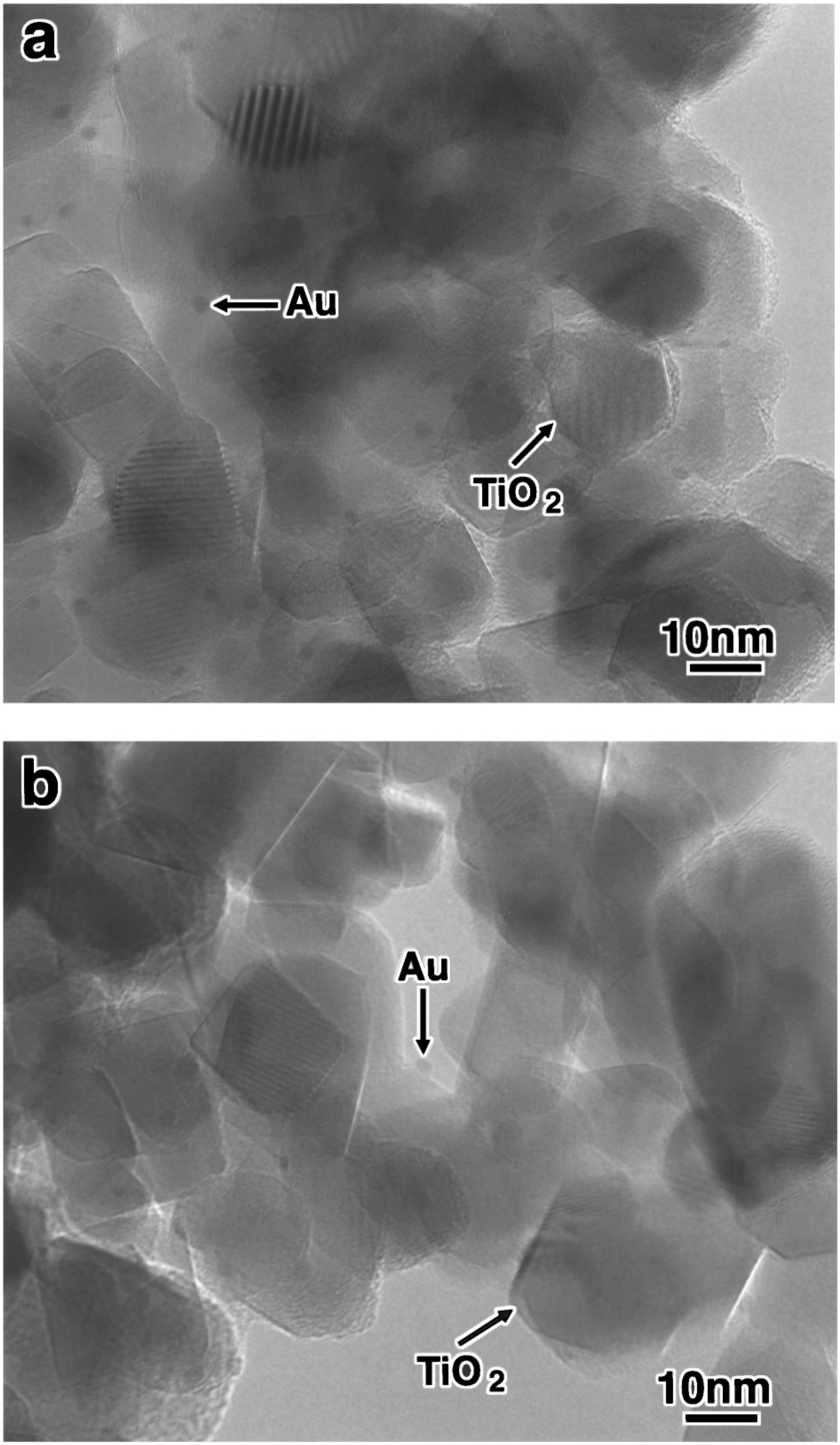


FIG. 1. TEM photographs for Au/TiO_2 catalysts. Au loading: (a) 0.98 wt%, (b) 0.02 wt%.

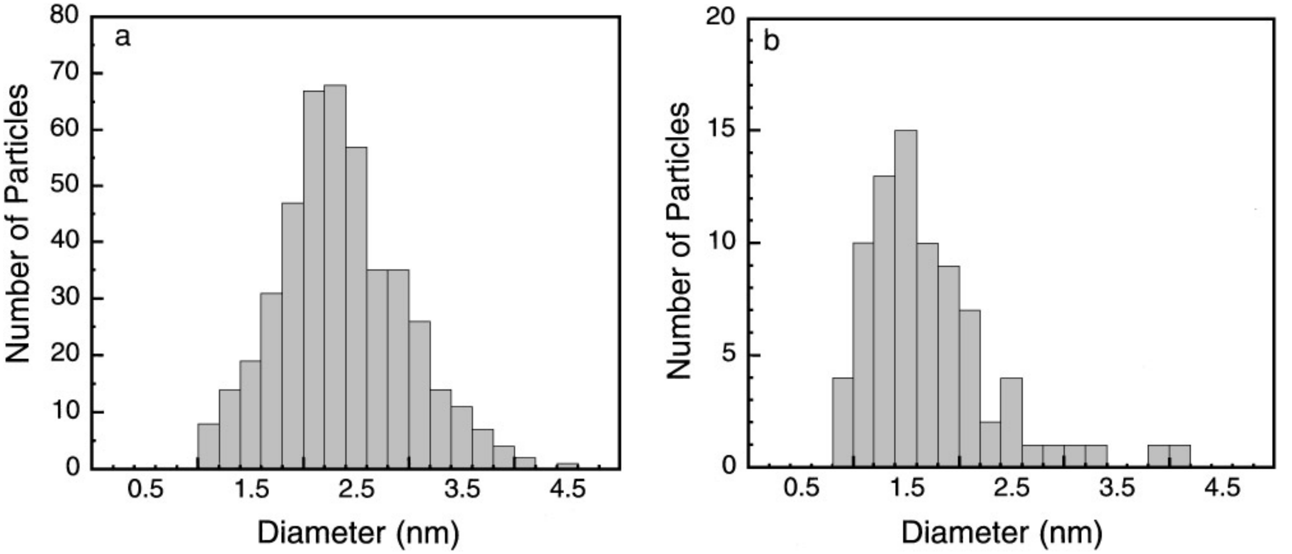


FIG. 2. Size distributions of gold particles for Au/TiO_2 catalysts. Au loading: (a) 0.98 wt%, (b) 0.02 wt%.

feed gas composition used for the $Au/TiO_2/SiO_2$ catalyst was also different from those of other catalysts: lower C_3H_6 concentration and larger H_2 concentration, both of which were advantageous for improving C_3H_6 conversion (see Fig. 4). The C_3H_6 conversion obtained was above 2% and the rate of PO formation per unit weight of Au was about five times as large as those of Au/TiO_2 catalysts.

Neither Au nor TiO_2 alone exhibited any notable catalytic activity and selectivity at a temperature range of 303 K to 573 K, indicating that the combination of Au with TiO_2 was indispensable for the selective oxidation of C_3H_6. However, it should be noted that PO did not form at all over Au/TiO_2 prepared by the conventional impregnation method, which produced spherical Au particles simply loaded on the TiO_2 support and with diameters above 10 nm. The combination of gold with other metal oxides, such as Al_2O_3, SiO_2, Fe_2O_3, Co_3O_4, ZnO, and ZrO_2 did not catalyze the partial oxidation of C_3H_6 and produced H_2O and CO_2. Over Pd/TiO_2 and Pt/TiO_2, C_3H_6 is mostly transformed into C_3H_8, a hydrogenated product, with only trace amounts of acetone formed as an oxygenate. Even at a lower temperature, at 298 K, the conversions of C_3H_6 and of H_2 are much larger than those at 323 K over Au/TiO_2. Over Cu/TiO_2 and Ag/TiO_2, neither partial oxygenates of C_3H_6 nor C_3H_8 were obtained and H_2 was preferentially converted to H_2O at temperatures above 393 K.

Figure 3 shows the rates of H_2-O_2, H_2-O_2-C_3H_6, and C_3H_6-O_2 reactions over Au(0.20 wt%)/TiO_2/SiO_2 as a function of temperature. The oxidation of C_3H_6, in the absence of H_2, occurs only above 473 K and produces mainly CO_2. While the oxidation of C_3H_6 is enhanced by H_2, the oxidation of H_2 to H_2O is retarded by C_3H_6. This provides optimal conditions for the selective low-temperature epoxidation of C_3H_6. The fact that H_2 consumption at 350 K is only about 1.4 times as the stoichiometric amount required to produce PO implies that the selective partial oxidation may principally proceed via Eq. [1]. Dioxygen may be transformed by reduction with H_2, to an active species which has the ability to selectively oxidize C_3H_6 to PO. However, as shown in Fig.3, the ratio of H_2 consumption to oxygenate formation increases with reaction temperature, indicating that the combustion of H_2 with O_2 is more enhanced than the partial oxidation of C_3H_6. From the economical point of view, it is requested to minimize the ratio down to unity by retarding the consumption of H_2 with O_2 to form H_2O.

Figure 4 shows the rate of PO formation as a function of partial pressure of feed gas, H_2, O_2, and C_3H_6, at the reaction temperature of 350 K and 393 K. The PO formation rate appreciably increases with increasing concentration of H_2 and O_2 and almost independent of the concentration of C_3H_6 up to 10 vol%. The rate dependency on oxygen concentration is the first order and saturates at around 10 vol%. The hydrogen-dependency does not level off and gives reaction orders of 0.9–0.6. The above reaction orders imply that C_3H_6 is strongly adsorbed on the catalyst surface nearly to saturation and that the active oxygen species are formed through the reaction of O_2 with H_2.

TPD of Propylene

In TPD spectra, as shown in Fig. 5, a single broad desorption peak is observed at around 313 K for TiO_2. This peak can be assigned to C_3H_6 adsorbed on the surface of TiO_2. Pretreatment in a stream containing H_2O before the introduction of C_3H_6 pulses reduces the intensity of the

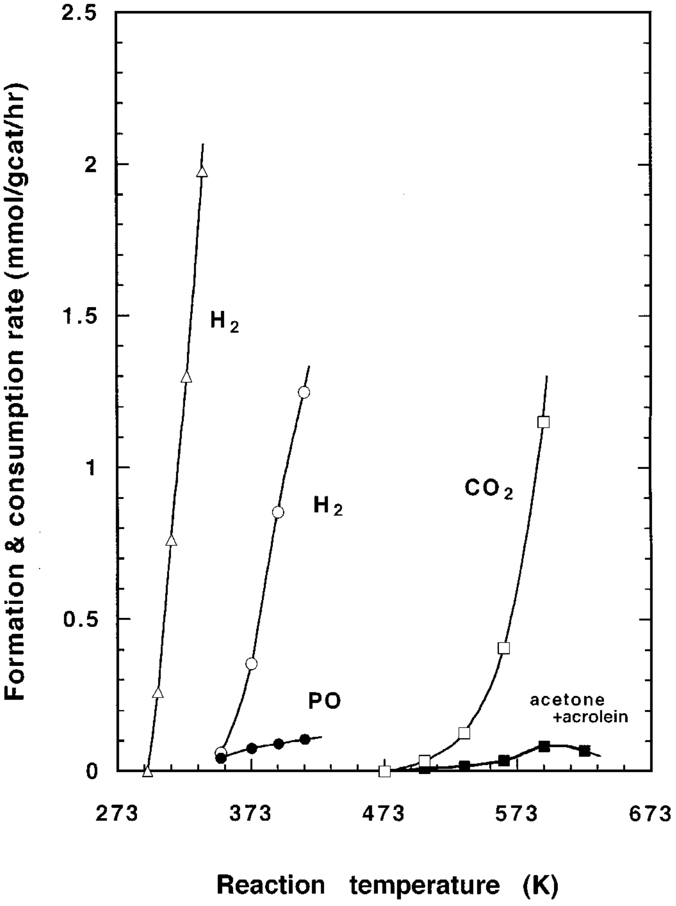


FIG. 3. Rate of oxygenate formation and of hydrogen consumption in the oxidation of hydrogen and/or propylene over $Au/TiO_2/SiO_2$. Flow rate, 2000ml/hr; catalyst, Au(0.20 wt%)/TiO_2/SiO_2 0.5g: △, hydrogen consumption in a feed gas of $H_2/O_2/Ar = 40/10/50$ (vol%); ○, hydrogen consumption and ●, PO (propylene oxide) formation in a feed gas of $H_2/O_2/C_3H_6/Ar = 40/10/2/48$ (vol%); □, CO_2 formation and ■, the formation of acetone and acrolein in a feed gas of $C_3H_6/O_2/Ar = 2/10/88$ (vol%).

desorption peak and brought about a new peak at around 423–573 K due to water desorption. For Au/TiO_2 the C_3H_6 desorption was observed in two peaks at around 313 K and around 323 K. The higher-temperature peak which does not disappear after the moisture pretreatment can be ascribed to the desorption of C_3H_6 from the surface of Au particles or/and the perimeter interface on the TiO_2 support. The former possibility is assumed to be much larger, because H_2 oxidation which occurs on the surface of Au particles is appreciably retarded in the copresence of C_3H_6. The whole peak intensity for C_3H_6 desorption decreases by moisture pretreatment (c) and (d) in the same ratio between TiO_2 and Au/TiO_2, 21% reduction from (b) to (c) and 51% reduction from (b) to (d), indicating that moisture affects the adsorption of C_3H_6 on the TiO_2 support and on the Au particles similarly. Since the exposed surface area of the gold particles occupies only less than 1% of the total surface area of the TiO_2 support in the Au (0.98 wt%)/TiO_2 sample (40), the peak intensity ratio of 4 (Au/TiO_2) to 3 (TiO_2) suggests that the population density of C_3H_6 adsorption is larger by more than 30 times on the Au surface than on the TiO_2 surface. The above results imply that C_3H_6 can preferentially adsorb on the surface of Au particles under reaction conditions where H_2O is continuously formed.

Effect of Au Loading: Switching of Product Selectivity

The unique behavior of Au/TiO_2 system is that the reaction pathway switches from oxidation to hydrogenation at a specific Au metal loading. Table 2 lists the yields of reaction products over Au/TiO_2 catalysts with different gold loadings ranging from 0.02 wt% to 0.98 wt%. The catalysts with Au loadings of 0.98 and 0.39 wt% catalyze oxidation to produce mainly PO with a by-product of CO_2. On the other

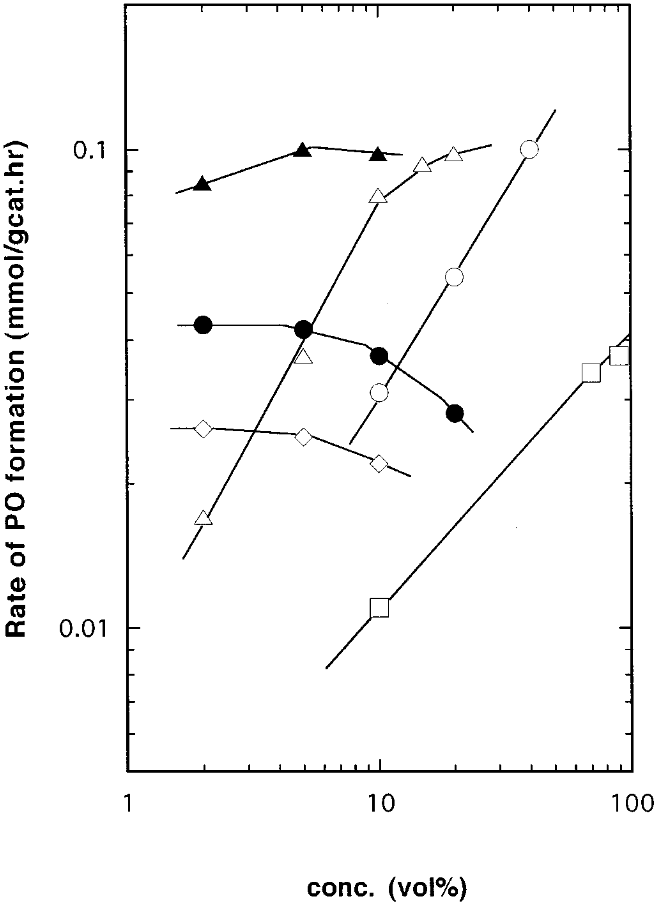


FIG. 4. Rate dependency on reactant concentration over $Au/TiO_2/SiO_2$: ○, $H_2/O_2/C_3H_6 = 10\text{-}40/10/5$ (393K); □, $H_2/O_2/C_3H_6 = 10\text{-}90/5/5$ (350K); △, $H_2/O_2/C_3H_6 = 40/2\text{-}20/5$ (393K); ◇, $H_2/O_2/C_3H_6 = 10/10/2\text{-}10$ (350K); ●, $H_2/O_2/C_3H_6 = 40/10/2\text{-}20$ (350K); ▲, $H_2/O_2/C_3H_6 = 40/10/2\text{-}10$ (393K). Each gas was diluted with Ar up to 100 vol% in total. Flow rate, 2000ml/hr; catalyst, Au(0.20 wt%)/TiO_2/SiO_2 0.5g.

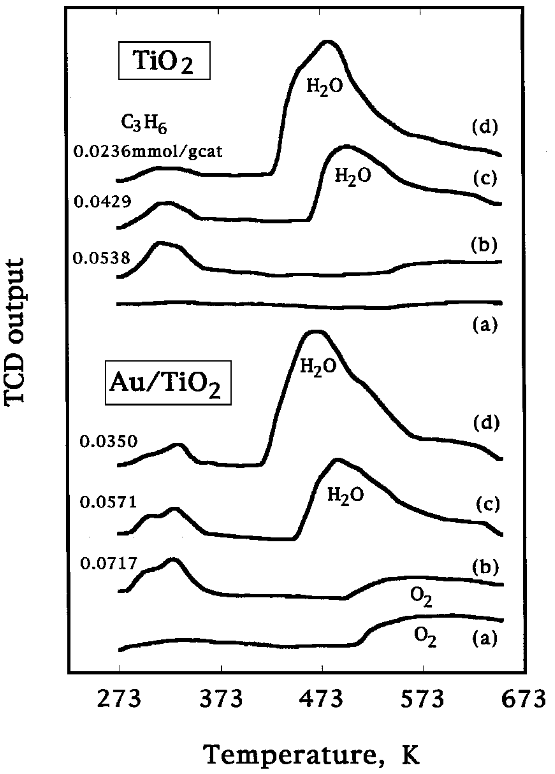


FIG. 5. TPD profile for Au/TiO_2 (Au loading, 0.98 wt%) and TiO_2. Pretreatment for Au/TiO_2 and TiO_2: (a) in O_2 at 573K for 1 h, (b) in O_2 at 573K for 1 h, followed by exposure to C_3H_6 pulses up to full uptake, (c) in O_2 at 573 K for 1 h, followed by exposure to He stream containing H_2O at 2.3 vol% for 10 min, then to C_3H_6 pulses up to full uptake, (d) in O_2 at 573 K for 1 h, followed by exposure to He stream containing H_2O at 2.3 vol% for 20 min, then to C_3H_6 pulses up to full uptake. Heating rate, 5 K/min; rate of flow, 50 ml/min; sample weight, 200 mg.

hand, for Au loadings smaller than 0.10 wt% hydrogenation is catalyzed to produce C_3H_8 alone. Both PO and C_3H_8 were competitively produced for metal loadings of 0.20 wt% and 0.10 wt%, and in the latter case C_3H_8 tended to exceed PO. The reaction products for each catalyst never changed under the different reaction conditions investigated. These results show that the reaction pathway switches over from oxidation to hydrogenation over Au/TiO_2 catalysts at a critical Au loading of 0.20 wt%.

Since the reaction pathway had been assumed to be correlated with the size of Au particles, we made careful TEM observation for every catalyst. In the case of 0.98 wt% and 0.39 wt% Au samples, Au particles having hemispherical shape were homogeneously dispersed with diameters of 1–4 nm. Although the number of Au particles observed was not large for the catalysts with loadings below 0.10 wt%, a major difference between Au loadings above 0.39 wt% and below 0.10 wt% is whether the majority of particles have diameters above or below 2 nm. The sample prepared with a Au loading of 0.20 wt% appeared to have smaller particles than those with lower Au loadings and the mean diameter of Au particles was not so different for Au/TiO_2 catalysts with Au loadings below 0.20 wt%. On the other hand, the contrast of Au particles in TEM observation become weaker with lower Au loadings. This implies that Au particles were thinner or flatter and that we might have been unable to observe all the small Au particles in the samples with low Au loadings. It is probable that not only particle size but also the particle shape (thick or thin) influence the reaction of C_3H_6. The flat shape of Au particles may account for the fact that the formation rate of C_3H_8 normalized per gram Au appreciably increases with a decrease in Au loading. However, it can be primarily concluded that gold particles larger than 2 nm are responsible for the formation of PO, whereas those below 2 nm catalyze the formation of C_3H_8. Gold particles smaller than 2 nm may be no longer intrinsically gold but may resemble Pt in catalytic nature which also selectively produces C_3H_8 under the same reaction conditions. Since Au clusters smaller than 1 nm could not be clearly observed by TEM the possibility of the contribution of such clusters to the catalytic reaction cannot be excluded.

DISCUSSION

The results obtained appear to show that over the Au/TiO_2-based catalysts molecular oxygen can be transformed through the reaction with molecular hydrogen to an active species, which is capable to selectively oxidize C_3H_6 adsorbed on Au particles to PO. Although we have attempted to detect oxygen species by ESR, no significant information has yet been obtained. Many intermediates, for example H_2O_2, are known to be involved during the reaction between H_2 and O_2 (41). Naito and Tanimoto have speculated that oxygen molecules on small Au particles behave as a peroxo-like adsorbed species, which enhances the dissociation of hydrogen molecules (42). Moreover, the products, epoxides from alkenes, are similar to those of the oxidations of hydrocarbons by H_2O_2 over titanium silicates, on which a peroxo or hydroperoxo species is regarded to be responsible for the selective oxidation (4, 43). From this we speculate that the active oxygen species may be a similar peroxo-like species, formed on a Ti cation site at the boundary between the Au particles and the TiO_2 support. This assumption can also explain why Au/TiO_2 prepared by impregnation does not lead to PO formation; the larger spherical Au particles simply loaded on TiO_2 have much weaker interactions and a much shorter perimeter interface with the TiO_2 on which the peroxo-like species may be produced.

Figure 6 shows a probable formation route for the active oxygen species on the Au/TiO_2 catalyst. Although it is speculative at the present stage of our research, at the border between the gold particless and the TiO_2 support there may be an equilibrium state between $Ti^{4+}{=}O\cdots Au^0 \Leftrightarrow Ti^{3+}\text{-}O\text{-}Au^+$. The presence of positively charged gold species has been

TABLE 2

Product Yield for the Reaction of Propylene with Oxygen and Hydrogen over Au/TiO_2 with Different Gold Loadings and the Results of TEM Observation

	Yield of products,[b] %			TEM observaiton			
Au loadings,[a] wt%	Propane	Propylene oxide	CO_2	Total number of Au particles	Mean diameter, nm	Most frequent diameter, nm	Standard deviation, %
0.98	—	0.61 [0.109][c] (11.1)[d]	0.08 [0.014] (1.4)	446	2.4	2.2-2.4	25
0.39	-	0.56 [0.100] (25.6)	0.20 [0.036] (9.2)	258	2.2	2.2-2.4	30
0.20	0.33 [0.059] (29.5)	0.54 [0.096] (48.0)	0.05 [0.009] (4.5)	393	1.5	1.2-1.4	25
0.10	1.9 [0.346] (346)	0.1 [0.018] (18.0)	-	35	1.8	1.0-1.2	36
0.05	3.1 [0.554] (1108)	-	-	79	1.5	0.8-1.0	25
0.02	2.5 [0.446] (2230)	-	-	80	1.7	1.4-1.6	25

[a] Actual Au loadings determined by X-ray fluorescence analysis.

[b] Reaction conditions: feed gas, $C_3H_6/O_2/H_2/Ar = 10/10/10/70$; flow rate, 2000ml/hr; catalyst, 0.5 g; temperature, 353K.

[c] Formation rate (mmol/hr/g-cat) is given in parenthesis [ ].

[d] Formation rate (mmol/hr/g-Au) is given in parenthesis ( ).

indicated by a smaller carbonyl peak at a higher wavenumber region (ν CO) in FT-IR (44). Molecular oxygen is taken up by a Ti^{3+} cation site and is activated, probably to a negatively charged molecular oxygen species, which forms hydropeoxo- or peroxo-like species directly through reaction with hydrogen. The oxygen species adsorbed on Ti site can react with C_3H_6 mainly adsorbed on the surface of Au particles to produce PO.

Monooxygenase enzymes can excellently catalyze the oxidation of alkenes to epoxides at ambient temperatures with high selectivities through the reductive activation of molecular oxygen (45, 46), as expressed in Eq. [2], where So is a substrate, hydrocarbon:

$$\mathbf{S_0 + O_2 + 2H^+ + 2e^- \rightarrow S_0O + H_2O}. \qquad [2]$$

Dioxygen is transformed to an activated species by the interaction with two protons and electrons. One oxygen atom is donated to the organic substrate and the other to form water. The catalytic features of Au/TiO_2 catalysts observed show reasonable similarity to the enzymes in terms of the reductive activation of dioxygen with molecular hydrogen and, also, by the presence of multifunctional active sites (46). The key role of Au appears to be in providing

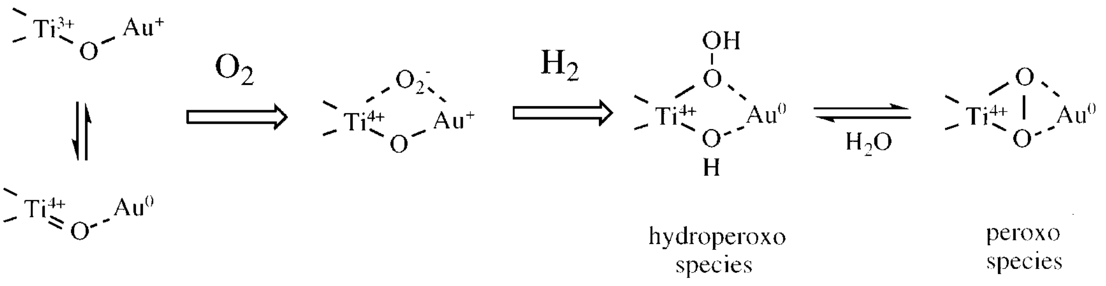


FIG. 6. A probable formation route for the active oxygen species on Au/TiO_2 catalyst.

binding sites for C_3H_6 and to aid electron transfer from H_2 to O_2.

Several attempts have been reported where the behavior of monooxygenase enzymes have also been successfully mimicked concerning the activation of molecular oxygen. Pd-Fe zeolite (47) and Pd-titanosilicate (6, 48) can catalyze the oxidation of both alkanes and alkenes to oxygenates in the liquid phase, by using H_2O_2 generated *in situ*. Vapor phase processes by use of oxygen and hydrogen have also been reported for CH_4 over $FePO_4$ (49) and benzene over Pd-Cu (50).

The occurrence of hydrogenation of C_3H_6 over Au/TiO_2 with very low Au loadings appears consistent with the results reported by Naito *et al.* for Au/SiO_2 catalyst (42), where using very low Au loadings it was found that the hydrogenation of olefins was accelerated by the presence of oxygen. Our work has further demonstrated that the reaction of C_3H_6 switches between partial oxidation and hydrogenation, depending on the size of Au particles. Flat Au particles with diameters smaller than 2 nm might be oxidic in nature in the copresence of O_2, namely, positively charged to a certain extent, whereas Au particles larger than 2 nm might be still metallic. The positively charged state of Au will have electronically some similarities to that of Pt metal and can catalyze hydrogen dissociation and then hydrogenation. It is probable that Au can remain oxidic only in the presence of O_2 which is electrophilic and therefore O_2 is necessary for hydrogenation over Au/TiO_2. Further investigation is now underway to understand the structure–catalytic function relations and to describe the concerted mechanism of metal and support.

CONCLUSION

The selective partial oxidation of propylene to propylene oxide has been achieved over a supported gold catalyst in a vapor-phase containing H_2 and O_2. Combination of Au and TiO_2 is indispensable for the selective oxidation. Over Au/TiO_2, the presence of H_2 not only enhances the oxidation of C_3H_6 but also leads to the epoxidation to produce propylene oxide at 303 K to 393 K with selectivities above 90%. It appears that the reaction pathway can be tuned, by carefully controlling the size of the Au particles and switches from oxidation to hydrogenation at a critical size of around 2 nm. Although no direct experimental evidence was obtained, it can be suggested that the active oxygen species are produced by the reductive activation of molecular oxygen with molecular hydrogen at the perimeter boundary between the Au particles and the TiO_2 support.

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