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# Monoatomically dispersed $Pd/TiO_2$ catalyst effective for epoxidation of propylene at ambient temperature in the presence of $H_2$ and $O_2$

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#### ABSTRACT

The catalytic activity of monoatomically dispersed Pd supported on TiO<sub>2</sub> toward propylene epoxidation in the presence of H<sub>2</sub> and O<sub>2</sub> was studied at ambient temperature, and both propylene oxide (PO) and propane were obtained. Short-chain alkanes also reacted but epoxide formation was not observed in those reactions except in the case of isobutane, which formed isobutylene oxide at a low rate. The optimum surface concentration of Pd on TiO<sub>2</sub> was 0.005–0.01 atom/nm<sup>2</sup>; because the supported amount of Pd is extremely small relative to the surface area of the support, the supported Pd is thought to be monoatomically dispersed. Pd/TiO<sub>2</sub> catalysts prepared from a tetraphenylporphyrin–Pd chloride complex showed almost the same product distribution for propylene epoxidation as did catalysts prepared from Pd(NO<sub>3</sub>)<sub>2</sub>. Isotope exchange between H<sub>2</sub> and D<sub>2</sub> proceeded over Pd/TiO<sub>2</sub> with a low surface concentration (0.0001 atom-Pd/nm<sup>2</sup>), and chemical potential calculations suggested that H<sub>2</sub> molecules could dissociatively adsorb onto the monoatomically dispersed Pd/TiO<sub>2</sub>. A PO formation mechanism over the catalyst is proposed on the basis of these results. The results presented here may provide the first clear evidence of catalysis by monoatomically dispersed noble metals.

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#### 1. Introduction

Propylene oxide (PO) is one of the most important raw materials for organic syntheses and is produced on a large scale industrially. Its major applications are the production of polyether polyols, which are used in making polyurethane plastics, and propylene glycol, which is used as a water keeping agent and as a surfactant for foodstuffs and cosmetics. In contrast to the epoxidation of ethylene, the catalytic epoxidation of propylene is very difficult [1]. Industrially, the Chlorohydrin process and Halcon process are used to produce PO [2]. The former of these processes requires use of hazardous chlorine and produces CaCl<sub>2</sub> as a byproduct. The latter process requires the use of expensive cumen hydroperoxide. To circumvent the drawbacks associated with the Chlorohydrin and Halcon processes, the development of a safe and low-cost propylene epoxidation process is desired.

Propylene epoxidation has been explored using many oxidizing agents, including molecular oxygen [6], nitrous oxide [7–9], hydrogen peroxide [10-14], and organic hydroperoxide [15,16]. Ovama and co-workers [3] reported that  $MoO_x/SiO_2$  effectively epoxidized gas-phase propylene; propylene conversion of 17.6% and PO selectivity of 43.6% were obtained at 5 atm, 573 K, and  $C_3H_6/O_2/He$  flow rates of  $10/5/10 \text{ cm}^3/\text{min}$ . The same study also reported that crystalline MoO<sub>3</sub> nanoparticles were more effective for propylene epoxidation to PO than was a molecularly dispersed Mo oxide. Murata and co-workers [4] reported that a Ti- and Al-containing hexagonal mesoporous silica catalyst produced 47.8% propylene conversion and 30.6% PO selectivity for propylene epoxidation by molecular oxygen at 523 K. They proposed that an epoxide-like intermediate that formed at the Ti and Al sites produced a synergistic effect for the two metals. Furthermore, extra-framework Ti4+ ions improved the PO yield only slightly and the extra-framework Al<sup>3+</sup> ions greatly decreased the selectivity for PO, because the ions' strong acidity promoted the oligomerization and cracking of propylene. Takahashi et al. [5] reported that Ag-based catalysts containing an added 3d transition-metal species (Mn, Fe, Co, or Ni) catalyzed PO formation, and that Ag-Ni (33 mol%) exhibited PO selectivity about 4 times that observed for Ag alone at 4-6% propylene conversion. Since the dispersion of Ag particles in the Ag-Ni catalysts increased with increasing Ni

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content, the authors concluded that Ni atoms controlled the Ag particle size by suppressing the sintering of Ag particles. Miyaji et al. reported that propylene oxide was obtained selectively over Ti-MCM-41 impregnated with metal nitrates. The PO yield increased with increasing Ti content of Ti-MCM-41 and reached a maximum at an optimum Si/Ti ratio of 100. It is of interest that calcium nitrate was the most suitable additive and the acid treatment of the catalyst improved the PO formation. The presence of both nitrate and molecular oxygen was essential for the PO formation [6].

In the epoxidation of propylene by N<sub>2</sub>O, Zhang et al. [7] studied the use of alkali metal salt (KCl)-modified Fe-MFI and Fe-MCM-41 and reported that extra-framework Fe species (e.g.,  $FeO_x$  clusters) exhibited higher PO formation activity after KCl modification. A PO selectivity of 80% was achieved at a propylene conversion of 3.3% over the KCl-modified Fe-MCM-41. The modification with KCl increased the dispersion of extra-framework Fe species in tetrahedral coordination. Moens et al. [8] investigated the catalytic activity of alkaline- and alkaline-earth-modified silica-supported metal oxides for epoxidizing propylene with nitrous oxide, and Fe and Cr oxides showed the highest activities among the oxides tested. After modification by Rb<sub>2</sub>SO<sub>4</sub>, the oxidation rate increased significantly, and PO was the principal product, with selectivities as high as 85–90%. Rb<sub>2</sub>SO<sub>4</sub> severely reduced the acidity of the catalyst, and thus PO isomerization was drastically reduced. The authors proposed that well-dispersed, distorted tetrahedral Fe<sup>3+</sup> sites were the active sites for epoxidation and that Fe dispersion was controlled by the promoter salts, with both anions and cations being essential for catalysis. Epoxidation of propylene in liquid-phase by H<sub>2</sub>O<sub>2</sub> and organic hydroperoxide was also achieved with these catalysts.

Recently, propylene epoxidation in the presence of both H<sub>2</sub> and O<sub>2</sub> has been reported. Haruta and co-workers reported that nanoscale Au particles on titania supports in the presence of H<sub>2</sub> and O<sub>2</sub> provide a means for highly selective, vapor-phase propylene oxide production [17-19]. According to their reports, Au nanoparticles with 2-5 nm diameter catalyzed PO formation, whereas smaller particles catalyzed propylene hydrogenation. They also reported that among the noble metals, only Au and Ag were active for PO formation. Haruta and co-workers also found that nanoparticles of Au-Ti-MCM-41 were effective for propylene epoxidation in the presence of H<sub>2</sub> and O<sub>2</sub> [20,21]. Ti was hydrothermally incorporated into the mesoporous MCM-41 framework, and the authors found that the catalyst prepared by hydrothermal incorporation followed by post-synthesis was higher activity than the catalyst by hydrothermally during synthesis or by post-synthesis grafting. The presence of more Ti sites isolated from each other is thought to be responsible for the enhanced activity of the catalysts comprising of titanium incorporated by two-step method [20,21]. In another report, Haruta et al. studied Au nanoparticles supported on nonporous  $TiO_2$ -SiO<sub>2</sub> and concluded that isolated  $TiO_4$  sites incorporated in silica surface layers are an important structural factor for the selective deposition of Au particles and for selective PO formation [22]. Au supported on Ti-MCM-48 and Ti-MCM-41 was also investigated, and the authors concluded that guick deactivation of Au catalysts within hours is mainly affected by the surface properties rather than the pore structure and diffusion limitation of the supports [23,24]. Delgass and co-workers [25] studied the location of Au in TS-1 catalysts and concluded that although a Au particle diameter of 2-5 nm is essential for PO formation, PO formation rates are not strongly influenced by the TS-1 particle size and are thus not proportional to the specific external surface area of the support. These investigators also concluded that PO formation might have occurred on Au particles residing in the channels of the TS-1 because the observable gold particles decorating the TS-1 surface account for only  $\sim$ 30% of the total Au content of the

catalyst. Extremely small Au clusters of 2-5 nm located near Ti sites inside the TS-1 pores or on the TS-1 surface were active for propylene epoxidation. Au/TS-1 catalysts with mesoporous-scale defects that were induced through the addition of carbon pearls during synthesis had the highest PO formation rate, despite relatively high Au loading, considerable contamination with octahedral Ti species, and the presence of a significant portion of Au deposited on the support surface that might have been inactive for epoxidation [26]. Explaining the resultant fractional reactant orders  $(O_2 = 0.31 \pm 0.04, H_2 = 0.60 \pm 0.03, and C_3H_6 = 0.18 \pm 0.04)$  on Au/TS-1 using the statistical software package JMP requires a sequence of elementary kinetic steps having a minimum of two active sites participating in the rate-determining step. The proposed reaction sequence requires that Ti and Au sites must generate and use the epoxidation oxidant simultaneously rather than sequentially [27]. After investigating the catalytic activity of a series of Au/TS-1 catalysts with varying Au and Ti contents prepared by deposition-precipitation and observing transmission electron microscopy (TEM) images, Delgass and co-workers reported that Au loading is closely related to Ti loading and that significant activity is attributable to Au particles much smaller than 2 nm [28]. Oyama et al. studied propylene epoxidation in H<sub>2</sub> and O<sub>2</sub> concentrations as high as 40% over a highly dispersed Au/TS-1 catalyst in a packed-bed catalytic membrane reactor and found that the rate of PO production was improved by 100-200% compared with that observed in a conventional packed-bed reactor [29]. The above-mentioned studies indicate that Au/TiO<sub>2</sub> catalysts containing Au particles with diameters of 2-5 nm supported on TiO<sub>2</sub> effectively catalyze PO formation

We have investigated noble metals for their ability to promote the oxidation of isobutane and have found that extremely small concentrations of noble metals supported on SiO<sub>2</sub> and Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> affected the catalytic activity and product distribution in the partial oxidation of iso-butane [30]. Pt, Pd, and Rh supported on SiO<sub>2</sub> at a concentration of  $1 \times 10^{-6}$  atom/nm<sup>2</sup> enhanced the catalytic activity, increased the selectivity of the partial oxidation products isobutene, methacrolein, acetaldehyde, and acetone, and decreased  $CO_x$  selectivity. Electron paramagnetic resonance (EPR) measurements indicated that two valent Rh ions were monoatomically dispersed on the surface and played a role in the oxidation of iso-butane. Pd, Ir, Rh, and Au supported on  $Bi_2 Mo_3 O_{12}$  at a concentration of  $1.1 \times 10^{-5} \, atom/nm^2$ increased the conversion of iso-butane, but Pt and Ru decreased it. The catalytic activity was increased by decreasing the concentration of noble metals to  $2 \times 10^{-6}$  atom/nm<sup>2</sup>; in particular, Rh supported on Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> at this concentration exhibited increased catalytic activity without affecting the methacrolein selectivity. We concluded that supported noble metals interact with active oxygen ions bridging Mo and Bi on the Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> surface.

More recently, we studied the reaction of  $C_3H_6$  over supported noble metal catalysts in the presence of  $O_2$  and  $H_2$  and found that Pd/TiO<sub>2</sub> with extremely low Pd concentration is effective for epoxidation of olefins at ambient temperature [31]. In that study, PO was obtained from propylene (1–2% yield; 30–60% selectivity) together with propane. The difference between the Pd/TiO<sub>2</sub> catalyst used in that study and a Au catalyst is that the active site for Pd/TiO<sub>2</sub> is so small that is monoatomic. Unfortunately, the amount of Pd used in the catalyst was too small to detect by any spectroscopic means.

In this paper, we provide a detailed report of the catalytic activity of Pd/TiO<sub>2</sub> toward oxidation of lower-molecular-weight alkanes in the presence of  $H_2$  and  $O_2$ , and the structure of the catalyst's active site. The effects of catalyst preparation conditions on the reaction rates and the reaction mechanism of PO formation are discussed.



**Fig. 1.** Schematic diagram of the reaction apparatus. (a) Mixer, (b) electric furnace, (c) catalyst, (d) SiO<sub>2</sub> wool, (e) thermocouple, (f) gas sampling port, and (g) vent.

#### 2. Experimental

#### 2.1. Catalyst preparation

Aerosil TiO<sub>2</sub> P-25 ( $50 \text{ m}^2/\text{g}$ ) was used as the catalyst support. Pd standard solution (Wako Pure Chemical Co., 5 mg/ml in HNO<sub>3</sub> (1+1)) was added to a beaker in which the support material was soaked in pure water. The solvent was evaporated to dryness with a rotary evaporator, and the remaining solid was dried at 333 K overnight. The dried material was calcined at 773 K for 4 h in air and then was reduced in a H<sub>2</sub> stream (40 cm<sup>3</sup>/min) at 723 K for 2 h, yielding the Pd/TiO<sub>2</sub> catalyst.

Pd/TiO<sub>2</sub>-tetraphenylporphyrin (TPP) catalysts were prepared from a solution of Pd-TPP chloride dissolved in a mixed solvent of tetrahydrofuran and water (molar ratio 1:1). Pd/TiO<sub>2</sub>-TPP catalysts were prepared by means of the experimental procedure described above for preparing Pd/TiO<sub>2</sub> catalysts from Pd(NO<sub>3</sub>)<sub>2</sub>. The Pd concentrations on both types of prepared catalysts were 0.0001-0.02 atom-Pd/nm<sup>2</sup> (8.8 × 10<sup>-8</sup>-0.0176 wt%).

#### 2.2. Experimental procedure and product analysis

Propylene and alkanes (Sumitomo Seika Chem. Co., 99.5 vol% up) obtained from were used. Catalytic reactions were carried out with an ordinal-flow-type reactor made of Pyrex glass (Fig. 1). The gas composition was 20 mol%  $C_3H_6$ , 20 mol%  $O_2$ , 10 mol%  $H_2$ , and 50 mol%  $N_2$ , and the flow rate was 30 cm<sup>3</sup>/min at ambient temperature. For each reaction, 0.50 g of catalyst was used. Reactants and produced gases were analyzed by gas chromatography, and the products were identified by gas chromatography–mass spectrometry (GC–MS).

#### 2.3. Hydrogen isotope exchange reaction

Isotope exchange reaction was carried out using a circulation reaction system with 105.0 ml at 293 K. Catalysts prepared from Pd nitrate and Pd-TPP with 0.0001 atom Pd/nm<sup>2</sup> were used. The samples which were calcined at 773 K for 5 h and then reduced by hydrogen at 723 K for 2 h, were evacuated at 723 K for 0.5 h and then the temperature was cooled to 293 K. A mixture of H<sub>2</sub> and D<sub>2</sub> (molar ratio of H<sub>2</sub>/D<sub>2</sub> was 1.0) was introduced the circulation system and equilibration was commenced. Gaseous hydrogen was analyzed by MS.



**Fig. 2.** Time course of the rates of product formation at ambient temperatures (a), the product distribution at several temperatures (b) for the reaction of propylene over Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> prepared from Pd(NO<sub>3</sub>)<sub>2</sub> and the consumption rate of hydrogen (c)  $\square$  CH<sub>3</sub>CHO,  $\square$  PO,  $\blacksquare$  CH<sub>3</sub>COCH<sub>3</sub>,  $\square$  CO<sub>2</sub>,  $\square$  C<sub>3</sub>H<sub>8</sub>,  $\boxed{\square}$  CH<sub>2</sub>O.

#### 3. Results and discussion

#### 3.1. Oxidation of propylene and lower alkanes

In our previous paper [31], we reported epoxide formation from propylene, 1-butene, and isobutene over Pd/TiO<sub>2</sub>. The corresponding epoxide was obtained from alkenes other than ethylene. Typical results obtained for propylene epoxidation over Pd/TiO2 prepared from  $Pd(NO_3)_2$  are shown in Fig. 2. One minute after  $H_2$  was introduced to the system, the major product observed was propane. After 10 min, the formation rate of propane decreased, and formation of PO was observed. The formation rates of both products gradually decreased over time between 10 and 60 min at ambient temperature (Fig. 2(a)). The production of acetone also was observed during this time frame, but its formation rate was negligible. When temperature was increased to 373 K (Fig. 2(b)), however, the formation rate of acetone increased (0.49% yield) and both acetaldehyde and  $CO_2$  were formed with yields of 0.075% and 0.72%, respectively. No PO formation was observed at 373 K. The formation rates of acetaldehyde and CO<sub>2</sub> increased when the temperature was increased to 423 K. However, the rate of acetaldehyde formation was the same at 423 K as that at 373 K, and the rate of propane formation decreased at 423 K. To determine whether acetone was formed from PO at the two elevated temperatures, PO reactivity was studied using Pd/TiO<sub>2</sub> prepared from  $Pd(NO_3)_2$  and a mixture of PO, O<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub>, and the results are shown in Fig. 3. Hydrocarbons such as methane, ethane, and propane, and oxygenated products such as acetaldehyde and acetone, were formed from this reaction at ambient temperature (Fig. 3(a)); but the formation rates were small, and no substantial reaction of PO proceeded at this temperature. As shown in Fig. 3(b), at 373 K, however, PO did react, and the observed products were acetaldehyde, acetone,



**Fig. 3.** Time course of the rates of PO consumption at ambient temperature (a) and the consumption rate at various reaction temperatures (b) over Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd(NO<sub>3</sub>)<sub>2</sub>).  $\square$  CH<sub>3</sub>CHO,  $\blacksquare$  CH<sub>3</sub>COCH<sub>3</sub>,  $\square$  C<sub>2</sub>H<sub>5</sub>CHO,  $\boxtimes$  CH<sub>3</sub>COOCH=CH<sub>2</sub>,  $\square$  CO,  $\square$  CO<sub>2</sub>,  $\square$  C<sub>2</sub>H<sub>6</sub>,  $\square$  CH<sub>4</sub>,  $\square$  C<sub>3</sub>H<sub>8</sub>.

propionaldehyde, vinyl acetate, and CO<sub>2</sub>. The rate of acetone formation at this temperature was 6.3% and 11% of the formation rates (0.64 mmol/min at 373 K and 1.17 mmol/min at 423 K) observed for the reaction of propylene. Therefore, we concluded that acetone was not formed from PO by isomerization. The product distribution observed at 473K suggests that PO isomerizes to propionaldehyde at higher temperatures of above 473 K. Additionally, all the H<sub>2</sub> introduced to the reactor was consumed at the initial stage of the reaction of propylene (Fig. 2(c)). When propylene and  $O_2$  were introduced to the Pd/TiO<sub>2</sub> catalyst in the absence of H<sub>2</sub>, no reaction proceeded. Therefore, H<sub>2</sub> clearly participated in the formation of the propylene oxidation products. However, among the oxidation products observed here, only the reaction equation for propane formation from propylene contains H<sub>2</sub>; therefore, the amount of H<sub>2</sub> required to form the other oxidation products is not known. The selectivity of H<sub>2</sub> for the formation of these products was calculated under the assumption that 1 mol of H<sub>2</sub> contributed to the production of each oxidation product. One minute after the reaction commenced, almost all the H<sub>2</sub> introduced into the reactor was consumed to form water. However, the rate of this simple oxidation of H<sub>2</sub> decreased sharply, and the selectivity of H<sub>2</sub> for PO formation increased with reaction time from 0% at 1 min to 6.3%, 14.8%, and 26.0% at 10, 30, and 60 min, respectively. These results indicate that further optimization of the reactor system is needed to avoid the consumption of H<sub>2</sub> to form oxidation products other than PO.

We also studied oxidation reactions of short-chain alkanes (2–4 carbon atoms) to better understand the reaction mechanism for PO formation, and the results obtained for ethane, propane, and iso- and *n*-butanes are shown in Figs. 4–7. For the oxidation of ethane (Fig. 4) and propane, the major product observed was CO<sub>2</sub>. Acetaldehyde, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> also formed in the reaction of ethane, but the formation rates for these compounds were low, below 0.3  $\mu$ mol/min. The catalytic activity of the Pd/TiO<sub>2</sub> catalyst toward ethane gradually decreased with reaction time, and the product distributions at 373 and 423 K were similar to the distribution at ambient temperature (Fig. 4(b)). For the reaction of propane (Fig. 5), acetone was formed at about 60% of the rate observed for CO<sub>2</sub> formation. Acetone is formed by the oxidative



**Fig. 4.** Time course of the rates of product formation for reactions of  $C_3H_8$  at ambient temperature (a) and the formation rate at various temperature (b)  $Pd(0.005 \text{ atom}/nm^2)/TiO_2 (Pd(NO_3)_2)$ .  $CH_3CHO, CH_3COCH_3, CO_2, CO_2, CO_3, CO_4, CO_4,$ 





**Fig. 6.** Time course of the rates of product formation (a) and the formation rates at various temperature (b) for reaction of  $i-C_4H_{10}$  over Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd(NO<sub>3</sub>)<sub>2</sub>).



**Fig. 7.** Time course of the rates of product formation (a) and the formation rates at various temperature (b) for reaction of *n*-C<sub>4</sub>H<sub>10</sub> over Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd(NO<sub>3</sub>)<sub>2</sub>). *IIII* CH<sub>3</sub>CHO, **CH**<sub>3</sub>COCH<sub>3</sub>, **CO**<sub>2</sub>, **CH**<sub>3</sub>CH<sub>4</sub>K, **CH**<sub>3</sub>cbuta-neoxide, **IIII** tert-butanol.

dehydrogenation of isopropanol (IPA); therefore, acetone likely was formed here via IPA, although the formation of IPA, which has low vapor pressure at ambient temperature, was not observed in this experiment. The total formation rate was almost independent of temperature (Fig. 5(b)), and the decrease in acetone formation at 373 and 423 K suggests that acetone may have been successively oxidized to CO<sub>2</sub> at elevated reaction temperatures. Although no products were observed in the initial stages (30 s for propane and 1 min for ethane, respectively) of the reactions, H abstraction from propane to form an isopropyl radical, and the subsequent recombination of the H radical and isopropyl radical to regenerate propane, may have occurred rapidly. Because the observed rate of propane formation was high in the initial stage of the propylene reaction, dissociatively adsorbed hydrogen was probably present at a high density on the catalyst, and the reaction rate between propylene and this adsorbed hydrogen would also have been fast. For the ethane reaction, almost all the H<sub>2</sub> introduced to the system was consumed, and the major product was water. For propane oxidation, the H<sub>2</sub> conversion was about 90% at ambient temperature and about 99% at 373 and 423 K.

For the oxidation of isobutene (Fig. 6), acetone was the major product, with a relatively high formation rate of 2.51 µmol/min. The rate of CO<sub>2</sub> formation was one-third of the rate observed for acetone, and the epoxide isobutylene oxide was formed at a rate of 0.1 µmol/min. Epoxide formation was not observed in the oxidation of *n*-butane. At present, it is not clear whether isobutylene oxide was formed via a compound derived from isobutane, such as tertbutylhydroperoxide, or via isobutene. In the reaction of *n*-butane (Fig. 7), CO<sub>2</sub> and methylethylketone (MEK) each were formed at a formation rate of 1 µmol/min, and acetaldehyde and acetone were formed at 0.1–0.2 µmol/min. MEK might have been formed from nbutane by a mechanism similar to that of acetone formation from propane. The rate of acetaldehyde formation in *n*-butane oxidation was higher than that observed in the oxidation of the other alkanes studied here. This high formation rate might indicate that acetaldehyde was formed by oxidation of MEK, since the oxidation of one MEK molecule produces two acetaldehyde molecules. The results of lower alkane oxidation confirmed that, in general, no products were obtained at early in the reaction (about 1 min), and that the formation of CO<sub>2</sub> and ketones increased with increasing reaction time (more than 10 min). These results also confirmed that epoxides were not obtained as major products in alkane oxidation, in contrast to the results observed for alkene oxidation. For *n*-butane oxidation at ambient temperature (Fig. 7(a)), the H conversion was 87% after 30 s, and the conversion decreased to 70% after 60 min.



**Fig. 8.** Effect of Pd loading on products of propylene epoxidation at ambient temperature over (a) Pd(0.02 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd(NO<sub>3</sub>)<sub>2</sub>) and (b) Pd(0.01 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd(NO<sub>3</sub>)<sub>2</sub>). 2 (Pd(NO<sub>3</sub>)<sub>2</sub>) CH<sub>3</sub>CHO, 2 PO, CH<sub>3</sub>COCH<sub>3</sub>, 2 CO<sub>2</sub>, 2 C(3)H<sub>8</sub>.

For isobutene oxidation at ambient temperature (Fig. 6(a)), H conversion decreased from 98.4% after 30 s to 49.0% at 60 min. For both butanes, 99% H conversion was observed at 373 K. In the reaction of alkanes that adsorption is weaker than the corresponding alkenes, the adsorption of  $H_2$  would not be hindered by alkenes. As a result, the simple oxidation of  $H_2$  seems to be promoted.

#### 3.2. Effect of Pd loading on PO formation

The Pd/TiO<sub>2</sub> catalysts prepared here were sensitive to Pd loading. When a support material is added to a Pd solution, an ionexchange reaction occurs between surface protons on the support material and Pd-complex ions, such as  $Pd(NO_3)^+$  or aquo-complex ions. Since the concentration of such exchangeable support-surface protons is low, the surface concentration of Pd ions adsorbed by ion exchange is also low, thus causing the Pd ions to be mono-atomically dispersed. The amount of Pd ions adsorbed from Pd(NO<sub>3</sub>)<sub>2</sub> solution onto TiO<sub>2</sub> by ion exchange was measured, and the obtained surface concentration was 0.0083 atom-Pd/nm<sup>2</sup>. In the process of catalyst preparation, after Pd was adsorbed to TiO<sub>2</sub> by ion exchange, the excessive Pd compound will be in a water solution. When this system is heated to evaporate the water, the Pd left in a water solution has a chance to adsorb near to Pd that adsorbed by ion exchange. However, if the quantity of the Pd less than the max amount of ion exchange is taken, all of the Pd will be mono-atomically adsorbed on ion exchange site and may be well dispersed. From this point of view, the effect of Pd loading on the products of propylene epoxidation at ambient temperature was studied, and the results are shown in Fig. 8. The formation rate of propane over Pd(0.01 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Fig. 8(a)) was much higher than that over Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Fig. 2). However, the PO formation rate at 10 min over Pd(0.01 atom/nm<sup>2</sup>)/TiO<sub>2</sub> was higher than that over  $Pd(0.005 \text{ atom}/\text{nm}^2)/\text{TiO}_2$ , and the PO formation rate over Pd(0.01 atom/nm<sup>2</sup>)/TiO<sub>2</sub> decreased more rapidly over time. For propylene epoxidation over  $Pd(0.02 \text{ atom}/\text{nm}^2)/\text{TiO}_2$ , the formation rate of PO decreased to 27% of that observed over  $Pd(0.01 \text{ atom}/\text{nm}^2)/\text{TiO}_2$  at 10 min, and to 18% at 30 and 60 min. The major partial oxidation product for  $Pd(0.02 \text{ atom}/nm^2)/TiO_2$ , was acetone with a formation rate of 1.57 mol/min at 10 min, which increased to 2.54 mol/min at 60 min which is 1.62 times of that at 10 min.

The CO<sub>2</sub> formation rates over Pd( $0.02 \text{ atom}/\text{nm}^2$ )/TiO<sub>2</sub> were 13.7 and 12.4 times the rate observed over Pd( $0.01 \text{ atom}/\text{nm}^2$ )/TiO<sub>2</sub> at 10 and 30 min, respectively. Interestingly, the CO<sub>2</sub> formation



**Fig. 9.** Product distributions obtained from propylene epoxidation over  $Pd(0.005 \text{ atom}/nm^2)/TiO_2$  ( $Pd(NO_3)_2$ ) catalysts calcined at various temperatures and then reduced at 723 K. 2002 CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>.

rate decreased with increasing reaction time while the formation rate of propane increased. For Pd(0.01 atom/nm<sup>2</sup>)/TiO<sub>2</sub>, H<sub>2</sub> conversion was 80% complete at 1 min and decreased to 20.2% with increasing reaction time. However, almost all the H<sub>2</sub> was converted over Pd(0.02 atom/nm<sup>2</sup>)/TiO<sub>2</sub> after 60 min. Assuming a homogeneous dispersion of Pd atoms on the TiO<sub>2</sub> surface, one Pd atom would have occupied about 120 nm<sup>2</sup> of the surface of the Pd(0.0083 atom/nm<sup>2</sup>)/TiO<sub>2</sub> catalyst. If these Pd atoms are assumed to be arranged in a hexagonal lattice, the length of one side of the hexagon is 6.81 nm, and thus the average distance between adjacent Pd atoms is 11.8 nm. This distance is about 45 times the diameter of a Pd atom. Similarly, the average distances between adjacent Pd atoms would have been 15.2, 10.7, and 7.6 nm for 0.005 atom/nm<sup>2</sup>, 0.01 atom/nm<sup>2</sup>, and 0.02 atom/nm<sup>2</sup> surface densities, respectively. From the experimental results, we concluded that Pd was completely monoatomically dispersed on the surface of the Pd( $0.005 \operatorname{atom}/\operatorname{nm}^2$ )/TiO<sub>2</sub> catalyst, and that most of the Pd was monoatomically dispersed on the Pd $(0.01 \text{ atom}/\text{nm}^2)/\text{TiO}_2$ catalyst. However, Pd pair sites may have been present on the  $Pd(0.02 \text{ atom/nm}^2)/TiO_2 \text{ catalyst.}$ 

#### 3.3. Effect of oxidation temperature on PO formation rate

In the previous section, we reported that Pd was found to be monoatomically dispersed on the surface of Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> catalysts with Pd concentrations of 0.01 atom/nm<sup>2</sup> or lower. Unfortunately, such concentration of Pd is too small to be detected by common electron microscopy. Since Pd is not paramagnetic, electron paramagnetic resonance cannot be used to distinguish single Pd atoms from pairs of Pd atoms on the catalysts. After Pd was adsorbed on TiO<sub>2</sub> below 393 K during catalyst synthesis, the Pd/TiO<sub>2</sub> catalysts were calcined at 773 K in air for 5 h and then reduced in H<sub>2</sub> at 723 K for 2 h. Pd is believed to be monoatomically dispersed when it is supported on TiO<sub>2</sub> at temperatures below 293 K. We conducted additional studies to determine whether the Pd atoms on the catalysts aggregated during propylene epoxidation.

The product distribution obtained from propylene epoxidation over catalysts calcined at various temperatures and then reduced at 723 K is shown in Fig. 9. The major products observed for the catalyst calcined at 573 K were PO and propane, with acetaldehyde and acetone byproducts. The PO formation rate increased only slightly over the catalyst calcined at 673 K, but the rates of propane, acetaldehyde, and acetone formation increased to approximately



**Fig. 10.** Product distributions obtained from propylene epoxidation over  $Pd(0.005 \text{ atom}/nm^2)/TiO_2 (Pd(NO_3)_2)$  catalysts calcined at 773 K and then reduced at various temperatures.  $\boxtimes CH_3CHO$ ,  $\square PO$ ,  $\blacksquare CH_3COCH_3$ ,  $\boxtimes CO_2$ ,  $\blacksquare C_3H_8$ .

200%, 140%, and 195%, respectively, of the rates observed for the catalyst calcined at 573 K. For the catalyst calcined at 773 K, the rates of acetaldehyde, acetone, and PO formation increased, but the rate of propane formation decreased. However, for the catalyst calcined at 873 K, only the rate of acetone formation increased, whereas the rates of the other products decreased. Hydrogenation, but not oxidation, of propylene proceeded over the catalyst calcined at 973 K. As mentioned in the previous section, the formation of acetone increased as the surface concentration of Pd increased on the catalysts. Notably, the PO formation rate increased up to calcination temperatures of 773 K and then decreased with a corresponding increase in acetone formation at a calcination temperature of 873 K. This result may suggest that a catalyst calcination temperature of 773 K did not promote the aggregation of Pd ions on the Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub> catalyst surface.

#### 3.4. Effect of reduction temperature on PO formation rate

As mentioned in the previous section, we concluded that a catalyst calcination temperature of 773K did not promote the aggregation of Pd ions on the Pd( $0.005 \text{ atom}/\text{nm}^2$ )/TiO<sub>2</sub> catalyst surface. Next we examined the effect of the temperature used for H<sub>2</sub> reduction of the catalysts, which occurred immediately after calcination in the synthetic procedure, and the results are shown in Fig. 10 for Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub>. All these catalysts were calcined at 773K prior to reduction. Catalysts reduced at 573 and 623 K showed no activity toward PO formation, perhaps because the Pd ions were not reduced to metal at these relatively low temperatures. However, the observed formation of propane at these temperatures suggests that at least some small portion of Pd was reduced. At 673 K, PO was formed at an intermediate rate of 0.4 µmol/min, and the propane formation rate increased to 250% of that observed over the catalyst reduced at 623 K. The rate of PO formation over the catalyst reduced at 723 K increased further, to about 3 µmol/min, and the catalyst reduced at 773 K showed further increased activity for PO formation. However, the rates of PO and propane formation over the catalyst reduced at 823 K decreased, and the formation rates of acetaldehyde and acetone increased compared to the rates over the catalyst reduced at 723 K. Acetone is a typically observed product over catalysts with high Pd concentration. Therefore, these results suggest that a reducing temperature of 723 K is not sufficiently high to reduce all the Pd



**Fig. 11.** Product distribution observed for propylene epoxidation over  $Pd/TiO_2$  prepared from Pd-TPP.Pd loading (atom-Pd/nm<sup>2</sup> TiO<sub>2</sub>): (a) 0.005, (b) 0.01, and (c) 0.02.

ions on the  $TiO_2$  surface. From the viewpoint of maximizing the PO formation rate, 773 K is the optimum reducing temperature. The PO formation rate of the catalyst reduced at 773 K shows that catalytic activity has still a great surplus for improvement by about 2 times compared to catalyst prepared by the standard pretreatment in this paper. We concluded that Pd was monoatomically dispersed on the surface of the catalysts reduced at 723 and 773 K.

#### 3.5. PO formation over Pd/TiO<sub>2</sub> catalysts prepared from Pd-TPP

In the previous sections, the effects of calcination and reduction temperatures on propylene epoxidation suggested that Pd was monoatomically dispersed on the Pd/TiO<sub>2</sub> catalysts pretreated by calcination at 773 K and subsequent reduction at 723 K. Specifically, we observed that PO was formed over monoatomically dispersed Pd on TiO<sub>2</sub>, whereas acetone was formed over pairs of Pd atoms on TiO<sub>2</sub>. All the Pd/TiO<sub>2</sub> catalysts described thus far in this report were prepared from Pd(NO<sub>3</sub>)<sub>2</sub>. However, many types of Pd complexes with varying geometries exist, so we also examined catalysts prepared from a different Pd precursor, Pd-tetraphenylporphyrin (Pd-TPP). Pd-TPP is bulkier than Pd(NO<sub>3</sub>)<sub>2</sub>, with Pd located in the center of the bulky TPP molecule. It is thought that when Pd-TPP is adsorbed on TiO<sub>2</sub>, because bulky ligand will hinder the approach of Pd ions on the support surface, no Pd pair may be formed. The product distribution observed for propylene epoxidation over Pd/TiO<sub>2</sub> catalysts prepared from Pd-TPP and with varying Pd loadings are shown in Fig. 11. The product distributions over Pd(0.005 atom/nm<sup>2</sup>)/TiO<sub>2</sub>(TPP) and Pd(0.01 atom/nm<sup>2</sup>)/TiO<sub>2</sub>(TPP) were quite similar to those observed over the corresponding catalysts prepared from Pd(NO<sub>3</sub>)<sub>2</sub> (Fig. 6(b)). Pd/TiO<sub>2</sub> prepared from Pd-TPP with a surface concentration of 0.02 atom-Pd/nm<sup>2</sup> also showed a product distribution that was similar to that of  $Pd(0.02 \text{ atom}/nm^2)/TiO_2$  prepared from  $Pd(NO_3)_2$ , except that  $CO_2$ was formed at 1 min for the catalyst prepared from Pd-TPP. Acetone, CO<sub>2</sub>, and propane were formed at 10 min for this catalyst, and the formation rates of acetone and CO<sub>2</sub> decreased with increasing reaction time while the rate of propane formation increased. Similar trends again were observed for Pd(0.02 atom/nm<sup>2</sup>)/TiO<sub>2</sub> prepared from Pd(NO<sub>3</sub>)<sub>2</sub>. These results strongly suggest that the structure of the Pd active site on Pd/TiO<sub>2</sub>(TPP) was similar to that on Pd/TiO<sub>2</sub> prepared from Pd(NO<sub>3</sub>)<sub>2</sub>, and that PO was formed over the monoatomically dispersed Pd in both cases.



**Fig. 12.**  $H_2-D_2$  exchange reaction over (a) Pd(0.0001 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd(NO<sub>3</sub>)<sub>2</sub>), (b) Pd(0.0001 atom/nm<sup>2</sup>)/TiO<sub>2</sub> (Pd-TPP), (c) TiO<sub>2</sub> without supported Pd. The total catalyst weight for each experiment was 2.50 g. Volume of gas circulation system: 105 ml, H<sub>2</sub> 20 Torr, D<sub>2</sub> 20 Torr. Temperature: 293 K.

### 3.6. Isotope exchange between $H_2$ and $D_2$ over monoatomically dispersed Pd catalysts

The results discussed thus far all indicate that the Pd on the Pd/TiO<sub>2</sub> catalysts was well-dispersed as single atoms. To confirm that Pd was present in atomic form, we tried to obtain spectroscopic evidence for the structure of active sites by means of EPR and Raman spectroscopy. We also attempted to use temperatureprogrammed reduction with H<sub>2</sub> to characterize the catalysts, but we did not obtain any meaningful evidence from either the spectroscopic or the temperature-programmed experiments, perhaps because the Pd concentration in the catalysts might have been below the detection limit of the instruments. On the basis of our hypothesis that Pd is monoatomically dispersed on the surface of the TiO<sub>2</sub> support, we next tried to determine whether a hydrogen molecule would have dissociatively adsorbed onto these dispersed Pd atoms. None of the published literature that we found clearly addressed this question, so we studied isotope exchange between H<sub>2</sub> and D<sub>2</sub> on Pd/TiO<sub>2</sub> prepared from Pd(NO<sub>3</sub>)<sub>2</sub> and from Pd-TPP, as well as on TiO<sub>2</sub> without supported Pd. To achieve monoatomic dispersion, we used a surface concentration of 0.0001 atom-Pd/nm<sup>2</sup>  $(Pd(NO_3)_2)$ , which is at about 1/100 of the maximum amount of Pd adsorption observed on TiO<sub>2</sub> in the experiments described above (0.0083 atom-Pd/nm<sup>2</sup>). The results of the isotope exchange experiments are shown in Fig. 12. The effect of the supported Pd was clear: the isotope exchange reaction proceeded over catalysts prepared both from Pd(NO<sub>3</sub>)<sub>2</sub> and from Pd-TPP, but no isotope exchange reaction proceeded on the TiO<sub>2</sub> without supported Pd. These results clearly show that hydrogen was dissociatively adsorbed on Pd/TiO<sub>2</sub> on which Pd was monoatomically dispersed.

## 3.7. Computational investigation of dissociative adsorption of hydrogen on monoatomically dispersed Pd

To determine how isotope exchange proceeded on the catalysts, we performed calculations to determine the adsorption structure of  $H_2$  on the monoatomically dispersed Pd. Potential energy calculations were carried out for  $H_2$  adsorption onto a Pd atom, and the resulting potential energy diagram is shown in Fig. 13. The diagram shows that the  $H_2$  molecule can be adsorbed associatively, with a distance of 0.1753 nm between the Pd atom and  $H_2$  molecule. The stabilization energy obtained by adsorption is-14.4 kcal/mol. The  $H_2$  molecule can also be dissociatively adsorbed onto the Pd



Fig. 13. Potential energy diagram for  $\rm H_2$  adsorption onto a Pd atom. TS I: transition state I.

atom, with a stabilization energy is -10.7 kcal/mol. This dissociative adsorption occurs via transition state I (Fig. 13), which has a stabilization energy of -9.2 kcal/mol. The activation energy for dissociative adsorption is 5.2 kcal/mol; thus, the diagram shows that the dissociative adsorption of hydrogen molecule is feasible. The adsorption of a H<sub>2</sub> molecule onto Pd/TiO<sub>2</sub> also was examined, and the results are shown in Fig. 14. For the stabilization energy for associative adsorption of H<sub>2</sub> onto Pd/TiO<sub>2</sub> is -12.7 kcal/mol. The bond distance between hydrogen atoms of the associatively adsorbed H<sub>2</sub> molecule on Pd/TiO<sub>2</sub> is 0.0801 nm, which is somewhat smaller than that observed for associative adsorption on the single Pd atom (Fig. 13). This result suggests that the electron density on Pd/TiO<sub>2</sub> was slightly smaller than that on single Pd atoms. In the dissociative adsorption process, one hydrogen atom of the adsorbed H<sub>2</sub> molecule approaches a nearest oxygen ion; the H<sub>2</sub> molecule then dissociates, and the hydrogen atom adsorbs onto the oxygen ion. The transition state II that accompanies this reaction process is unstabilized (1.6 kcal/mol), but the stabilization energy for dissociative adsorption of  $H_2$  is calculated to be -55.9 kcal/mol. Clearly, the dissociative adsorption of H<sub>2</sub> onto the Pd atom and oxygen ion is much more stabilized than dissociative adsorption onto the Pd atom alone. These results suggest that H<sub>2</sub> was able to adsorb dissociatively onto the monoatomically dispersed Pd/TiO<sub>2</sub> catalysts and that the isotope exchange reaction proceeded via migration and recombination of these adsorbed hydrogen atoms on Pd. In other words, monoatomically dispersed Pd supported on TiO<sub>2</sub> catalyzed the dissociative adsorption of H<sub>2</sub>. The results presented here may provide the first clear evidence of catalysis by monoatomically dispersed noble metals.

## 3.8. Proposed reaction mechanism for epoxidation of propylene over $Pd/TiO_2$

On the basis of the above-presented results, we proposed a reaction mechanism for the epoxidation of propylene over Pd/TiO<sub>2</sub>. Because no reaction proceeded over TiO<sub>2</sub> alone, Pd must have catalyzed the epoxidation of propylene. When a mixture of propylene and O<sub>2</sub> was introduced to Pd/TiO<sub>2</sub> at ambient temperature, no oxidation proceeded, suggesting that the epoxidation of propylene required the presence of both H<sub>2</sub> and O<sub>2</sub>. Epoxidation of propylene proceeded over Pd/TiO<sub>2</sub> reduced at 673–823 K, but not over catalysts that had not been subjected to H<sub>2</sub> reduction. When a mixture of propylene and H<sub>2</sub> was introduced to Pd/TiO<sub>2</sub>, hydrogenation of propylene to propane proceeded, and when a mixture of H<sub>2</sub> and O<sub>2</sub> was introduced, oxidation of H<sub>2</sub> proceeded at ambient temperature. These observed reactions suggest that H radicals were present on the catalyst. Evidently several adsorbed species exist on the catalyst surface, including H, propylene, and a certain species participating in PO formation. To clarify the quantitative relationship between these surface-adsorbed species, a transientresponse experiment was carried out. In this transient-response experiment, the changes of product formation rates were observed when propylene was introduced to the reaction system achieving a steady state in a flow of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. The results are shown in Figs. 15 and 16. A mixture of H<sub>2</sub> (10 mol%), O<sub>2</sub> (20 mol%), and N<sub>2</sub> (70 mol%) gases was fed over Pd $(0.005 \text{ atom}/\text{nm}^2)/\text{TiO}_2$  at ambient temperature, and then all the H<sub>2</sub> fed over the catalyst was oxidized to water. After 60 min, propylene (20 mol%) was introduced into the  $H_2 + O_2$  stream, at which point the simple oxidation of  $H_2$  sharply decreased and the formation of PO and propane was observed. This result suggests that (1) propylene disturbed the adsorption of  $H_2$  (in other words, adsorption of propylene was stronger than that of  $H_2$ ) and that (2) water formed during the reaction did not inhibit PO and propane formation. Since no reaction between O<sub>2</sub> and propylene proceeded on Pd/TiO<sub>2</sub>, O<sub>2</sub> must not have adsorbed onto Pd/TiO<sub>2</sub>. Moreover, the oxidation of H<sub>2</sub> must have proceeded via reaction between H radicals and molecular O<sub>2</sub>.

One of the most important results observed from the reactions over the Pd/TiO<sub>2</sub> catalysts was that epoxides were formed only from alkenes, and not from alkanes. This result suggests that PO was formed by direct reaction between propylene on Pd and an active



Fig. 14. Potential energy diagram for H<sub>2</sub> adsorption onto a Pd atom supported on TiO<sub>2</sub>. TS II: transition state II.



Fig. 15. Rates of  $\Box$  PO and  $\bigcirc$  propane formation observed during transitionresponse measurement of propylene oxidation over Pd/TiO2. The arrow indicates the introduction of propylene over the catalyst.



**Fig. 16.** Rates of  $\Box$  H<sub>2</sub>O and  $\bigcirc$  H<sub>2</sub> formation observed during transition-response measurement of propylene oxidation over Pd/TiO<sub>2</sub>.



Fig. 17. Proposed reaction mechanism for PO formation on Pd/TiO<sub>2</sub>.

preparation. On the basis of our results, we propose the reaction mechanism depicted in Fig. 17 for PO production over Pd/TiO<sub>2</sub>. Hydrogen molecules adsorb dissociatively on Pd, and O<sub>2</sub> reacts with the adsorbed hydrogen atoms to form •OOH. Propylene adsorbed on individual Pd atoms reacts with •OOH on TiO<sub>2</sub>, which is slightly positive by adsorbing onto TiO<sub>2</sub> and is reactable to electron rich double bond to give PO and  $H_2O[32,25]$ .

optimizing the reaction conditions and by improvements in catalyst

#### 4. Conclusion

Monoatomically dispersed Pd on TiO<sub>2</sub> catalyzed the epoxidation of lower alkenes (except ethylene) at ambient temperature in the presence of H<sub>2</sub> and O<sub>2</sub>. PO formation was sensitive to the surface concentration of Pd active sites, and the optimum surface Pd concentration for PO formation was 0.005–0.01 atom-Pd/nm<sup>2</sup>, which was comparable to the amount of Pd that was spontaneously adsorbed on TiO<sub>2</sub> (0.0083 atom-Pd/nm<sup>2</sup>) from a diluted aqueous solution of  $Pd(NO_3)_2$  that was used to prepare the  $Pd/TiO_2$  catalysts. Monoatomically dispersed Pd on TiO<sub>2</sub> also catalyzed the dissociative adsorption of H<sub>2</sub> at ambient temperature. PO seems to have been formed by reaction of propylene on Pd with an active species, perhaps •OOH, generated from reaction of H<sub>2</sub> and O<sub>2</sub> on TiO<sub>2</sub>.

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