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A Career in Catalysis: Masatake Haruta

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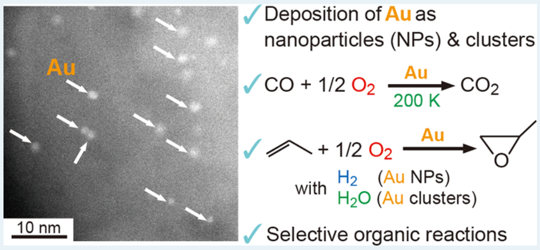

ABSTRACT: Professor Masatake Haruta's distinguished scientific achievements are highlighted in heterogeneous catalysis by gold (Au). In 1982, he discovered that Au became highly active for CO oxidation even at 200 K when gold was deposited as nanoparticles (NPs) smaller than 5 nm on 3d transition metal oxides. After this finding, he and his co-workers have developed many preparation methods for the deposition of Au as NPs and clusters onto a wide variety of supports. By kinetic, theoretical, and surface science studies, Haruta and co-workers revealed interesting catalytic features of Au, including reaction mechanisms which are greatly different from those of Pd and Pt. Haruta and co-workers also found that supported Au NPs catalyzed direct oxidation of propylene to propylene oxide using O_2 and H_2, and subsequently O_2 alone in the presence of H_2O.

KEYWORDS: *gold nanoparticles, gold clusters, CO oxidation, propylene epoxidation, alcohol oxidation*

1. INTRODUCTION

More than 30 years have passed since heterogeneous catalysis by Au was discovered independently by Professor Masatake Haruta[1] and Professor Graham J. Hutchings.[2] Before their finding, Au had been considered as an almost catalytically inert metal. Thermodynamically, Au cannot be oxidized according to the Gibbs free energy ($\Delta G^\circ_f < 0$), and the smooth flat surfaces of Au neither chemisorb nor dissociate molecular oxygen. This common understanding was dramatically changed by the appearance of small Au nanoparticles (NPs) supported on metal oxides, which were prepared by Haruta. Supported Au-catalyzed hydrochlorination of acetylene to vinyl chloride, found by Hutchings, also had a great impact on chemical industry. Since then, Au has fascinated many researchers in the field of not only catalysis but also surface science and organic chemistry. As interesting catalytic features of Au have been revealed year by year, papers on gold catalysis have exponentially increased. Haruta and Hutchings have always been on the leading edge of the research field in Au catalysis for these three decades.

Professor Masatake Haruta, who was born in Gifu prefecture, Japan, in 1947, graduated from Nagoya Institute of Technology in 1970. He received his Ph.D. from Kyoto University in 1976. Then, he joined Osaka National Research Institute (the predecessor of National Institute of Advanced Industrial Science and Technology (AIST), Kansai Center) as a research scientist in 1976 and started his research on hydrogen combustion catalysts. He tried to prepare mixed oxides of base metals with Ag or Au by coprecipitation (CP). He found that Ag−Co−Mn mixed oxides showed significantly improved catalytic activity compared to Ag_2O and single metal oxides for H_2 oxidation.[3] During this work, he stayed as a visiting scientist in Professor Bernard Delmon's group of Université Catholique de Louvain, Belgium, in 1981. He worked on the preparation of homodisperse colloidal NPs of Mo and Co sufides.[4]

After coming back to Japan in 1982, he began to prepare Au-containing mixed metal oxides by CP. In the end of the same

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year, he discovered that the Au-containing catalysts obtained exhibited extremely high catalytic activity for the oxidation of H_2 and CO at room temperature and at 200 K, respectively.[1,5−7] Haruta examined the reproducibility of active Au catalysts and confirmed by XRD that Au crystallites with diameters of around 5 nm were dispersed on Fe_2O_3, and he reported these findings in 1987.[1] Haruta collaborated with Professor Sumio Iijima for transmission electron microscopy, and they ascertained that Au NPs with diameters of around 4 nm were almost homogeneously dispersed on 3d transition metal oxides such as Fe_2O_3 and Co_3O_4.[6] On the other hand, Hutchings predicted in 1985[2] and confirmed experimentally in 1988[8] that Au cations (as $HAuCl_4$) supported on activated carbon showed superior catalytic activity to conventional mercury chloride on carbon for hydrochlorination of acetylene to vinyl chloride in the gas phase.

Although catalysis by Au had been known, catalytic activity was low.[9] This was due to the fact that Au could be only deposited as large NPs by a conventional catalyst preparation method, impregnation (IMP). Such large Au NPs show very low catalytic activity. In contrast, small Au NPs deposited on the above metal oxides obtained by CP can catalyze CO oxidation even at 200 K. With this finding as a trigger, Haruta initiated an extensive research on catalysis by Au. He developed many catalyst preparation methods, and now Au can be deposited as NPs and clusters smaller than 2 nm onto a wide variety of supports, including inert supports such as carbonaceous materials and polymers. These methods facilitated the research on Au catalysis for a variety of reactions in both of gas and liquid phase.

He also investigated the mechanism of CO oxidation and proposed that the periphery between Au NPs and metal oxide supports was the active sites.[10] Although other hypotheses were proposed by many researchers, Haruta's hypothesis is now most widely accepted. Haruta and Hayashi also found the epoxidation of propylene to propylene oxide (PO) over Au catalysts, which was first reported in 1998.[11] Recently, he has been focusing on Au clusters, which are defined as particles consisting of less than 200 Au atoms. In this article, we highlight his major achievements, focusing on selected topics.

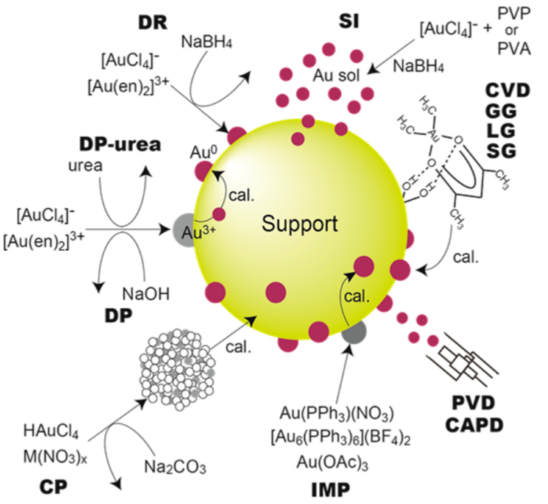


Figure 1. Schematic representation of preparation methods for supported gold catalysts. Modified with permission from ref 16. Copyright 2012 Elsevier Inc. DR: deposition-reduction, DP: deposition−precipitation, CP: coprecipitation, IMP: impregnation, PVD: physical vapor deposition, CAPD: cathodic arc plasma deposition, CVD: chemical vapor deposition, GG: gas-phase grafting, LG: liquid-phase grafting, SG: solid grinding, SI: sol immobilization, cal.: calcination.

2. DEPOSITION OF GOLD NANOPARTICLES

In order to prepare highly active Au catalysts, it is important to generate Au NPs with diameters smaller than 10 nm and to deposit them onto the supports as hemispherical shapes.[12] However, the conventional preparation method, such as IMP using $HAuCl_4$, is not applicable to the preparation of highly dispersed Au catalysts, because the mean diameter of the Au NPs deposited by IMP is larger than 10 nm. This is due to the effect of the residual Cl on the support surface,[6] and a theoretical study has been recently proposed the mechanism for the aggregation of Au NPs in the presence of Cl ions.[13] On the other hand, Au NPs often keep their sizes smaller than 5 nm in diameter by using IMP when the Au loading is very low. When other suitable Au precursors, such as $Au(PPh_3)(NO_3)$[14] and $Au(OAc)_3$,[15] are selected instead of $HAuCl_4$, the IMP method is also applicable to the preparation of Au catalysts. Accordingly, special preparation methods are essential to generate highly active Au catalysts by using various supports. Nowadays, a lot of preparation methods are used for the creation of highly dispersed Au catalysts (Figure 1).[16]

2.1. Coprecipitation (CP).

The CP method is the first accomplishment for the preparation of well-dispersed Au NPs supported on metal oxide supports.[1,6,17] The precursor is a mixture of metal hydroxides or carbonates of support metals with $Au(OH)_3$. Hydroxides or carbonates of metal components of the supports are converted to metal oxides, whereas $Au(OH)_3$ is reduced to metallic Au NPs under the subsequent calcination process in air. The CP method can be applicable to the 3d transition metal oxides, such as MnO_x, Fe_2O_3, Co_3O_4, NiO, ZnO, and to other metal oxides like La_2O_3.[18] The mean diameter of Au NPs can be controlled to some extent by tuning the calcination temperature. The coprecipitated precursors are generally calcined in air at 573 K or higher temperatures in order to form crystalline metal oxide supports.

2.2. Deposition−Precipitation (DP).

Because highly dispersed small Au NPs were hardly obtained by CP method when Al_2O_3 and TiO_2 were used as supports, Haruta and coworkers subsequently developed the deposition−precipitation (DP) method.[19−24] The DP method is useful to the basic metal oxide supports. The pH of $HAuCl_4$ solution is adjusted to be in the range from 7 to 10 by adding NaOH. In this condition, $[Au(OH)_4]^-$ and $[AuCl(OH)_3]^-$ are formed by ligand exchange of $[AuCl_4]^-$ ions and interact with positively charged oxide surfaces or hydroxy groups on the support surfaces. Then $Au(OH)_3$ precipitates on the support surfaces. Therefore, the positive charges on the support surface play an important role for the interaction between negatively charged $[Au(OH)_4]^-$ or $[AuCl(OH)_3]^-$ and the support surface. In other words, there is repulsion between negatively charged surfaces and negatively charged Au-containing ions. Consequently, it is difficult to apply the DP method to SiO_2 and WO_3 supports because these oxide surfaces are negatively charged in a wide pH region. On the other hand, the positively charged ion, $[Au(en)_2]^{3+}$ (en: ethylenediamine), is a useful Au precursor for these negatively charged solid surfaces. The subsequent reduction of Au(III) to Au(0) gives Au NPs with diameters of 1.5−5 nm.[25−27] In this DP method, NaOH is usually used as a reagent for pH control. Instead of NaOH, urea was employed as a reagent for pH control by Zanella et al.[28,29] This is called DP-urea.

2.3. Catalyst Preparations Using Volatile Organogold Complexes as Precursors. To deposit Au NPs onto a wide variety of supports such as SiO_2, acidic supports, and so on, Haruta and co-workers used gas-phase grafting (GG) method, which is a modified chemical vapor deposition (CVD).[30−32] An organogold complex, $(CH_3)_2Au(acac)$ (acac: acetylacetonate), which has a vapor pressure of 1.1 Pa at room temperature, is vaporized in a vacuum preparation apparatus and adsorbed on the support. Then, the Au precursor adsorbed on the support is calcined in air at 573 K or higher temperatures to remove organic ligands. Au NPs can be deposited not only on metal oxides but also on other materials such as carbons and organic polymers. Additionally, $(CF_3)_2Au(acac)$, which has much higher vapor pressure than that of $(CH_3)_2Au(acac)$, is also applicable to this method.

The above-mentioned volatile organogold complexes easily dissolve in organic solvents, such as ethanol and acetone. To a solution of the organogold complex, a certain amount of support is introduced, and the mixture is kept in a refrigerator for several hours. Finally, the mixture is filtered, and the organogold complex absorbed on the support is calcined in air at 673 K. This method is called the liquid-phase grafting (LG).[33] This LG method is also an effective and simple technique for the deposition of Au NPs on selected metal oxide supports.

It is a simple and valid procedure to mix a solid volatile organogold complex with a support material directly for the preparation of supported Au NP catalysts. The solid grinding (SG) is carried out by use of an agate mortar or a ball mill.[34−37] In some cases, the gold complex is mixed with organic solvents. The gold complex vaporizes during grinding and adsorbs onto the surfaces of the support. In particular, the gold complexes interact with the surface hydroxy groups on the metal oxide surfaces in this adsorption process. The SG method is applicable to a wide variety of support materials, including conventional metal oxides, carbons, and organic polymers. Moreover, Au particles with a diameter ranging from 1.5 to 4 nm can frequently be generated.

2.4. Other Preparation Methods. Fujitani et al. prepared Au NPs on single crystal TiO_2 (110) surfaces with precise control of the size distribution of 4.2 ± 0.3 nm in diameter by using cathodic arc plasma deposition (CAPD).[38,39] Because precise control of the size and surface coverage of deposited Au NPs is one of the special features of CAPD, this method is useful for the investigations of the size dependency of the catalytic properties under the same metal loadings.

A wide variety of preparation methods have been developed for Au catalysts to generate very small Au NPs with less than 5 nm in diameter with homogeneous dispersions on different types of the supports. Nowadays, a lot of preparation methods have also been developed for highly dispersed Au catalysts, such as deposition−reduction (DR),[40−44] sol immobilization (SI),[45−51] physical vapor deposition (PVD),[52−54] and so on.[55] The development of the new preparation methods for Au catalysts is one of the crucial subjects in the research of catalysis by Au.

3. CO OXIDATION

In 1987, Haruta reported for the first time that Au NPs deposited on metal oxide supports exhibited surprisingly high catalytic activity for CO oxidation at low temperatures.[1] After this discovery, Haruta has energetically carried out research on the elucidation of the Au catalysis for more than 30 years and has obtained a few important conclusions on the active sites for CO oxidation in Au NPs catalysts and on reaction mechanism. Among many significant findings by his research work on oxidation of CO on Au catalysts, a few highlights are the following: catalysis by Au NPs is remarkably sensitive to (i) the contact structure between the Au particles and the support, (ii) the type of metal oxide supports, (iii) the size of Au particles, and (iv) the presence of moisture. The above findings and the proposed mechanism for CO oxidation are briefly summarized below.

3.1. Contact Structure between Au Particles and Support. Haruta and co-workers examined the reaction rates of CO oxidation at 300 K over Au/TiO_2 prepared by DP, photochemical deposition (PCD), and IMP methods.[56] The reaction rate of the catalysts prepared by DP is higher by 4 orders of magnitude than those of the catalysts prepared by PCD and IMP. The DP method yields hemispherical Au particles with their flat planes strongly attached to the TiO_2 support by epitaxial contact between Au(111) and anatase TiO_2 (112),[57] while PCD and IMP methods yield spherical particles, which are simply loaded on the TiO_2 support. Over Pt/TiO_2, the rates of CO oxidation did not depend on the methods of preparation, because the reaction of CO with O_2 takes place preferentially on the Pt surfaces. In contrast, the reaction rate of Au catalyst prepared by DP is higher by 4 orders of magnitude than those of catalysts prepared by PCD and IMP. The dramatic difference in the reaction rates indicates that the contact structure is the most critical factor in supported Au catalysts, strongly demonstrating that the reactions might take place at the perimeter interfaces around the Au NPs.

Haruta et al. also examined the CO oxidation over Au/TiO_2 prepared by mechanically mixing a colloidal solution of 5 nm diameter Au NPs with TiO_2 powder, followed by calcination in air at different temperatures.[58] The reaction rate was enhanced with increasing calcination temperature, indicating that the stronger contact between Au and TiO_2 is important to generate higher catalytic activity.

3.2. Type of Metal Oxide Supports. Most of the supported Au catalysts are able to catalyze CO oxidation at low temperatures. Among them, Au NPs and clusters supported on TiO_2, α-Fe_2O_3, Co_3O_4, NiO, $Be(OH)_2$, and $Mg(OH)_2$ are highly active.[20] It is interesting to note that these supports are the oxides of Group VIII of 3d transition metals[6,20] and the hydroxides of alkaline earth metals.[59,60] It should be noted that Au particles of larger than 2 nm are formed on 3d transition metal oxides, whereas Au clusters are formed on alkaline earth metal hydroxides.[61] With high Au loadings above 10 wt %, these supports make Au active even at a temperature as low as 197 K.

Recently, Haruta and co-workers have demonstrated that morphological control of Co_3O_4 is very rewarding: the nanorods of Co_3O_4 not only exhibit remarkably high catalytic activity for CO oxidation at temperatures as low as 196 K but also show sufficient stability in feed gases containing large amounts of H_2O and CO_2 at 473−673 K.[62] This finding has revealed that the morphological control of base transition metal oxides leads to the preferential exposure of catalytically active sites and will most probably be applicable to the development of highly efficient and stable oxidation catalysts of the next generation.

3.3. Size of Au Particles. Figure 2 shows the turnover frequencies (TOFs) of CO oxidation over Pt/CeO_2 and Au/CeO_2 as a function of the mean diameter of metal particles. A

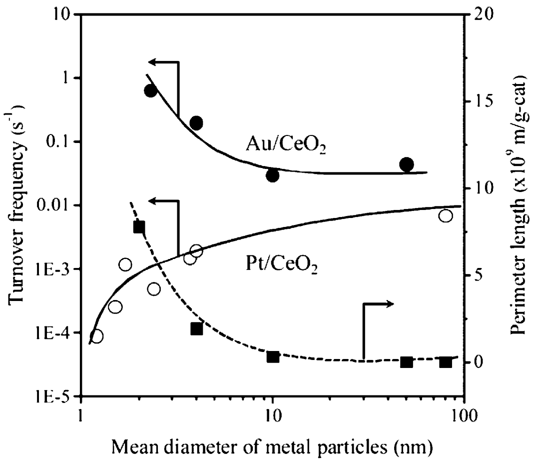


Figure 2. Turnover frequency for CO oxidation over 1 wt % Pt/CeO_2 and 1 wt % Au/CeO_2 at 303 K with the relationships between particle diameters and perimeter length.

sharp increase in the TOF is observed with a decrease in the diameter from 4 nm. In contrast, Pt shows a decreasing or steady TOF.[63−65] TOFs are almost independent of the kind of metal oxide supports (Co_3O_4, Fe_2O_3, and TiO_2), whereas they are significantly dependent on the diameter of Au NPs. At this point, we superimpose in Figure 2 the curve how the perimeter interface length increases at a metal particle diameter less than 10 nm. These relationships lead to a conclusion that the active site for CO oxidation is perimeter interface between Au and metal oxide support.

3.4. Moisture.

Haruta et al.[66,67] investigated quantitatively the effect of moisture in the reactant gas on CO oxidation over Au/TiO_2 at 270 K in the concentration range of 0.1 to 6,000 ppm. He constructed special experimental equipment by using ultraclean technology developed for the semiconductor industry.[68] The presence of moisture was found to enhance the reaction by more than 10 times up to 200 ppm of H_2O, whereas a further increase in the moisture content suppressed the reaction, which was probably due to the blocking of active sites by a thick layer of adsorbed water. The apparent activation energies were almost the same between 0.1 and 3 ppm of H_2O, indicating that the reaction mechanism was not significantly influenced by moisture, but only the pre-exponential factor in the rate law was changed.[66]

Although the degree of rate enhancement for CO oxidation by moisture depends on the type of metal oxide supports (Al_2O_3, SiO_2, and TiO_2), the apparent activation energies for Au/Al_2O_3 and Au/TiO_2 are almost independent of moisture concentration, indicating that moisture did not significantly change the reaction mechanism for CO oxidation on these two catalysts.[69] The amount of accumulated carbonate-like species at the perimeter sites during CO oxidation on Au/Al_2O_3 is reduced by the addition of moisture, leading to the enhancement of CO_2 production.[70]

The experimental evidence for O_2 activation by moisture has been obtained from FT-IR experiments using an isotope.[71] The interaction of dry or wet $C^{16}O$ ($H_2O/CO \doteqdot 1/3$) on $^{18}O_2$ preadsorbed Au/TiO_2 at 90 K was examined. The weak bands assigned to $C^{16}O^{18}O$ (2323 cm^{-1}) and $C^{16}O_2$ (2340 cm^{-1}) were observed in the case of dry CO. In contrast, in the presence of moisture in the gas phase, only a strong $C^{16}O^{18}O$ band (2323 cm^{-1}) was observed during the reaction, without any participation of the oxygen of the support or of the water, indicating that water activates oxygen dissociation on the surfaces of Au NPs and promotes CO oxidation.

3.5. Reaction Mechanism.

Haruta and co-workers found that there is a transition in reaction mechanism of CO oxidation at around 333 K.[72] This result has been reproduced by model single crystal catalysts in their Arrhenius plots.[39] The apparent activation energy is very small, 2−3 kJ mol^{-1} at temperatures above 333 K, but at lower temperatures, the energy is in the range of 26−34 kJ mol^{-1}.

The rate of CO oxidation over Au/TiO_2, Au/Fe_2O_3, Au/Co_3O_4 is independent of the concentration of CO and is slightly dependent on the concentration of O_2 (on the order of 0 to 0.25),[20] whereas the rate is almost independent of the concentrations of CO and O_2 over unsupported Au powder with mean diameters of 17 nm.[73] This independency suggests that CO and O_2 are adsorbed on the catalyst surfaces nearly to saturation and that the reaction of the two adsorbed species is the rate-determining step.

$^{18}O_2$ isotope experiments[71] and ESR measurements[74] indicate that molecularly adsorbed O_2, most likely O_2^- at the perimeter interface, is involved in the oxidation of CO. Haruta and co-workers measured FT-IR by introducing $C^{16}O$ at 300 K on Au/TiO_2 preadsorbed with $^{18}O_2$.[71] $C^{16}O_2$ is formed in a quantity comparable to that of $C^{16}O^{18}O$, meaning that the oxygen species (^{16}O) contained in the surface layer of the TiO_2 support is also involved in CO oxidation at room temperature.

On the basis of catalytic activity differences of Au NPs deposited on different kind of supports and on kinetics and spectroscopic investigations, a probable reaction route at room temperature has been schematically shown in Figure 3.[10] The rate-determining step is the reaction of CO adsorbed on Au surfaces and oxygen adsorbed at the periphery, meaning that the reaction rate of CO oxidation depends on the length of perimeter interface. Accordingly, this conclusion has been supported widely both by experimental and theoretical approaches.[39,75−77]

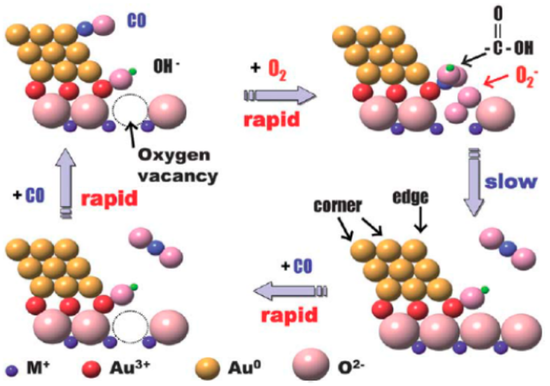


Figure 3. Probable mechanism for CO oxidation on supported Au catalysts at room temperature.[10]

4. PROPYLENE EPOXIDATION

Propylene oxide (PO) is one of the most important organic chemicals and is widely used to produce polyurethane, propylene glycols, and so on. Its annual worldwide market capacity exceeds 7.0 million tons. In 1930, the chlorohydrin process was set up to commercially produce PO, but a large amount of $CaCl_2$ (2.2 tons per ton of PO) was produced together with hazardous chlorinated organic compounds.[78] In approximately 1970, two organic hydroperoxide processes were developed; however, a large amount of styrene (2.3 tons per ton of PO) or *tert*-butanol (2.7 tons per ton of PO) was coproduced.[79] In 2003, Sumitomo Chemical developed an improved organic hydroperoxide process.[80] This process selectively produces PO with H_2O as the only byproduct using cumene hydroperoxide (CMHP), which is reused by hydrogenation of α-cumyl alcohol to cumene and subsequent oxidation of cumene to CMHP. In 2008, a hydrogen peroxide process was started to produce PO commercially.[81] This process selectively produces PO with H_2O as the only byproduct. However, H_2O_2 is relatively expensive and dangerous to transport and thus has to be synthesized on site.

Propylene epoxidation with O_2 and H_2, where H_2O_2 is *in situ* synthesized, is an environmentally benign and atomic economical process to produce PO because only one reaction step is required and water is the only byproduct. Although this reaction has been extensively studied in the liquid phase using Pt, Pd, and other noble metals as the catalysts, PO selectivity was usually very low.[82,83] In 1998, Hayashi and Haruta found that 2−5 nm Au NPs deposited on TiO_2 (P-25) could efficiently catalyze propylene epoxidation with O_2 and H_2 in the gas phase, giving a very high PO selectivity (>90%) at a propylene conversion of about 1%.[11] This outstanding finding immediately received extensive attention from both academic and industrial sectors because it opened a new field of research, selective oxidation with molecular oxygen in gas phase, together with the finding of selective oxidation of alcohols in water by Prati.[84,85] Until now, Haruta and co-workers have made great efforts to investigate propylene epoxidation with O_2 and H_2 in the gas phase and achieved great progresses toward commercialization of this process.[86−105]

In 1998, Haruta and co-workers found that the preparation method of Au catalysts was very important for PO synthesis.[11,86] Hemispherical Au NPs on TiO_2 prepared by DP were highly selective for PO synthesis, whereas spherical ones prepared by IMP and CVD favored the combustion of propylene to CO_2. In addition, the support was also crucial for PO synthesis.[86] Anatase TiO_2 and mesoporous titanosilicate, Ti-MCM-41, resulted in the formation of PO with high selectivity, but rutile TiO_2 caused propylene combustion to CO_2.

Further studies carried out by Haruta and co-workers indicated that, as well as TiO_2 and Ti-MCM-41, microporous titanosilicates such as TS-1, TS-2, and Ti-beta could be used as the supports.[87] Among these supports, Ti-MCM-41 was found to be the best one. The washing step after Au deposition was also important for PO synthesis. Simple washing led to the selective synthesis of PO, whereas repeated washing caused the formation of propionaldehyde as the major product.[87]

Then, Haruta and co-workers focused on mesoporous titanosilicates as supports for propylene epoxidation, such as Ti-MCM-41, Ti-MCM-48, and 3D wormhole-like mesoporous Ti-SiO_2.[88,89,91−102] The results indicated that large mesopores and three-dimensional interconnected porous structure were more beneficial to the diffusion of reactants and products, leading to high propylene conversion and PO selectivity. On Au NPs supported on 3D wormhole-like mesoporous Ti-SiO_2, a high propylene conversion of 9.8% was achieved with PO selectivity of 90.3% and H_2 efficiency of 27.1% at a space velocity of 4000 mL $g_{cat.}^{-1}$ h^{-1} and a feed gas of $C_3H_6/O_2/H_2/Ar = 10/10/10/70$.[97]

The surfaces of mesoporous titanosilicates are relatively hydrophilic due to the presence of large amount of surface hydroxy groups and thus strongly adsorb hydrophilic PO molecules during propylene epoxidation. The adsorbed PO molecules easily oligomerize to form low-molecular weight polymers catalyzed by surface acidic sites such as Ti−OH and Si−OH. This will cover the surface active sites and then lead to the serious deactivation of Au catalysts. Haruta and co-workers found that organic silylation such as trimethylsilylation (Figure 4) and incorporation of organic functional groups into mesoporous walls could convert the surface of mesoporous Ti-SiO_2 strongly hydrophobic and thus enhance the desorption of PO molecules and improve the catalytic stability of Au/mesoporous Ti-SiO_2.[91,92,95−97,99,100] Haruta and co-workers have also found that the introduction of $Ba(NO_3)_2$ and trimethylamine (TMA) as a solid and a gas promoter, respectively, could neutralize the surface acid sites and then significantly suppress the oligomerization of PO molecules (Figure 4).[97,100] In addition, TMA adsorbed on Au surface could greatly suppress H_2 combustion and then improve H_2 utilization efficiency to about 35%.

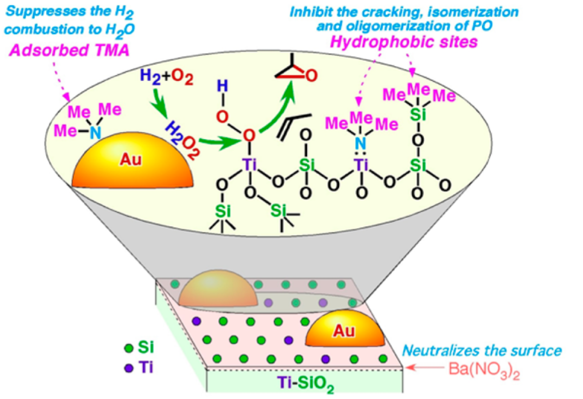


Figure 4. Propylene epoxidation with O_2 and H_2 on trimethylsilylated Au/mesoporous Ti-SiO_2 with $Ba(NO_3)_2$ and trimethylamine (TMA) as a solid and a gas promoter, respectively.[100]

In 2008, Haruta and co-workers invented SG method to prepare highly active Au catalysts for glucose oxidation.[35] Later, SG method was used to deposit Au clusters on alkali-treated TS-1, which were found to be highly active for propylene epoxidation with O_2 and H_2.[103] Further comparison experiments indicated that Au clusters deposited on the exterior surface of TS-1 were more active than tiny Au clusters incorporated into microporous channels of TS-1.[104]

Propylene epoxidation with O_2 and H_2 over Au catalysts has also been widely investigated by other research groups.[106−109] Nijhuis and co-workers found that Au/TS-1 and Au/TiO_2−SiO_2 (TiO_2 dispersed on SiO_2) displayed higher PO yields and better catalytic stability than Au/TiO_2.[106] They also found that PO formation rate was most dependent on H_2 concentration, and the deactivation of Au catalysts was mainly caused by consecutive oxidation of PO.[107] Delgass and co-workers have found that the catalytic performance of Au/TS-1 for propylene oxidation with O_2 and H_2 was significantly improved by the pretreatment of TS-1 with NH_4NO_3 and the introduction of mesoporous scale defects into TS-1.[108,109]

Haruta has estimated that the targets for the commercialization of propylene epoxidation with O_2 and H_2 are propylene conversion of 10%, PO selectivity of 90%, and H_2 efficiency of

50%. Until now propylene conversion and PO selectivity have been greatly improved and attained the target values, but H_2 efficiency was still much lower than 50%. For propylene epoxidation, the catalytic stability of Au catalysts is also one of the most important targets. Therefore, great efforts should be devoted to further improving catalytic properties, especially H_2 efficiency, and catalytic stability of Au catalysts.

Propylene epoxidation with O_2 alone is the most admired route to manufacture PO because it does not produce any byproducts. However, this is one of the most difficult reactions to achieve and is regarded as the Holy Grail in catalysis research.[110] Ethylene epoxidation with O_2 alone has been commercialized since the 1950s by utilizing Ag grain catalysts. However, for propylene epoxidation with O_2 alone, no suitable catalysts have yet been developed to exhibit good performance, especially high PO selectivity.

In 2009, Huang and Haruta found that Au clusters with diameters smaller than 2.0 nm deposited on alkali-treated TS-1 could catalyze propylene epoxidation with O_2 alone in the presence of a small amount of H_2O (about 2.0 vol %).[111−113] PO selectivity of 52% and C_3H_6 conversion of 0.88% were achieved. Interestingly, when H_2O was absent from the feed gas, PO could not be produced, and CO_2 was produced as the major product with the selectivity above 80%.[111] Iglesia and co-workers reported that Au/TiO_2 could catalyze propylene epoxidation with O_2−H_2O, giving PO selectivities of 20−70%.[114] However, C_3H_6 conversion was too low, below 0.1%. Vajda and co-workers found that Au_{6-10} clusters could catalyze propylene epoxidation with O_2−H_2O, giving PO selectivities up to 90%.[115] However, there remained a great challenge to scale up the production of Au_{6-10} clusters, because they were produced in a laser ablation source and selected by a mass spectrometer quadrupole deflector assembly. A possible reaction route for propylene epoxidation with O_2−H_2O over Au/alkali-treated TS-1 was proposed in Figure 5. First, O_2 reacted with H_2O over Au cluster surfaces to produce hydroperoxide radical (*OOH) species. The *OOH species were then reversibly transferred from Au cluster surfaces to neighboring Ti sites to form Ti−OOH species, which have been identified by *in situ* UV−vis spectroscopy.[111] The Ti-OOH species were responsible for the subsequent propylene epoxidation to PO.

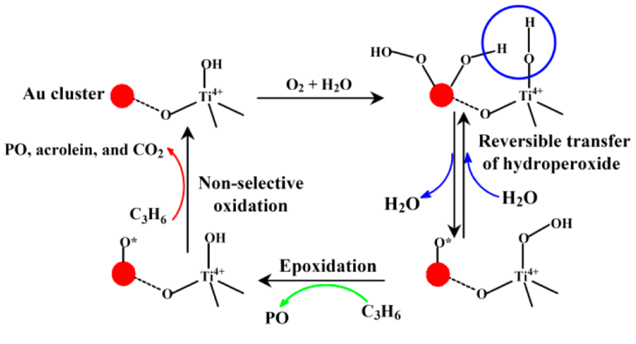


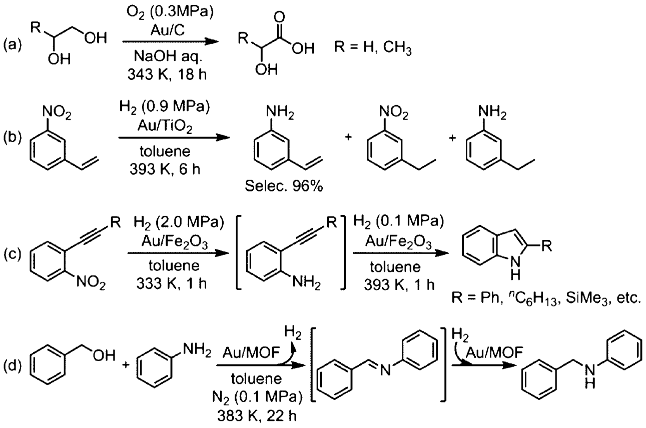
Figure 5. Possible route for C_3H_6 epoxidation with O_2 on Au/alkali-treated TS-1 in the presence of H_2O.[111]

So far, propylene epoxidation with O_2 and H_2O has not provided adequate yield and selectivity to PO for an industrial process, and thus great efforts should be devoted to optimizing this catalyst system. As shown in Figure 5, It is likely that O* radicals might be formed during the reaction and further used to oxidize propylene to PO, acrolein, and CO_2. Accordingly, if the reactivity of oxygen radicals can be tuned for propylene epoxidation, PO selectivity will be improved significantly.

5. ORGANIC REACTIONS

In 2005, Haruta moved to Tokyo Metropolitan University. At that time, catalysis by Au NPs supported on activated carbon (Au/C) in liquid phase had been revealed in the oxidation of alcohols[84,85] and glucose[116] by Prati and Rossi. Until their reports, carbon was considered to be an unsuitable support for Au NPs because Au/C shows poor catalytic activity in gas phase. In addition, the surface of activated carbon is negatively charged in water, so that well-dispersed Au NPs in diameters of smaller than 5 nm were hardly obtained on carbonaceous supports. However, Prati and Rossi found that Au/C exhibited superior catalytic activity to Au/Al_2O_3 for the aerobic oxidation of diols to hydroxy acids (Scheme 1a).[85] These results suggested that catalysis by Au in liquid phase might be largely different from that in gas phase. Subsequently, Hutchings reported the oxidation of glycerol to glyceric acid over Au/C with 100% selectvities at moderate conversions.[117] Corma and his co-workers reported that Au/CeO_2 catalyzed aerobic oxidation of alcohols to give aldehydes and carboxylic acids selectively in the absence and presence of base, respectively.[118] In alcohol oxidations, Au exhibited superior product selectivity to Pd and Pt catalysts for a variety of substrates. These findings led Haruta to start Au-catalyzed organic reactions in liquid phase.

Scheme 1. Organic Reactions Catalyzed by Supported Au NPs



Although the oxidation of alcohol to carboxylic acid over Au catalysts is generally carried out in the presence of base, base-free oxidation of alcohol to carboxylic acid is also an important issue, because the neutralization of carboxylate salts to carboxylic acid can be avoided. Christensen et al. succeeded the base-free oxidation of ethanol to acetic acid in H_2O over $Au/MgAl_2O_4$[119] and Au/TiO_2.[120] $Au/MgAl_2O_4$ and Au/TiO_2 showed similar catalytic activity, and the acetic acid selectivity was 86% at >90% conversion for $Au/MgAl_2O_4$. The selectivity was much higher than those obtained by $Pd/MgAl_2O_4$ (65%) and $Pt/MgAl_2O_4$ (20%).[119] Haruta and co-workers investigated the ethanol oxidation both in gas and liquid phase using Au NPs supported on a wide variety of metal oxides. In the gas phase, the nature of metal oxide supports plays a determinant role for the product selectivity.[121] Acetaldehyde, which is an economically preferred product, was obtained as a major product (up to 94% yield) over Au NPs on inert acidic or basic metal oxides such as MoO_3. Further oxidation occurred to produce acetic acid in yields up to 46% together with acetaldehyde over Au NPs on n-type semiconductive metal oxides such as ZnO. Complete oxidation to CO_2 takes place over Au NPs on p-type semiconductive one such as NiO and MnO_2. The reaction tendency was explained by the adsorbed ethanol species and by the reactivity of oxygen species on the metal oxide supports. On the other hand, acetic acid was obtained as a major product with selectivities of >50% over Au catalysts regardless of the kind of supports in aqueous media.[122] Among single metal oxide supports, NiO was the best in terms of catalytic activity and selectivity. Further, doping of Cu into NiO supports improved the selectivity of acetic acid as a result of enhancing semiconductivity of support oxides and a decrease in the size of Au NPs. Au/NiO was also effective for the base-free oxidation of less reactive aliphatic alcohol, 1-octanol, and gave octanoic acid in 97% yield at a full conversion.[123]

Gold catalysts also show superior product selectivity to Pd and Pt in hydrogenations. Corma and co-workers demonstrated the selective hydrogenation of nitroaromatics to aniline derivatives keeping other reducible substituents intact.[124] In the case of 3-nitrostyrene hydrogenation, Au/TiO_2 and Au/Fe_2O_3 exhibited excellent selectivity to 3-aminostyrene of 96% at conversions of >95%, whereas Pd and Pt catalysts promoted the hydrogenation of both of nitro group and C=C double bond to give 3-ethylaniline (Scheme 1b). Tokunaga, a collaborator with Haruta, exploited Au-catalyzed selective hydrogenation of nitroalkynes to aminoalkynes for one-pot indole synthesis over Au/Fe_2O_3 (Scheme 1c).[125] Haruta and co-workers also reported that the hydrogen-atom transfer was facilitated when Au clusters (<2 nm in a diameter) were deposited on inert supports for one-pot *N*-alkylation of benzyl alcohol with aniline to give the corresponding secondary amine (Scheme 1d).[126]

In 2012, Haruta became a director of Gold Catalysis Research Center, Dalian Institute of Chemical Physics, China, and a director of Research Center for Gold Chemistry, Tokyo Metropolitan University. The keyword of both centers is Au clusters. In the Chinese center, Haruta and co-workers aim to develop new reactions on supported Au clusters. In the Japanese center, Haruta also aims at utilizing synergy effects between Au clusters and biocatalysts. The aerobic oxidation of glucose over Au catalysts is generally performed under basic conditions in the range of pH 9−10,[116] because the reaction is greatly suppressed under acidic or neutral conditions. Haruta and co-workers found that the reaction rate of glucose oxidation was enhanced at pH 7 by combining Au/ZrO_2 with glucose oxidase as compared to those obtained by individual catalysts.[127] At pH 7, glucose oxidase is the catalytically active species to produce gluconic acid with H_2O_2 as a byproduct. Au/ZrO_2 decomposed H_2O_2 and suppressed the deactivation of glucose oxidase by H_2O_2, resulting a synergistic effect.

6. SUMMARY

Prof. Masatake Haruta has had a distinguished career in catalysis by Au NPs and clusters. He has contributed a great deal of fundamental studies that deepen the understanding of gold catalysis, while continuously tackling challenges of industrially important reactions such as propylene epoxidation. Other examples include development of gold catalysts commercialized as a deodorizer. Gold catalysts were commercialized as a deodorizer (decomposition of *N*-containing odor compounds) in modern Japanese toilets in 1992[72] and are now being commercialized as an air purifier (oxidation of CO and formaldehyde)[128] by collaborating works with him. A new process for the production of methyl methacrylate by the oxidative esterification of methacrolein has been operated using the Au-NiO core−shell catalyst by Asahi Kasei Chemicals since 2008.[129] Mercury chloride has been replaced by Au catalysts for the acetylene hydrochlorination process, which was first found by Prof. Hutchings, by Johnson Matthey and Jacobs in China.[130] This process significantly reduced the use of Hg. The recent successive commercialization of Au catalysts proved that Au can contribute to sustainable developments and human health. In 2013, Haruta established a venture company, Haruta Gold Inc., to accelerate the research and development on Au catalysis both in academia and industries. We wish him continuous success in his career.

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Notes

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■ REFERENCES

(1) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405−408.

(2) Hutchings, G. J. *J. Catal.* **1985**, *96*, 292−295.

(3) Haruta, M.; Sano, H. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1983; Vol. *16*, pp 225−236.

(4) Haruta, M.; Lemaitre, J.; Delannay, F.; Delmon, B. *J. Colloid Interface Sci.* **1984**, *101*, 59−71.

(5) Haruta, M.; Sano, H. *Shokubai (Catalyst)* **1984**, *26*, 140.

(6) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301−309.

(7) Haruta, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 52−56.

(8) Nkoshi, B.; Coville, N. J.; Hutchings, G. J. *J. Chem. Soc., Chem. Commun.* **1988**, 71−72.

(9) Bond, G. C.; Sermon, P. A.; Webb, G.; Buchanan, D. A.; Wells, P. B. *J. Chem. Soc., Chem. Commun.* **1973**, 444b−445.

(10) Haruta, M. *Faraday Discuss.* **2011**, *152*, 11−32.

(11) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566−575.

(12) Haruta, M. *Catal. Today* **1997**, *36*, 153−166.

(13) Tada, K.; Sakata, K.; Yamada, S.; Okazaki, K.; Kitagawa, Y.; Kawakami, T.; Yamanaka, S.; Okumura, M. *Mol. Phys.* **2014**, *112*, 365−378.

(14) Yuan, Y.; Asakura, K.; Wan, H.; Tsai, K.; Iwasawa, Y. *Chem. Lett.* **1996**, *25*, 755−756.

(15) Sakurai, H.; Koga, K.; Iizuka, Y.; Kiuchi, M. *Appl. Catal., A* **2013**, *462−463*, 236−246.

(16) Takei, T.; Akita, T.; Nakamura, I.; Fujitani, T.; Okumura, M.; Okazaki, K.; Huang, J.; Ishida, T.; Haruta, M. *Advances in Catalysis*; Elsevier: Amsterdam, 2012; Vol. *55*, pp 1−126.

(17) Haruta, M.; Kageyama, H.; Kamijo, N.; Kobayashi, T.; Delannay, F. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1989, Vol. *44*, pp 33−42.

(18) Takei, T.; Okuda, I.; Bando, K. K.; Akita, T.; Haruta, M. *Chem. Phys. Lett.* **2010**, *493*, 207−211.

(19) Tsubota, S.; Haruta, M.; Kobayashi, T.; Ueda, A.; Nakahara, Y. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1991; Vol. *63*, pp 695−704.

(20) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175−192.

(21) Tsubota, S.; Cunningham, D. A. H.; Bando, Y.; Haruta, M. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1995; Vol. *91*, pp 227−235.

(22) Wolf, A.; Schüth, F. *Appl. Catal., A* **2002**, *226*, 1−13.

(23) Moreau, F.; Bond, G. C.; Taylor, A. O. *J. Catal.* **2005**, *231*, 105−114.

(24) Moreau, F.; Bond, G. C. *Catal. Today* **2007**, *122*, 260−265.

(25) Zanella, R.; Sandoval, A.; Santiago, P.; Basiuk, V. A.; Saniger, J. M. *J. Phys. Chem. B* **2006**, *110*, 8559−8565.

(26) Zhu, H.; Liang, C.; Yan, W.; Overbury, S. H.; Dai, S. *J. Phys. Chem. B* **2006**, *110*, 10842−10848.

(27) Zhu, H.; Ma, Z.; Clark, J. C.; Pan, Z.; Overbury, S. H.; Dai, S. *Appl. Catal., A* **2007**, *326*, 89−99.

(28) Zanella, R.; Giorgio, S.; Henry, C. R.; Louis, C. *J. Phys. Chem. B* **2002**, *106*, 7634−7642.

(29) Zanella, R.; Delannoy, L.; Louis, C. *Appl. Catal., A* **2005**, *291*, 62−72.

(30) Okumura, M.; Nakamura, S.; Tsubota, S.; Nakamura, T.; Azuma, M.; Haruta, M. *Catal. Lett.* **1998**, *51*, 53−58.

(31) Okumura, M.; Tanaka, K.; Ueda, A.; Haruta, M. *Solid State Ionics* **1997**, *95*, 143−149.

(32) Okumura, M.; Tsubota, S.; Iwamoto, M.; Haruta, M. *Chem. Lett.* **1998**, *27*, 315−316.

(33) Okumura, M.; Haruta, M. *Chem. Lett.* **2000**, *29*, 396−397.

(34) Ishida, T.; Nagaoka, M.; Akita, T.; Haruta, M. *Chem. - Eur. J.* **2008**, *14*, 8456−8460.

(35) Ishida, T.; Kinoshita, N.; Okatsu, H.; Akita, T.; Takei, T.; Haruta, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 9265−9268.

(36) Ishida, T.; Watanabe, H.; Bebeko, T.; Akita, T.; Haruta, M. *Appl. Catal., A* **2010**, *377*, 42−46.

(37) Jiang, H.-L.; Lin, Q.-P.; Akita, T.; Liu, B.; Ohashi, H.; Oji, H.; Honma, T.; Takei, T.; Haruta, M.; Xu, Q. *Chem. - Eur. J.* **2011**, *17*, 78−81.

(38) Fujitani, T.; Nakamura, I.; Akita, T.; Okumura, M.; Haruta, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9515−9518.

(39) Fujitani, T.; Nakamura, I. *Angew. Chem., Int. Ed.* **2011**, *50*, 10144−10147.

(40) Ishida, T.; Kuroda, K.; Kinoshita, N.; Minagawa, W.; Haruta, M. *J. Colloid Interface Sci.* **2008**, *323*, 105−111.

(41) Kuroda, K.; Ishida, T.; Haruta, M. *J. Mol. Catal. A: Chem.* **2009**, *298*, 7−11.

(42) Ishida, T.; Okamoto, S.; Makiyama, R.; Haruta, M. *Appl. Catal., A* **2009**, *353*, 243−248.

(43) Villa, A.; Chan-Thaw, C. E.; Prati, L. *Appl. Catal., B* **2010**, *96*, 541−547.

(44) Sunagawa, Y.; Yamamoto, K.; Takahashi, H.; Muramatsu, A. *Catal. Today* **2008**, *132*, 81−87.

(45) Prati, L.; Martra, G. *Gold Bull.* **1999**, *32*, 96−101.

(46) Porta, F.; Prati, L.; Rossi, M.; Coluccia, S.; Martra, G. *Catal. Today* **2000**, *61*, 165−172.

(47) Önal, Y.; Schimpf, S.; Claus, P. *J. Catal.* **2004**, *223*, 122−133.

(48) Dimitratos, N.; Villa, A.; Bianchi, C. L.; Prati, L.; Makkee, M. *Appl. Catal., A* **2006**, *311*, 185−192.

(49) Hammer, N.; Kvande, I.; Xu, X.; Gunnarsson, V.; Tøtdal, B.; Chen, D.; Rønning, M. *Catal. Today* **2007**, *123*, 245−256.

(50) Biella, S.; Porta, F.; Prati, L.; Rossi, M. *Catal. Lett.* **2003**, *90*, 23−29.

(51) Li, B.; He, P.; Yi, G.; Lin, H.; Yuan, Y. *Catal. Lett.* **2009**, *133*, 33−40.

(52) Brey, L. A.; Wood, T. E.; Buccellato, G. M.; Jones, M. E.; Chamberlain, C. S.; Siedle, A. R. WO Patent 2005/030382, 3M Innovative Properties Co., 2005.

(53) Brady, J. T.; Berey, L. A.; Buccellato, G. M.; Chamberlain, C. S.; Huberty, J. S.; Siedle, A. R.; Wood, T. E. WO Patent 2006/074126 A2, 3M Innovative Properties Co., 2006.

(54) Corti, C. W.; Holliday, R. J.; Thompson, D. T. *Top. Catal.* **2007**, *44*, 331−343.

(55) Bonelli, R.; Lucarelli, C.; Pasini, T.; Liotta, L. F.; Zacchini, S.; Albonetti, S. *Appl. Catal., A* **2011**, *400*, 54−60.

(56) Bamwenda, G. R.; Tsubota, S.; Nakamura, T.; Haruta, M. *Catal. Lett.* **1997**, *44*, 83−87.

(57) Akita, T.; Tanaka, K.; Tsubota, S.; Haruta, M. *J. Electron Microsc.* **2000**, *49*, 657−662.

(58) Tsubota, S.; Nakamura, T.; Tanaka, K.; Haruta, M. *Catal. Lett.* **1998**, *56*, 131−135.

(59) Haruta, M.; Kobayashi, T.; Tsubota, S.; Nakahara, Y. *Chem. Express* **1988**, *3*, 159−162.

(60) Tsubota, S.; Yamada, N.; Haruta, M.; Kobayashi, T.; Nakahara, Y. *Chem. Express* **1991**, *5*, 349−352.

(61) Vogel, W.; Cunningham, D. A. H.; Tanaka, K.; Haruta, M. *Catal. Lett.* **1996**, *40*, 175−181.

(62) Xie, X.; Li, Y.; Liu, Z.; Haruta, M.; Shen, W. *Nature* **2009**, *458*, 746−749.

(63) Shimada, S.; Takei, T.; Akita, T.; Takeda, S.; Haruta, M. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 2010; Vol. *175*, pp 843−847

(64) Haruta, M. *Gold Bull.* **2004**, *37*, 27−36.

(65) Haruta, M. In *Catalysis and Electrocatalysis on Nanoparticles*; Wieckowski, A.; Savinova,E. R.; Vayenas, C. G., Eds.; Marcel Dekker: New York, 2003; p 645.

(66) Daté, M.; Haruta, M. *J. Catal.* **2001**, *201*, 221−224.

(67) Daté, M.; Ichihashi, Y.; Yamashita, T.; Chiorino, A.; Boccuzzi, F.; Haruta, M. *Catal. Today* **2002**, *72*, 89−94.

(68) Cunningham, D. A. H.; Yoshizaki, M.; Haruta, M. *Ultra Clean Technol.* **1996**, *8*, 117−120.

(69) Daté, M.; Okumura, M.; Tsubota, S.; Haruta, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2129−2132.

(70) Daté, M.; Imai, H.; Tsubota, S.; Haruta, M. *Catal. Today* **2007**, *122*, 222−225.

(71) Boccuzzi, F.; Chiorino, A.; Manzoli, M.; Lu, P.; Akita, T.; Ichikawa, S.; Haruta, M. *J. Catal.* **2001**, *202*, 256−267.

(72) Haruta, M. *Chem. Rec.* **2003**, *3*, 75−87.

(73) Iizuka, Y.; Tode, T.; Takao, T.; Yatsu, K.; Takeuchi, T.; Tsubota, S.; Haruta, M. *J. Catal.* **1999**, *187*, 50−58.

(74) Okumura, M.; Coronado, J. M.; Soria, J.; Haruta, M.; Conesa, J. C. *J. Catal.* **2001**, *203*, 168−174.

(75) Widmann, D.; Behm, R. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 10241−10245.

(76) Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T., Jr. *Science* **2011**, *333*, 736−739.

(77) Saavedra, J.; Doan, H. A.; Pursell, C. J.; Grabow, L. C.; Chandler, B. D. *Science* **2014**, *345*, 1599−1602.

(78) Kahlich, D.; Wiechern, U.; Lindner, J. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2012.

(79) Buijink, J. K. F.; Lange, J. P.; Bos, A. N. R.; Horton, A. D.; Niele, F. G. M. In *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*; Oyama, S. T., Ed.; Elsevier: Amsterdam, 2008; pp 355−371.

(80) Ishino, M.; Yamamoto, J. *Shokubai (Catalyst)* **2006**, *48*, 511.

(81) Cavani, F.; Teles, J. H. *ChemSusChem* **2009**, *2*, 508−534.

(82) Sato, A.; Miyake, T.; Saito, T. *Shokubai (Catalyst)* **1992**, *34*, 132.

(83) Meiers, R.; Dingerdissen, U.; Hölderich, W. F. *J. Catal.* **1998**, *176*, 376−386.

(84) Prati, L.; Rossi, M. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1997; Vol. *110*, pp 509−516.

(85) Prati, L.; Rossi, M. *J. Catal.* **1998**, *176*, 552−560.

(86) Haruta, M.; Uphade, B. S.; Tsubota, S.; Miyamoto, A. *Res. Chem. Intermed.* **1998**, *24*, 329−336.

(87) Uphade, B. S.; Tsubota, S.; Hayashi, T.; Haruta, M. *Chem. Lett.* **1998**, *27*, 1277−1278.

(88) Uphade, B. S.; Okumura, M.; Tsubota, S.; Haruta, M. *Appl. Catal., A* **2000**, *190*, 43−45.

(89) Uphade, B. S.; Yamada, Y.; Akita, T.; Nakamura, T.; Haruta, M. *Appl. Catal., A* **2001**, *215*, 137−148.

(90) Qi, C. X.; Akita, T.; Okumura, M.; Haruta, M. *Appl. Catal., A* **2001**, *218*, 81−89.

(91) Uphade, B. S.; Akita, T.; Nakamura, T.; Haruta, M. *J. Catal.* **2002**, *209*, 331−340.

(92) Kapoor, M. P.; Sinha, A. K.; Seelan, S.; Inagaki, S.; Tsubota, S.; Yoshida, H.; Haruta, M. *Chem. Commun.* **2002**, 2902−2903.
(93) Sinha, S. K.; Seelan, S.; Akita, T.; Tsubota, S.; Haruta, M. *Catal. Lett.* **2003**, *85*, 223−228.
(94) Sinha, A. K.; Seelan, S.; Akita, T.; Tsubota, S.; Haruta, M. *Appl. Catal., A* **2003**, *240*, 243−252.
(95) Qi, C. X.; Akita, T.; Okumura, M.; Kuraoka, K.; Haruta, M. *Appl. Catal., A* **2003**, *253*, 75−89.
(96) Sinha, A. K.; Seelan, S.; Tsubota, S.; Haruta, M. *Top. Catal.* **2004**, *29*, 95−101.
(97) Sinha, A. K.; Seelan, S.; Tsubota, S.; Haruta, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1546−1548.
(98) Qi, C. X.; Okumura, M.; Akita, T.; Haruta, M. *Appl. Catal., A* **2004**, *263*, 19−26.
(99) Sinha, A. K.; Seelan, S.; Okumura, M.; Akita, T.; Tsubota, S.; Haruta, M. *J. Phys. Chem. B* **2005**, *109*, 3956−3965.
(100) Chowdhury, B.; Bravo-Suárez, J. J.; Daté, M.; Tsubota, S.; Haruta, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 412−415.
(101) Chowdhury, B.; Bravo-Suárez, J. J.; Mimura, N.; Lu, J. Q.; Bando, K. K.; Tsubota, S.; Haruta, M. *J. Phys. Chem. B* **2006**, *110*, 22995−22999.
(102) Bravo-Suárez, J. J.; Bando, K. K.; Lu, J. Q.; Haruta, M.; Fujitani, T.; Oyama, S. T. *J. Phys. Chem. C* **2008**, *112*, 1115−1123.
(103) Huang, J. H.; Takei, T.; Akita, T.; Ohashi, H.; Haruta, M. *Appl. Catal., B* **2010**, *95*, 430−438.
(104) Huang, J. H.; Lima, E.; Akita, T.; Guzmán, A.; Qi, C. X.; Takei, T.; Haruta, M. *J. Catal.* **2011**, *278*, 8−15.
(105) Qi, C. X.; Huang, J. H.; Bao, S. Q.; Su, H. J.; Akita, T.; Haruta, M. *J. Catal.* **2011**, *281*, 12−20.
(106) Nijhuis, T. A.; Huizinga, B. J.; Makkee, M.; Moulijn, J. A. *Ind. Eng. Chem. Res.* **1999**, *38*, 884−891.
(107) Chen, J. Q.; Halin, S. J. A.; Schouten, J. C.; Nijhuis, T. A. *Faraday Discuss.* **2011**, *152*, 321−336.
(108) Cumaranatunge, L.; Delgass, W. N. *J. Catal.* **2005**, *232*, 38−42.
(109) Taylor, B.; Lauterbach, J.; Delgass, W. N. *Catal. Today* **2007**, *123*, 50−58.
(110) McCoy, M. *Chem. Eng. News* **2001**, *79* (43), 19−20.
(111) Huang, J. H.; Akita, T.; Faye, J.; Fujitani, T.; Takei, T.; Haruta, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7862−7866.
(112) Huang, J. H.; Takei, T.; Ohashi, H.; Haruta, M. *Appl. Catal., A* **2012**, *435−436*, 115−122.
(113) Huang, J. H.; Haruta, M. *Res. Chem. Intermed.* **2012**, *38*, 1−24.
(114) Ojeda, M.; Iglesia, E. *Chem. Commun.* **2009**, *48*, 352−354.
(115) Lee, S.; Molina, L. M.; López, M. J.; Alonso, J. A.; Hammer, B.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Pellin, M. J.; Vajda, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 1467−1471.
(116) Biella, S.; Prati, L.; Rossi, M. *J. Catal.* **2002**, *206*, 242−247.
(117) Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Hutchings, G. J. *Chem. Commun.* **2002**, *38*, 696−697.
(118) Abad, A.; Concepción, P.; Corma, A.; García, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4066−4069.
(119) Christensen, C. H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S. K.; Hansen, S. M.; Hansen, M. R.; Andersen, H. C.; Riisager, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4648−4651.
(120) Jørgensen, B.; Christiansen, S. E.; Thomsen, M. L. D.; Christensen, C. H. *J. Catal.* **2007**, *251*, 332−337.
(121) Takei, T.; Iguchi, N.; Haruta, M. *New J. Chem.* **2011**, *35*, 2227−2233.
(122) Takei, T.; Suenaga, J.; Ishida, T.; Haruta, M. *Top. Catal.* **2015**, *58*, 295−301.
(123) Ishida, T.; Ogihara, Y.; Ohashi, H.; Akita, T.; Honma, T.; Oji, H.; Haruta, M. *ChemSusChem* **2012**, *5*, 2243−2248.
(124) Corma, A.; Serna, P. *Science* **2006**, *313*, 332−334.
(125) Yamane, Y.; Liu, X.; Hamasaki, A.; Ishida, T.; Haruta, M.; Yokoyama, T.; Tokunaga, M. *Org. Lett.* **2009**, *11*, 5162−5165.
(126) Ishida, T.; Kawakita, N.; Akita, T.; Haruta, M. *Gold Bull.* **2009**, *42*, 267−274.
(127) Taketoshi, A.; Takenouchi, S.; Takei, T.; Haruta, M. *Appl. Catal., A* **2014**, *474*, 257−262.
(128) Ikegami, M.; Matsumoto, T.; Kobayashi, Y.; Jikihara, Y.; Nakayama, T.; Ohashi, H.; Honma, T.; Takei, T.; Haruta, M. *Appl. Catal., B* **2013**, *134−135*, 130−135.
(129) Suzuki, K.; Yamaguchi, T.; Matsushita, K.; Iitsuka, C.; Miura, J.; Akaogi, T.; Ishida, H. *ACS Catal.* **2013**, *3*, 1845−1849.
(130) *The Catalyst Review*; The Catalyst Group Resources, Inc.: Lower Gwynedd, 2015; Vol. *28*; pp 8−13.