

# The production of propylene oxide over nanometer Au catalysts in the presence of H<sub>2</sub> and O<sub>2</sub>

Caixia Qi\*

Institute of Applied Catalysis, College of Chemistry and Biology, Yantai University, Yantai 264005, P.R. China

\*To whom correspondence should be addressed.  
Tel & Fax: 86-535-6902233, Email: qicx@ytu.edu.cn

## Abstract

**Direct gaseous-phase epoxidation of propylene over nanogold catalysts in co-presence of H<sub>2</sub> and O<sub>2</sub> has been extensively studied. Many researchers have made important progress in this field, and a survey of the literature published to date is presented in this article. The salient features are the nature of the nanogold particles and the Ti-based support materials.**

## Keywords

Nanometer Au catalysts; Epoxidation of propylene

## Introduction

Propylene oxide (PO) is the third largest propylene derivative, ranking behind polypropylene and acrylonitrile and is used primarily as a chemical intermediate to manufacture polyether polyols and propylene glycol, alkoxyates and glycol ethers. Its total production was 5.8 million tons/annum in 1999 and is annually growing by 4-5% [1]. Traditionally, PO is produced via the chlorohydrin route, which consumes a large amount of chlorine and causes environmental pollution [2]. The Halcon process (the hydroperoxide process) with various oxidants [3-5], has therefore been developed. Large-scale commercialization of this process depends on the cost of oxidants and the market demand for the co-products. In 2003, Sumitomo Chemical Co. Ltd. launched a new commercial plant of 150,000 t/y capacity that uses a co-product free route to propylene oxide utilizing cumene hydroperoxide as oxidant combined with cumene recycling in Japan. A recent development in the production of PO by using hydrogen peroxide is to integrate a hydrogen peroxide process and a propylene epoxidation process. The disadvantage of the high cost of hydrogen peroxide can be solved by local production of the hydrogen peroxide, for which plants are currently under construction by Dow-BASF and Degussa/Uhde in Belgium and Korea respectively [6].

A major research effort in industry and academia has been made to continually search for a more environmentally friendly and economical route using either direct epoxidation with O<sub>2</sub> alone or in the co-presence of reducing reagents, such as H<sub>2</sub>. Some developing techniques with oxygen include photocatalysis [7-8], electrocatalysis [9], and an extensively studied heterogeneous catalytic system based on Ag catalysts [10-18], which are used in industry for the epoxidation of ethene. Copper has also been reported to be effective for the epoxidation of propylene [19-22]. Quite recently, an interesting result with propylene conversion as high as 47.8% at 150°C was obtained over a Ti-Al-HMS catalyst without adding noble metal [23]. However, in all the above processes, the selectivity for PO is below 60% and this is too low for the commercial application.

At the same time, many studies focus on producing PO through in situ generation of hydrogen peroxide from hydrogen and oxygen. A typical example is that when using a tungsten-containing catalyst, 91% propylene conversion with 94% selectivity to PO was obtained using the 2-ethylanthraquinone (EAQ)/2-ethylanthrahydroquinone (EAHQ) system and the technique of reaction-controlled phase transfer [24]. Supported palladium- or palladium/platinum catalysts have also been reported active and selective for the epoxidation of propylene in methanol and butanol media [25-28].

In gas phase, via addition of H<sub>2</sub> into a feed of propylene and O<sub>2</sub>, a simpler process for PO synthesis can be devised over supported Au catalysts. In 1997 or so, Dr. Hayashi *et al* were the first to report a high selectivity for PO of up to 99% over a Au/anatase TiO<sub>2</sub> catalyst under mild conditions

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.887	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 * Lu 174.97	hafnium 71 Hf 178.49	tantalum 72 Ta 180.95	tungsten 73 W 183.84	rhenium 74 Re 186.21	osmium 75 Os 190.23	iridium 76 Ir 192.22	platinum 77 Pt 195.08	gold 78 Au 196.97	mercury 79 Hg 200.59	thallium 80 Tl 204.38	lead 81 Pb 207.2	bismuth 82 Bi 208.98	polonium 83 Po [209]	astatine 84 At [210]	radon 85 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * * Lr [260]	lawrencium 103 Lr [260]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [263]	bohrium 107 Bh [264]	hassium 108 Hs [265]	meitnerium 109 Mt [266]	unnilennium 110 Uun [271]	ununennium 111 Uuu [272]	ununbium 112 Uub [273]	ununquadium 114 Uuq [284]				
* Lanthanide series		lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04		
** Actinide series		actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]		

**Table 1**

PO selectivity higher than 62% was observed over Au on silicates containing elements indicated by "red hearts" (ref. 31-32)

[29-30], emphasizing the necessity of the presence of titanium in the support for PO activity. This exciting work was soon followed by a number of groups worldwide, and significant achievements with Au-Ti catalysts recently emerged. In contrast to this, Dr. Cunningham *et al* in 2001 [31-32] described the production of PO over Au catalysts with supports totally free of titanium. As indicated by red hearts in Table 1, Au particles smaller than 10nm on silicates containing one or more elements from the lanthanide series [31] and others near titanium in the Periodic Table [32], can produce PO in comparable quantities as the Au-Ti catalysts. Unfortunately, this very excellent work has been largely ignored and no further progress has been reported to date.

After almost a decade of effort, commercially viable results for PO synthesis over the Au-Ti catalyst system were recently obtained in two leading research groups, Prof. Haruta's group in Tokyo Metropolitan University, Japan [33-34] and Prof. W.N. Delgass's group in Purdue University, USA [35-36]. The former initially started on TiO<sub>2</sub> supported nanogold catalysts and gradually moved forward the mesoporous titanasilicates as the supports. The latter focused on TS-1 as the only support with very low Au loading, which presented even better results. It is interesting that a PO selectivity greater than 90% was also achieved over Ag catalysts when introducing H<sub>2</sub> in the feed

[37-41]. However, the conversion is below 2%. Although further research and development may improve the catalytic performance, the gold-titanium catalysts, at present, seem to be the only ones close to commercialization for the direct synthesis of PO in the gas phase.

Considerable effort has been made to understand the nature of the Au-Ti system and the contribution from each component in PO production. To date, some essential requirements for success with this system have become clear but some remain elusive. Concerning the pertinent work done in his lab, Prof. Haruta summarized results obtained up to 2002 when talking about catalysis of nanogold [42-43] and also reviewed his team's work in 2004 [44]. Quite recently he again provided an up-to-date summary as a chapter in a book entitled "Nanoparticle Catalysis" [45]. A brief evaluation on epoxidation over nanogold was also provided recently by Nijhuis *et. al* as one of the PO production processes [46].

Here, this review attempts to summarize and compare the results from different labs and discusses the possible questions remaining for this system based on the majority of publications available up until November 2007. Here we focus on the nature of nanogold particles and the Ti-based support materials and the synergism between Au and Ti, the reaction mechanism, promoters and future issues.

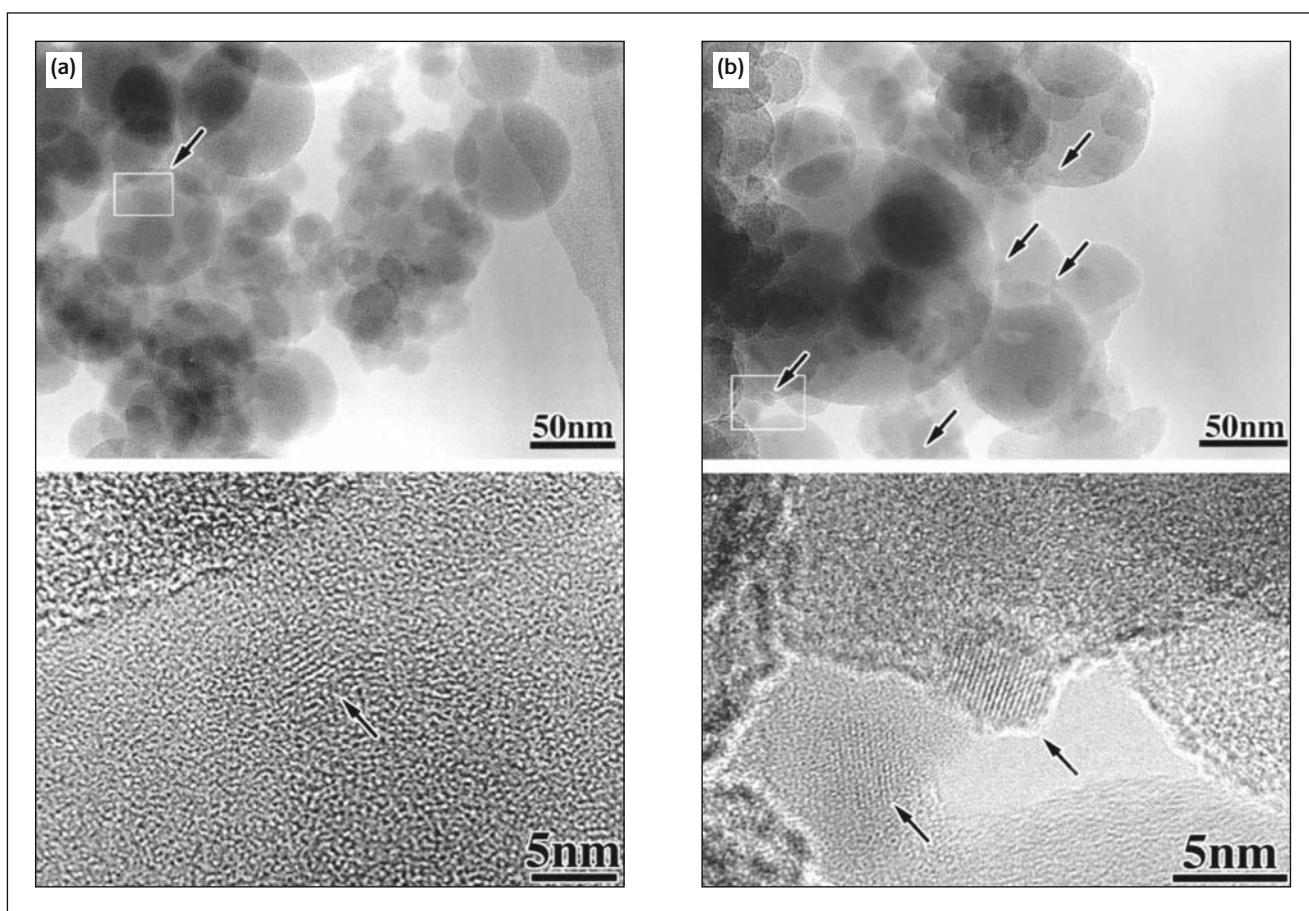
## Nature of titanium-containing supports

The properties of the Ti-based support materials required seem clearer than that for the gold nanoparticles at present. The effect of the titanium phase on reactivity to PO formation can be pieced together from its coordination environment, the distance between two neighboring titanium atoms, hydrophobicity/or acidity and porosity. For the Au/TiO<sub>2</sub> system, the pioneer work of Haruta *et. al* showed that only anatase TiO<sub>2</sub> rather than rutile and amorphous TiO<sub>2</sub> gave high selectivity for PO [29-30, 47]. In general, highly dispersed TiO<sub>2</sub> in the form of isolated tetrahedral coordination makes Au selective and more active. They strongly contact or embed in the framework of the substrate oxides such as silica [48-52] or zeolites such as TS-1[35-36, 47, 53-56], Ti-MCM-41/48 [44, 51, 57-62], Ti-HMM [63], 3D sponge- such as mesoporous Ti-silicates [33-34, 64] and Ti-TUD [65-66]. Our earlier work on Au deposited on Ti-doped nonporous silica [50] emphasizes the importance of the isolated tetrahedral coordinated TiO<sub>4</sub> units on the selectivity for PO. As shown in Table 2, Ti impregnated non-porous silica with heat treatment at high temperatures was found to be more selective and active than when heat treated at lower temperatures. In the case of low temperature treatment, amorphous TiO<sub>2</sub> is loosely dispersed on silica substrate while isolated Ti species are incorporated into the silica network at high temperatures. TEM images of

samples of titania-on-nonporous silica calcined respectively at 400 and 1000°C is shown in Figure 1.

The Au-Ti system of nanogold particles deposited on anatase TiO<sub>2</sub> possesses two inherent weaknesses: faster deactivation and low PO yields (<2%). It is only selective for PO at temperatures below 100°C [47]. Attempts to improve the rate of propylene conversion to PO by raising the temperature only resulted in PO combustion [48]. When using Ti-MCM-41/48, Ti-HMM etc. instead of TiO<sub>2</sub>, and the reaction temperature was increased from 50°C to 150°C while PO yields increased from 1-2% to 4-5% [44, 55, 57, 58, 60, 61, and 63]. This probably suggests that the distance between two neighboring Ti cations in Ti-O-Ti entities may determine the optimal reaction temperature to some extent. A significant enhancement in the optimal reaction temperature from 100°C to 250°C with maintenance of PO selectivity above 80% for the Au catalysts deposited on silylated Ti-MCM-48 supports [59] may support this assumption.

The accumulation of PO and other oxygenates on the catalyst surfaces via interaction with surface Ti-OH and Si-OH groups, which was confirmed by FT-IR analysis, temperature programmed desorption studies and the GC-MS analysis for the spent catalysts [58, 67-71], was thought to be mainly responsible for lower PO yield and rapid deactivation of the Au-Ti catalysts. The switch of the hydrophilic Ti-SiO<sub>2</sub> to



**Figure 1**

The low- and high-magnification TEM images of Ti-SiO<sub>2</sub> calcined at (a) 400°C and (b) 1000°C (ref.50)

**Table 2**

Propylene epoxidation at 60, 90, 120 & 150 °C over Au deposited on the Ti-SiO<sub>2</sub> supports calcined at different temperatures (Ti/Si atomic ratio: 1/100, ref.50)

Supports	Calcination temperature of Ti-SiO <sub>2</sub> (°C)					
	300	400	600	800	1000	
Surface Area of the Supports (m <sup>2</sup> /g)	77	77	73	69	61	
Actual Au loading (wt. %)	0.58	0.58	0.67	0.39	0.33	
Mean Diameter of Au (nm)	-	2.3	-	-	3.5	
Reaction at (°C)	60	86	81	89	99	-
		Selectivity for PO (%)				
		0.08	0.06	0.09	0.08	
	90	69	51	80	85	
		Conversion of Propylene (%)				
		0.15	0.13	0.14	0.15	
	120	10	16	48	62	80
		Conversion of Propylene (%)				
		0.30	0.25	0.28	0.28	0.27
	150	4.5	3.8	12	32	56
		Conversion of Propylene (%)				
		0.68	0.59	0.58	0.52	0.43

hydrophobic Ti-SiO<sub>2</sub> via silylation treatment has given a prominent positive effect on PO yields, the rate of deactivation and H<sub>2</sub> efficiency [33, 34, 58, 59, 64]. However, loss in activity with time on stream for the silylated Au catalyst is still an issue to be dealt with. Competitive adsorption of water or alcohols was thought to reduce PO adsorption and slow the deactivation [68, 72]. However, water, produced in the reaction process, probably acts as another contributor to the deactivation of the Au catalysts via the re-formation of hydroxide forms of Ti and Si sites (a reverse process of silylation), as indicated by FT-IR results for the spent catalyst [59]. A dynamic exchange between hydroxylation and silylation processes may maintain better stability of the silylated catalyst with time on stream, this probably could account for the significant contribution caused by the addition of gaseous trimethylamine as promoter to activity, stability and H<sub>2</sub> efficiency over the corresponding catalysts [33, 64].

Based on the experimental evidences described above, TS-1, which is a naturally hydrophobic microporous material, supported nanogold catalysts should give excellent stability. Recent results from the Prof. Delgass group indeed

demonstrated that this is the most active Au/TS-1 catalysts reported so far, with stable PO production in certain circumstances at temperatures ranging from 140-200 °C [35, 36]. However, poor stability has been observed over Au/TS-1 catalysts in some cases [35, 54-56], indicating that there are some other unknown factors which also cause deactivation of the Au catalysts for the epoxidation of propylene using O<sub>2</sub> and H<sub>2</sub>.

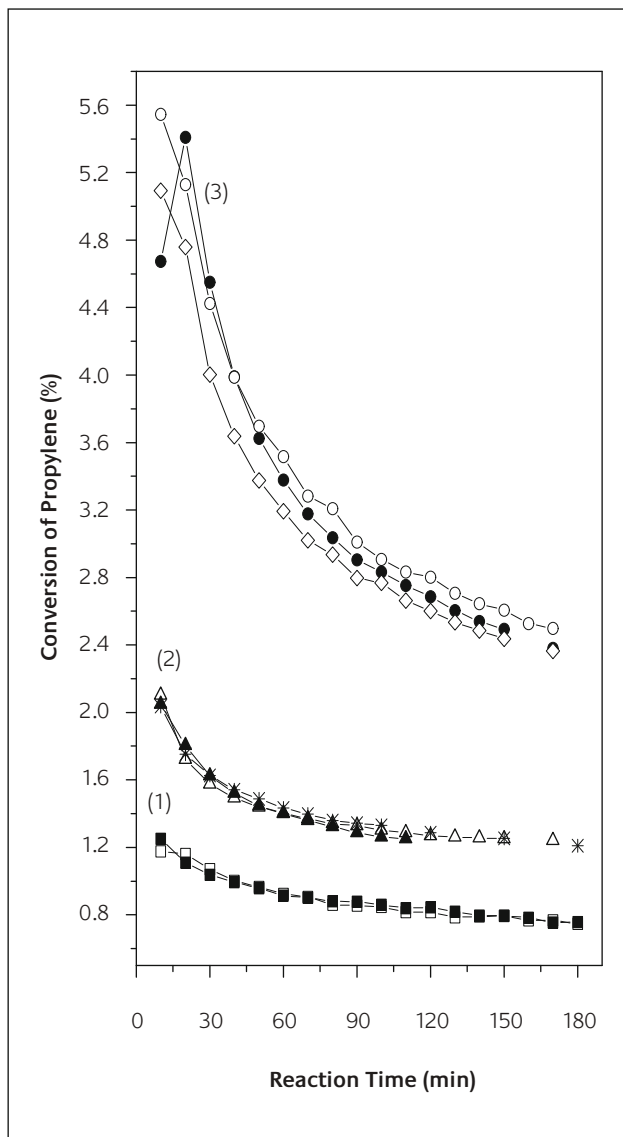
As compared to TS-1 materials with more globular or spheroidal particle morphologies, the Au deposited on TS-1 with prismatic crystallites was less active [36], suggesting that the morphology of the support may play an important role in determining the epoxidation activity. It has been claimed that Au deposited on Ti-MCM-48 with 3D pore structure gave better performance than nanogold deposited on Ti-MCM-41 with 2D pore structure [58]. Recently Dr. Sinha succeeded in obtaining an industrially relevant result over a highly dispersed Au catalyst supported by an amorphous sponge-like mesoporous titanium silicates with large 3D pores (>7nm) and higher Ti content plus the silylation treatment and promoting effect of Ba(NO<sub>3</sub>)<sub>2</sub> [33, 64], for which propylene conversions of up to 10% have been obtained at 90%

**Table 3**

Epoxidation of propylene on Au catalysts prepared by different methods

Preparation method	LG*				DP#			
	0.47		0.56		0.18		0.18	
Au loading, wt.%	Silylated Ti-MCM-48		Fresh Ti-MCM-48		Silylated aged Ti-MCM-48		Aged Ti-MCM-48	
Support	150	250	150	250	150	240	150	240
Reaction Temperature, °C	150	250	150	250	150	240	150	240
Propylene Conversion, %	trace	1.56	2.48	2.46	0.75	1.47	2.56	2.25
PO selectivity, %	>99	85	90	9.6	97	22	91	13
PO Yield, %	trace	1.33	2.23	0.24	0.73	0.32	2.32	0.29

The data of activity were collected after 30 minutes reaction. \*LG: the liquid grafting method, (CH<sub>3</sub>)<sub>2</sub>Au(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>) as precursor; #DP: the deposition-precipitation method, HAuCl<sub>4</sub>·4H<sub>2</sub>O as precursor



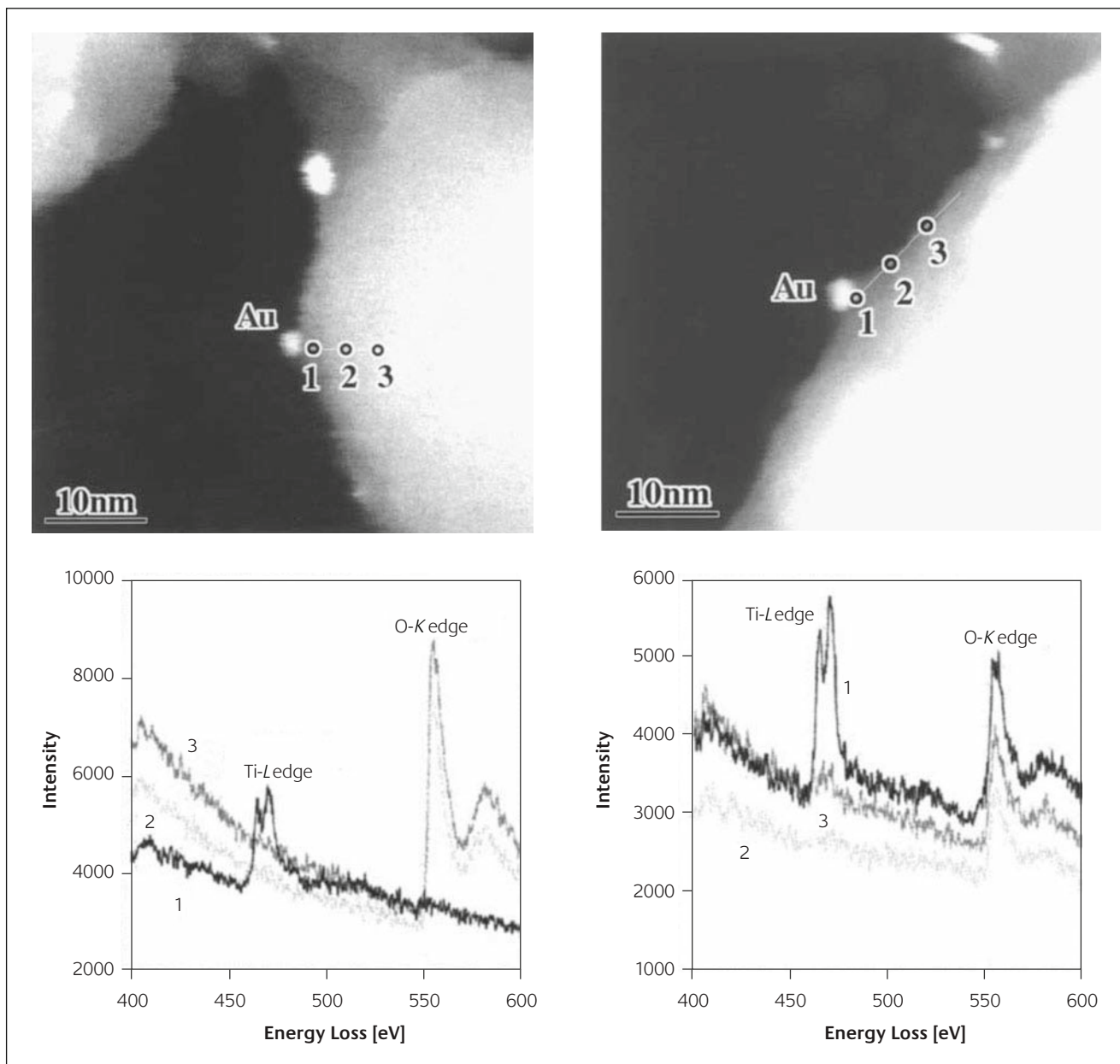
**Figure 2**  
*Epoxidation of propylene at 150°C over the three sets of Au catalysts supported on Ti-SiO<sub>2</sub> with varied Ti content and with different porosities and surface areas. (1) □: 8wt.% Au/Ti-nonporous SiO<sub>2</sub>, ■: 16wt.% Au/Ti-MCM-48 aged in air for more than one year. (2) ▲: 8wt.% Au/Ti-MCM-41, \*: 4wt.% Au/mixed TiO<sub>2</sub>/mesoporous SiO<sub>2</sub>, △: 2wt.% Au/Ti-MCM-48. (3) ●: 12wt.% Au/fresh Ti-MCM-48, ○: 16wt.% Au/fresh Ti-MCM-48, ◇: 12wt.% Au/Ti-MCM-41. All Au loadings are the theoretical Au contents in HAuCl<sub>4</sub> solution with respect to the support. (ref. 62)*

selectivity. Improved stability and regeneration of this catalyst have been reported when adding a trace of trimethylamine in the feed [34]. However, even better results were obtained when the catalysts were deposited on microporous TS-1 zeolite, as reported by Professor Delgass and his coworkers [35-36, 55] recently, and this gives rise to the necessity of defining the contribution made by the porosity of the titanosilicates materials. As shown in Figure 2, a similar starting conversion of propylene over various Au-Ti catalysts with Ti-doped nonporous SiO<sub>2</sub>, TiO<sub>2</sub> on mesoporous SiO<sub>2</sub> and mesoporous Ti-MCM-41/48, the observation of the same rate of deactivation with time on stream [62] also provides useful mechanistic insight.

## Nature of gold particles

It has been clear that the nature of the gold particles plays a key role in the epoxidation of propylene in the presence of H<sub>2</sub> and O<sub>2</sub> ever since the discovery of the reaction over nanogold. 2-5 nm Au particles were found to be highly selective for PO production by Professor Haruta and his coworkers [47]. This was widely justified by subsequent work in his lab and others around the world, regardless of the types of Ti-containing supports used. Interestingly, when using Au/TiO<sub>2</sub> catalyst prepared by the deposition-precipitation method, the propane/PO selectivity could be switched from the oxidation to the hydrogenation reaction when Au loadings below 0.1wt% and corresponding Au particle size less than 2 nm, whereas Au particles larger than 5 nm promoted complete combustion [47]. In contrast with this, working on a set of the modified mesoporous Ti-MCM-41, Professor Haruta and his coworkers firstly found that very low Au loadings (≤0.02wt. %) produced very active catalysts on the basis of per gram of Au with a PO selectivity of up to 80% and good stability for about 7 hours after a 30 min induction period [59]. This observation is further supported by the work of Professor Delgass's group [35, 54] on Au/TS-1 which confirmed that extremely small gold clusters (smaller than 2 nm) are active for propylene epoxidation [35, 54, 55]. Recently, McFarland and his coworkers reported that Au particles of about 8 nm in diameter, deposited onto TiO<sub>2</sub> favor the hydrogenation reaction: the catalyst was prepared by a micelle encapsulation method (PVP reducing method) that gave a narrow size distribution [73]. The presence of Cl<sup>-</sup> anions in final catalysts (ca. 0.5wt %) might not be the reason for this unexpected finding, as they proposed, when compared to Au/TiO<sub>2</sub> prepared from the same precursor: HAuCl<sub>4</sub>·4H<sub>2</sub>O [47]. Soon after this, they reported that PO could be highly selectively produced over Au on titania with an average Au size of 4.6±0.5nm, which was synthesized from chemically reduced, thiol-capped gold particles, another micelle encapsulation method [74]. The impact of nanogold size on product selectivity for propylene epoxidation, therefore highly depends on the preparation method, Au loading, support type and other unknown factors. This probably implies that the size of the nanogold particles is not the only factor controlling PO activity.

It has previously been shown that gold deposited by DP is sited near titanium [50] and the active epoxidation site is suggested to be the perimeter between the Au particles and the Ti sites [42, 43]. A typical ADF-STEM image of Au/Ti-SiO<sub>2</sub> prepared by DP and its EELS is displayed in Figure 3. Gold particles are shown as bright contrast spots in these ADF-STEM images. Ti-L edge signals are clearly observed at the position where Au particles are deposited. O-K edge signals come from the SiO<sub>2</sub> supports. It is clear that gold particles are deposited on titanium sites not on the SiO<sub>2</sub> surfaces. In comparison with the results on DP catalysts, Au deposition both on Ti<sup>4+</sup> and on the SiO<sub>2</sub> surface was claimed to lower the PO selectivity when using gas phase grafting (GG) of an



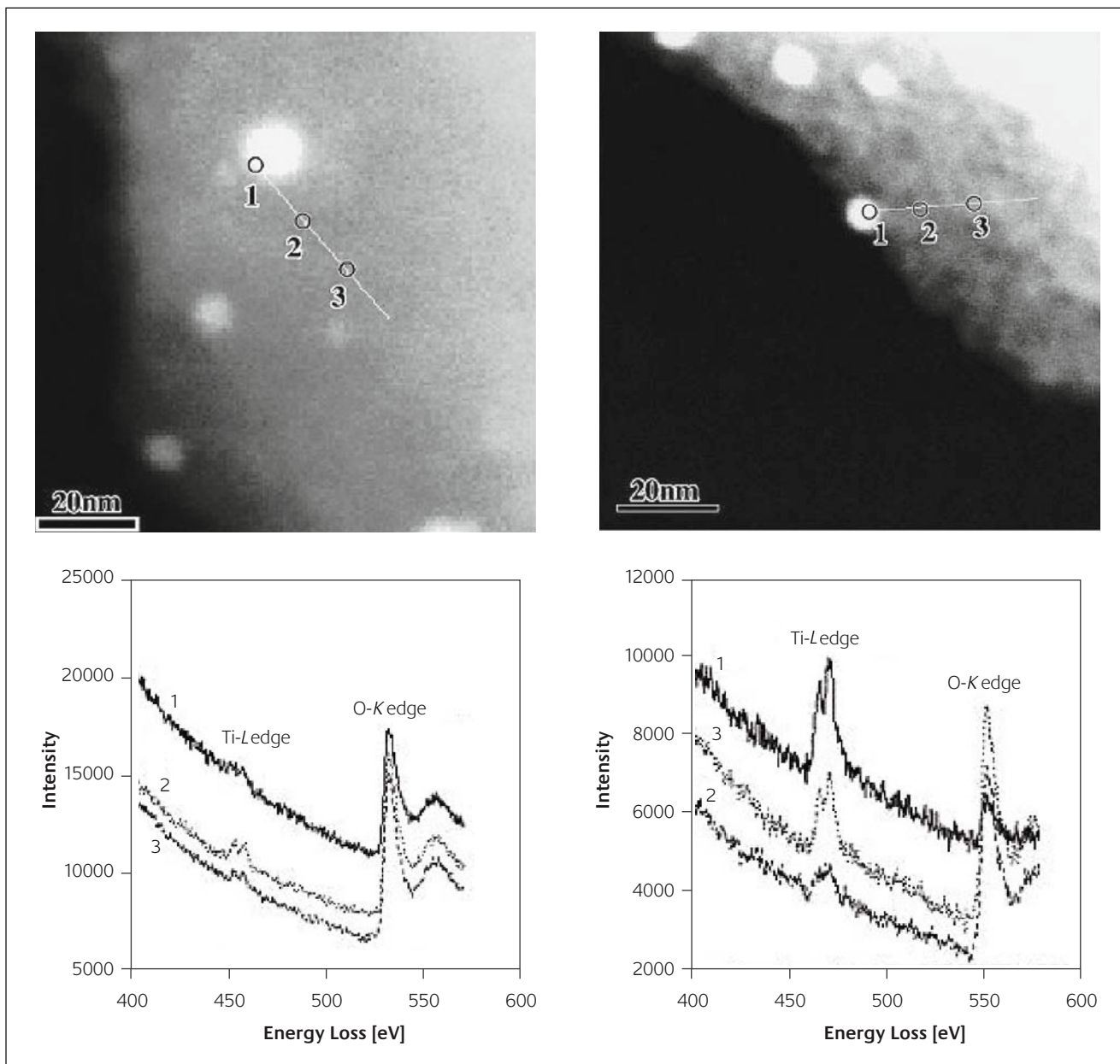
**Figure 3**

The ADF-STEM images of Au/Ti-SiO<sub>2</sub> and its EELS spectra obtained from each position indicated in the images (ref.50)

organic complex precursor dimethyl Au(III)acetylacetonate [75]. However, the above observation for the GG catalyst was obtained at only one temperature, which is much higher than that employed for the DP catalyst. The temperature used to compare may not be the optimal reaction temperature in terms of highest PO yield for the GG catalyst. Figure 4 shows the ADF-STEM images and EELS spectra of Au/Ti-MCM-48 prepared by liquid phase grafting (LG) using the same Au complex precursor [59]. It is clear that Au particles can be deposited on Si sites (Fig. 4(a)) as well as on Ti sites (Fig. 4(b)).

During my earlier work described above, some original, unpublished data, now summarized in Table 3 may be helpful in discussing how the position of Au nanoparticles affects the selectivity for PO. You may notice that the silylation treatment does not make a remarkable contribution to PO activity as claimed in Dr. Sinha's work [33]. This is because of an

unsuitable degree of silylation and shorter reaction time, as shown in Figure 5 [59]. The silylated catalysts were less active, when the molar ratio of MTEOS/(MTEOS+TEOS) in the synthesis gel was low, than the non-silylated one but became more active at higher ratios, particularly at a ratio of 0.75. All silylated catalysts presented better stability than Au/Ti-MCM-41 without silylation after an induction period, which is longer for the catalyst with lower methyl ratio. Information about catalyst preparation and the size of Au particles, etc may be obtained from reference 59. The PO selectivity higher than 80% at 150°C for non-silylated Ti-MCM-48 and 250°C for silylated Ti-MCM-48 suggests that nanogold particles deposited on Si sites, at least, are not detrimental to PO selectivity, and probably don't make a contribution to the activity if comparing two catalysts with almost the same Au loading but prepared by the DP or LG method. In fact, as claimed by Professor Delgass and his coworkers [36], for many



**Figure 4**

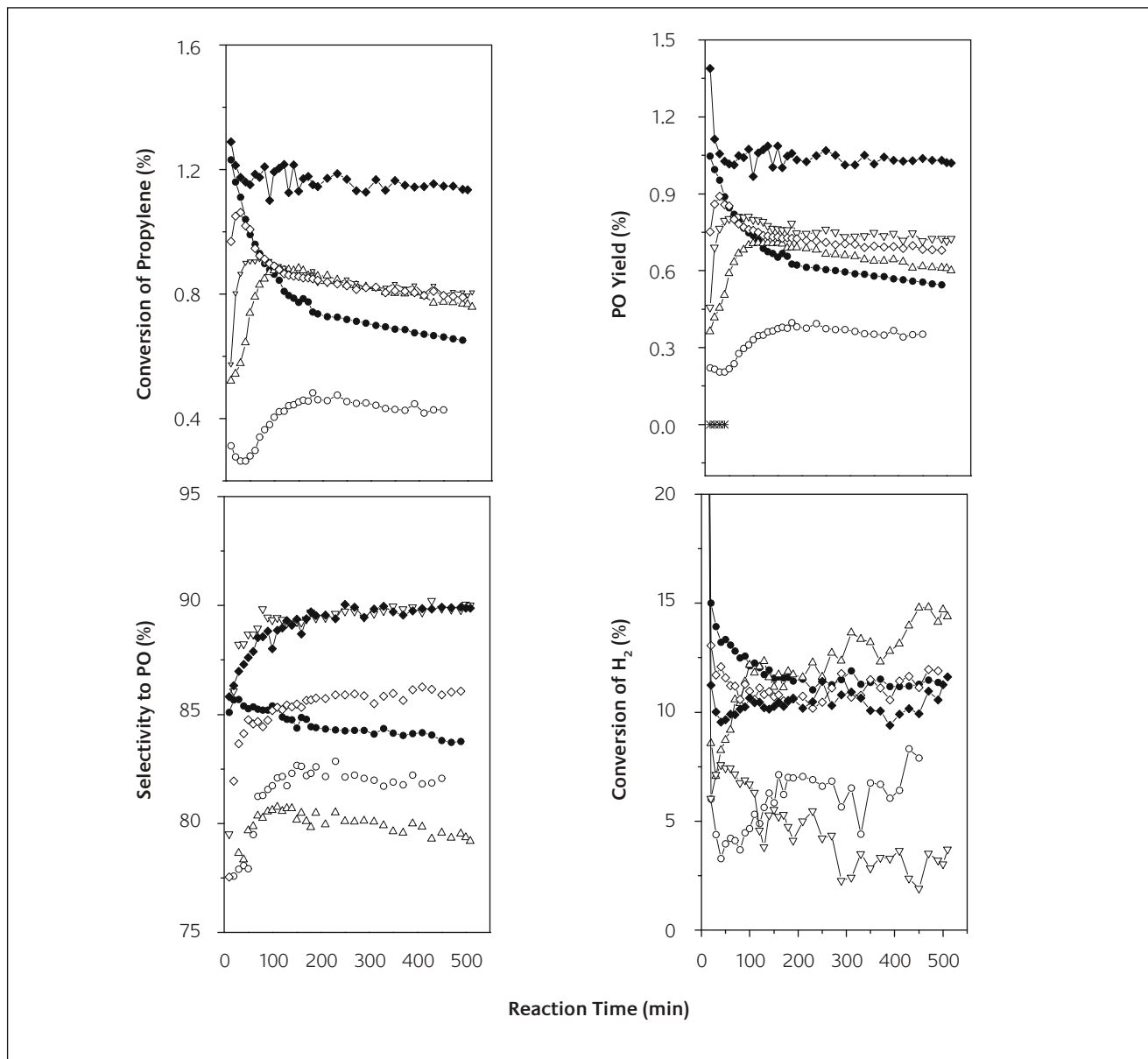
The ADF-STEM images of Au/Ti-MCM-48 and its EELS spectra of Au were deposited on: (a) Si sites and (b) Ti sites (ref.59)

Au catalysts with relatively high Au loading, low formation rate of PO based on the unit of per gold indicates that a significant portion of gold deposited on the support surface may be inactive for the epoxidation.

Little attention has also been paid to the oxidation state of active nanogold particles. Based on XPS and Mossbauer absorption spectroscopy analysis for Au/TiO<sub>2</sub> and Au/Ti-SiO<sub>2</sub> epoxidation catalysts [76], Professor Moulijn and his coworkers stated that only metallic gold contributed to catalytic activity, and a DP Au catalyst with oxidic Au species, observed by Au L<sub>3</sub>-edge EXAFS spectra, showed lower epoxide selectivity than other catalysts with only metallic gold [44]. However, it is too early to say oxidic Au is harmful or inactive for PO synthesis. Our dried Au catalysts deposited on Ti-MCM-48 [62, 77] or series of dried Au/TS-1 catalysts reported by Delgass and his coworkers [35, 36, 54-56] did give PO activity.

A PO selectivity higher than 90% over Au catalysts with at least 30% oxidized Au was disclosed by Dr. A. Kuperman (Dow Chemical) in 2000 [78]. Professor H. H. Kung and his coworkers provided direct evidence of oxidized gold on supported gold catalysts with Au diameters in the range of 2-5nm by time-of-flight secondary ion mass spectroscopy [79]. As they pointed out, oxidized Au particles were not detectable by a surface technique such as XPS in some cases.

So, the nature of active nanogold: its size, shape, residence position, and oxidative state as well as their impact on the performance of epoxidation of propylene is far from being understood at the present stage and further extensive investigation is needed to answer the questions concerning the magic effect of nanogold particles on the reaction of epoxidation and also on a variety of other reactions.



**Figure 5**

Epoxidation of propylene at 200 °C as a function of time on stream over (●) Au deposited on Ti-MCM-41, and on a series of methyl-tethered Ti-MCM-41-type with the molar ratio of MTEOS/(TEOS+MTEOS) in the synthesis gel of (○) 0.15, (△) 0.25, (▽) 0.35, (◇) 0.50, (◆) 0.75 and (★) 1.0 (ref. 59)

## Synergy of titanium and nanogold

It is known that neither nanogold nor tetrahedral titanium alone can produce PO from propylene in the presence of H<sub>2</sub> and O<sub>2</sub>. They have to work together as a two-site active centre to make PO [33, 48, 50, 65, and 67]. Lots of work has previously been done on searching the optimal Ti/Si ratio and simultaneous changing Au loading to search for the best catalysts. An optimum Au/Ti ratio has gradually been realized and demonstrated with very active catalysts [33, 35, 48, 54, 56, and 59]. However, the limitation in the formation of the isolated titanium entities limits the further enhancement in PO yields. How to break the current bottleneck of Au/Ti ratio and other factors to get high conversion of propylene with high selectivity for PO is quite challenging.

It is known that there are a number of elements which can replace titanium in silicate frameworks as the supports for Au catalysts for PO synthesis in co-presence of H<sub>2</sub> and O<sub>2</sub> [31-32]. This may provide a suitable approach toward understanding in greater depth the working mechanism between Au and these elements including Ti.

## Proposed mechanism

In 1999, Moulijn and his coworkers proposed three different types of mechanisms and finally concluded that there is a high possibility of formation of a hydroperoxide-like intermediate so that this can interact with hydrogen [48]. This possibility was further emphasized by other researchers



based on a theoretical prediction of H<sub>2</sub>O<sub>2</sub> generation over the surface of gold [80], further confirmed by computational evidence [81, 82] and the direct experimental observations of HOOH formation on Au/TiO<sub>2</sub> systems from molecular oxygen and hydrogen over nanogold particles [75, 83, 84] and of Ti-hydroperoxo species detected under reaction conditions over a mesoporous titanasilicate supported Au catalysts by in-situ UV-Vis spectroscopy [85].

Hydrogen peroxide formed on the Au surfaces is then converted into hydroperoxo species at tetrahedrally coordinated Ti cation sites. The Ti-hydroperoxo species can subsequently react with C<sub>3</sub>H<sub>6</sub> adsorbed either on Ti sites or Si sites to form PO. By means of a kinetic study [86] and DFT calculations [82, 87, and 88] for the Au/TS-1 catalysts, Professor Delgass and coworkers suggested a similar mechanism with a deduction of the final formation of PO on Ti sites. While Professor Haruta and his coworkers preferred the ultimate PO production on the SiO<sub>2</sub> surface for the epoxidation of propylene over Au on various titanosilicates [44, 58, and 85].

For the reaction pathway for the Au/TiO<sub>2</sub> catalysts, which is similar to that for the Au/Ti-SiO<sub>2</sub> system, the key step proposed is the formation of a peroxide species on the gold. There are some differences on details suggested by professor Haruta's group [44, 45] and Professor Nijhuis's group [88, 89]. Nijhuis and his coworkers stress that the role of gold in the epoxidation of propylene not only provides a peroxide species, but the gold particles also catalyze a consecutive oxidation of the bidentate propoxy species to form carbonate/carboxylate, which is possibly the cause of catalyst deactivation [70].

## Promoters

The deposition-precipitation (DP) method is the best method to prepare the Au-Ti catalysts using HAuCl<sub>4</sub> as the precursor. Professor Haruta *et al.* found that Au/TS-1 produced more propanal than PO, especially when the catalyst was thoroughly washed, suggesting that the presence of a small amount of Na<sup>+</sup> and/or Cl<sup>-</sup> are necessary for Au to be selective for the formation of PO [47]. Stangland *et al.* also noticed the enhancement in activity of sodium [49, 56]. The addition of CsCl to Au/Ti-CM-41 by impregnation and mechanical mixing depressed H<sub>2</sub> consumption whereas the presence of Cl<sup>-</sup> anions induced agglomeration of the gold particles [57]. Surprisingly high catalytic performance over Au/TS-1 was obtained recently via removal of extra Cl<sup>-</sup> using pretreatment of TS-1 with aqueous NH<sub>4</sub>NO<sub>3</sub> before Au deposition [55]. Addition of Ba(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub> and CsNO<sub>3</sub> during Au deposition can improve catalytic activity [64, 77]. Sodium, barium, rubidium, lithium, and magnesium [91] as well as potassium, calcium, and lanthanum [92] have been reported to improve the catalyst in patents. Also, alloying the gold with small quantities of platinum or palladium can improve the hydrogen efficiency [93]. Furthermore, anions can also dramatically change the reaction pathway to affect the final

product selectivity [77]. The conclusion is that the presence of surface alkali has a positive effect on PO activity and selectivity, presumably by blocking the consecutive PO reactions. It is not clear that one type of alkali is better than another or optimal amount of a specific alkali or anion reported so far due to lack of a deep and systematic investigation.

Amazing improvements in propylene conversion, PO selectivity and H<sub>2</sub> efficiency were observed by adding a trace amount (10-20 ppm) of trimethylamine in the feed [34]. Interestingly, regeneration of the spent catalysts in the presence of trimethylamine results in a more active, selective, and stable catalyst than the fresh one.

## Challenges

The recent results with the conversion of propylene close to 10% seem to make the epoxidation over the Au-Ti catalysts commercially viable [33-36]. However, the major problems to be overcome before the commercialization of this process are high cost in production, transportation and storage of H<sub>2</sub>, and the compression and separation of gaseous PO etc, making it impossible to run the process profitably at this moment. Sufficiently high PO yields are required to overcome these additional costs, or could similar conversions and selectivities be achieved without sacrificing H<sub>2</sub>? These two requirements are difficult to fulfill in a short period. Furthermore, the presence of minor amounts of by-products, not detected in lab-scale catalyst testing, might complicate the separation unit in an industrial process.

Deactivation of the Au catalysts with time on stream, is another unsolved obstacle, as is their stability in storage after preparation. These are common problems to be dealt with for Au catalysts, because Au particles growth starts at room temperature with the simultaneous formation of Au-OH species [94]. Many researchers working with Au catalysts have noticed that they lose their original activity after a few months or even a few days' exposure in air. Based on current relatively stable catalyst in a reactive stream, a relationship between the propylene epoxidation catalyst performance as a function of the storage time is anticipated. Furthermore, recent progress in the stability of Au catalysts for low temperature CO oxidation [95] may be helpful to some extent in designing and constructing new models for Au catalysts for other reactions.

## Conclusions

The extensive effort on the epoxidation of propylene over the nanogold catalysts in copresence of H<sub>2</sub> and O<sub>2</sub>, as summarized above, has led to an enhanced understanding of the chemical and physical properties of the Au-Ti system, and this has recently provided a definition of catalysts with industrially interesting rates and selectivities for propylene epoxidation.

However, both a higher conversion level to propylene oxide and higher hydrogen efficiency will be needed for the process economics to be profitable. One can say with certainty that synergy between nanogold particles and isolated tetrahedral titanium entities and hydrophobicity of the Ti-based support materials are helpful for the epoxidation. More work is needed to clarify the impact of the size, oxidation state and deposition position of nanogold on the epoxidation of propylene. The use of elements from lanthanides and others near to Ti in the Au catalyst support and the promotional effect of anions for the epoxidation reaction should be noted. Significant achievement based on further gathering insight into Au catalysis might soon enable the basis for an economic commercial process to be defined.

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## About the author



**Caixia Qi**, joined the Institute of Applied Catalysis of the College of Chemistry and Biology at Yantai University, China as a new faculty member in Sept. 2006 after a couple of years stay in Japan and Canada. Her research interests concern heterogeneous catalysis with emphasis in catalysis by gold and in energy conversion.

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