Catalysis Today 147 (2009) 186–195

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of composition and promoters in Au/TS-1 catalysts for direct propylene epoxidation using H_2 and O_2

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ARTICLE INFO

Article history:
Available online 29 October 2008

Keywords:
Au
TS-1
Propylene epoxidation
Alkaline earth metal
Capture efficiency
Promoters
Si/Ti ratio

ABSTRACT

A series of Au/titanium silicalite-1 (TS-1) catalysts with different Si/Ti ratios and promoted with alkali and alkaline earth cations were prepared by deposition–precipitation (DP) and tested for direct propylene epoxidation. It was found that the gold loading and catalytic activity was highly dependent on the pH of the DP synthesis solution and the final composition of the catalyst. Addition of Group 1 metals such as K or Cs had little effect on the gold content, but increased activity, while Group 2 metals such as Mg, Ca, Sr, and Ba increased both the gold content and the catalytic activity. The highest improvement was provided by a Mg promoted catalyst, which at 443 K and 0.1 MPa with a $H_2/O_2/C_3H_6/Ar = 1/1/1/7$ feed mixture gave a propylene oxide (PO) formation rate of 88 gPO h^{-1} $kg_{cat}{}^{-1}$, compared to 57 gPO h^{-1} $kg_{cat}{}^{-1}$ for an unpromoted catalyst, corresponding to a 50% enhancement of activity. Ammonia temperature-programmed desorption (NH_3-TPD) measurements indicated little change in adsorption amount with promotion indicating that the yield increase was not due to the elimination of acidic sites on the catalyst. Instead, the improved catalytic performance was ascribed to increased Au capture efficiency and dispersion by the catalyst. The effect of Si/Ti ratio, pH of synthesis, and the promoter ions on the gold content could be understood from their effect on the surface charge of the support.

1. Introduction

Propylene oxide (PO) is an important chemical intermediate used in the production of polyurethane, polyester resins, and surfactants [1]. PO is currently produced commercially by the chlorohydrin process and several organic hydroperoxide processes [2]. The chlorohydrin process produces a large amount of by-product salts and chlorinated organic compound wastes, and poses disposal and separation problems. The organic hydroperoxide processes produce large quantities of coproducts such as t-butylalcohol and styrene, which pose economic problems when their demand is lower than that of PO.

Although silver catalysts have been used for decades for ethylene epoxidation using molecular oxygen to produce ethylene oxide (EO), these catalysts cannot be used for propylene because the allylic hydrogen atoms in propylene are attacked by surface oxygen species and give rise to total combustion products [3–5].

The discovery by Haruta and coworkers that Au/TiO_2 catalysts with very finely dispersed gold particles could catalyze propylene epoxidation with H_2/O_2 mixtures with very high PO selectivity (>95%) at low propylene conversion (∼1%) [6] has given rise to considerable work in this area, including studies of gold supported on mesoporous titanosilicates [7–10]. However, most of these catalysts suffered from severe deactivation possibly because of PO adsorption or oligomerization on acidic sites. The group of Delgass found that Au supported on a microporous titanium silicalite-1 (TS-1) gave very active, stable catalysts [11–14]. One of their catalysts, a 0.05 wt% Au/TS-1 sample (Si/Ti = 36), gave a propylene conversion of 8.8% and a PO selectivity of 81% at 473 K, corresponding to a PO formation rate of 116 g_{PO} h^{-1} $kg_{cat}{}^{-1}$ [14]. In another study, the same group found that TS-1 pretreated with NH_4NO_3 solution could capture up to fourfold more Au than an untreated sample, which remarkably enhanced the PO formation rate [12]. The same group also prepared TS-1 samples with mesoporous scale defects by introduction of carbon pearl during

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doi:10.1016/j.cattod.2008.09.005

the synthesis procedure and got 132 $g_{PO}\ h^{-1}\ kg_{cat}{}^{-1}$ on a 0.33 wt% Au/TS-1 catalyst, which is the highest PO rate reported with standard reactors [15]. A membrane reactor which could increase the H_2 and O_2 levels to 40% each gave 200 $g_{PO}\ h^{-1}\ kg_{cat}{}^{-1}$ [16]. Another related stable catalyst system is gold supported on the mesoporous titanosilicate TUD [17]. The kinetics on Au/Ti-TUD [18] are similar to those reported on Au/TS-1 [19] indicating that the mechanisms of reaction are similar in both catalysts. It is believed that H_2 and O_2 react on gold to form H_2O_2, which then migrates to a Ti center to carry out the epoxidation reaction [13,17,18]. It has been shown that a hydroperoxide species on the Ti is the active epoxidizing species [20]. Furthermore, density functional theory studies by the group of Thomson on propylene epoxidation on TS-1 [21] and a neutral Au trimer [22] suggested that hydroperoxy (OOH) intermediates on defect Ti sites are more reactive than fully coordinated Ti sites.

It has been found that the best method of preparation of gold catalysts is the deposition–precipitation (DP) method, in which a support is added to a solution containing gold species [13]. However, in this method only a small fraction of Au can be deposited on the support (usually less than 5%), particularly when the neutralizing pH is high, the Ti content of the support is low, or the support is highly hydrophobic such as in the case of TS-1. The Au loading is generally related to the catalytic activity; therefore, an increase in Au loading is desirable for activity, provided the Au particles do not grow appreciably in size above 2–5 nm. In this paper, a series of Au catalysts modified with alkali and alkaline earth metal compounds have been examined, and the findings are explained by the effect of these additives on the isoelectric point (IEP) of the support. The latter also explains the effects of preparation pH and Si/Ti ratio. Results show that the alkali metals do not have a great effect, while alkaline earth metals can enhance the Au capture efficiency, which is beneficial for the activity. However, when the Au loading is too high clusters of gold that are too big form, and these promote the decomposition of H_2O_2 and reduce the formation of PO.

2. Experimental

2.1. Synthesis of titanium silicalite-1

TS-1 supports were synthesized using the method developed by Khomane et al. [23]. For a typical synthesis, 1.63 mmol (2.0 g) of polyoxyethylene 20-sorbitan monolaurate (Tween 20, Aldrich) was added to 24 g of deionized water under vigorous stirring. A quantity of 27 g of tetrapropylammonium hydroxide (TPAOH, TCI, 20–25% solution) and 173 mmol of tetraethylorthosilicate (TEOS, WAKO, 95%) was added under stirring. The clear solution was stirred for 1 h, and then a solution of 5.2 mmol titanium (IV) tetrabutoxide (TBOT, Chameleon Reagent, 99%) dissolved in 20 cm^3 of isopropanol (WAKO, 99.5%) was added drop-wise. The resulting solution was stirred for 1 h, and then was placed in a Teflon autoclave for crystallization at 448 K for 18 h. The solid was collected via centrifugation, and washed thoroughly with deionized water. It was dried in vacuum at room temperature overnight, followed by calcination at 773 K for 5 h. The TS-1 support with a Si/Ti ratio of 35 was labeled as TS-1_35. Other TS-1 supports with different Si/Ti ratios were synthesized in the same manner.

2.2. Preparation of Au/TS-1 catalysts

Au/TS-1 catalysts were prepared using the deposition–precipitation method [24]. A 100 cm^3solution of $HAuCl_4{\cdot}4H_2O$ was heated to 343 K under vigorous stirring. After adjusting the pH of the solution to 7 using 1 M and 0.1 M NaOH solutions, 1 g of TS-1 was added and the suspension was aged at 343 K for 1 h. For promoted Au/TS-1 catalysts, after 10 min of stirring, 1 cm^3 of metal nitrate solution (0.038 M) was added and the whole suspension was stirred for another 50 min. The addition of the metal nitrate did not change the pH of the solution, so no adjustment of pH was needed. The suspension was then cooled to room temperature. The solids were collected via centrifugation, washed with 50 cm^3 of deionized water, centrifuged again, and vacuum dried at room temperature overnight. The resulting solid was not further calcined. Actual Au, Ti, Cl, and promoter contents in the catalysts were determined by inductively coupled plasma (ICP) measurements. In the description of catalysts, a catalyst designated as 0.02 Au/TS-1_170 indicates that the Au loading in the catalyst was 0.02 wt% and that the support was TS-1 with a Si/Ti ratio of 170.

2.3. Characterization of the catalysts

Surface areas of the TS-1 supports were measured in a volumetric adsorption unit (Micromeritics ASAP 2020). X-ray diffraction (XRD) measurements were carried out with a Rigaku 2000 diffractometer operated at 40 kV and 20 mA. The ultraviolet–visible (UV–vis) spectra of the support were collected using a large compartment spectrometer (Varian Cary 5000) equipped with a praying mantis diffuse reflectance attachment (DRP-XXX) without pretreatment, using $BaSO_4$ as the reference. Transmission electron microscopy (TEM) images of the samples were obtained in a microscope (Hitachi H-9000) operated at 300 kV. Particle size distributions were obtained by measuring the diameters of Au particles in a representative region. Ammonia temperature-programmed desorption (NH_3-TPD) measurements were carried out in a chemical adsorption flow unit (BEL-CAT) using a small amount of sample (25–60 mg), which was heated at 573 K for 2 h in He prior to the experiment in order to remove the H_2O in the sample. Desorption gases were monitored by a thermal conductivity detector (TCD). Adsorbed amounts were calculated by comparing desorption peak areas with calibration values from pulses of a known volume. Fourier transform infrared (FTIR) measurements were carried out with a JASCO FT/IR-610 spectrometer provided with an MCT detector. Samples were loaded in an IR cell with KBr windows and provided with KBr rod inserts inside the cell to minimize gas-phase contributions to the spectra. Sample wafers (diameter = 1 cm) were prepared from 15 mg of sample by pressing at about 3 MPa. Spectra were recorded at 4 cm^{-1} resolution and averaged over 100 scans.

2.4. Catalytic testing

Epoxidation of propylene was carried out in a quartz tubular microreactor of 6 mm diameter and 180 mm length equipped with an axial quartz-sheathed thermocouple, and using 0.3 g catalyst of 100–140 mesh size without dilution. The catalyst was heated in a reaction gas mixture ($C_3H_6/H_2/O_2/Ar$ = 1/1/1/7 with flow rates of 3.5/3.5/3.5/24.5 $cm^3\ min^{-1}$, controlled by mass flow meters) from room temperature to reaction temperature in 6 h. Reaction products were analyzed online using two gas chromatographs (Shimazu GC-14) both equipped with a flame ionization detector (FID) and a thermal conductivity detector. One GC had a FFAP capillary column (0.32 mm × 60 m) and a Porapak Q compact column (3 mm × 2 m) and the other had a MS-5A 60/80 compact column (3 mm × 2 m) and a Gaskuropak 54 84/100 compact column (3 mm × 2 m). The FFAP capillary column and Porapak Q were used to detect oxygenates (acetaldehyde, PO, acetone, propionaldehyde, acrolein, acetic acid, and isopropanol) and H_2O and CO_2, respectively, while the MS-5A and Gaskuropak columns were used to detect H_2, O_2, CO, and hydrocarbons (propane, propylene, ethylene, and ethane), respectively. Carbon balances closed to near 100%. The propylene conversion, PO selectivity, H_2 conversion, and H_2 efficiency were defined as follows:

Propylene conversion = moles of (oxygenates + CO_2/3)/moles of propylene in feed.
PO selectivity = moles of PO/moles of (oxygenates + CO_2/3).
H_2 conversion = moles of H_2 converted/moles of H_2 in feed.
H_2 efficiency = moles of PO/moles of H_2O.

3. Results

Table 1 summarizes textural properties of the prepared TS-1 supports. The supports had a surface area of about 400 $m^2\ g^{-1}$.

The structures of the TS-1 supports with different Si/Ti ratios were obtained by XRD. Fig. 1 shows similar patterns consistent with the literature [23], indicating that all the supports are highly crystalline TS-1 with the MFI structure. The incorporation of Ti(IV) into the framework was evidenced by UV–vis spectroscopy (Fig. 2) by absorption peaks at 210 nm. The sample with high Ti content shows a tail in the 320–340 nm region.

Table 2 summarizes the effects of initial Au concentration in the DP solution, neutralizing pH, and TS-1 supports with different Si/Ti ratios on the resulting Au loading in the catalyst and catalytic performance. The first set of entries shows that increasing the gold concentration ($HAuCl_4{\cdot}4H_2O$) in the preparation solution from 0.33 to 5.0 mg cm^{-3} increases the gold loading in the catalyst from 0.005 to 0.23 wt%. The second set of entries shows that decreasing the Si/Ti ratio from 500 to 35 increases the gold loading from 0.009 to 0.10 wt%. The third set of entries shows that decreasing the preparation pH from 10 to 4 increases the gold loading from 0 to 0.07 wt%.

Fig. 3 presents TEM images of the Au/TS-1_170 catalysts with different Au loadings. It is clear that for the catalysts with extremely low Au loading (0.005 and 0.02 wt%), no visible Au particles were observed (Fig. 3a and b). As for the 0.09 Au/TS-1_170 catalyst, there were a few Au particles with 2–5 nm in diameter (Fig. 3c). On the spent 0.09 Au/TS-1_170 sample, slight aggregation of Au particles occurred (Fig. 3d).

The catalytic activity was clearly dependent on the Au loading, Si/Ti ratio, and pH of preparation during the DP process, as shown in Table 2. The main products in this reaction consist of CO_2, H_2O, and C3 compounds such as PO, acetone, propionaldehyde, and acrolein. No C2 compounds were found possibly because the C2 compounds were not formed or were under the detection limits of the analysis system. The catalysts generally have low propylene conversions but high PO selectivities, as is standard for these types of catalysts as well documented in the literature in this area. Although some exceptions occurred at the highest Au contents, generally, higher Au loading gave higher steady-state propylene conversion. For example, in the first set of entries, increasing the gold content in the Au/TS-1_170 catalyst from 0.005 to 0.02 and 0.09 wt% increased propylene conversion from 0.3 to 2.3 and 6.7%. However, a further increase in gold content in the same Au/TS-1_170 series to 0.23 wt% reduced the conversion to 4.7%. In contrast, the PO selectivity uniformly decreased with gold content. Again, for the same series the PO selectivity decreased from 98.4 to 91.9, 78.1 and 75.6%.

The same positive effect of gold loading on conversion was seen in the samples prepared with different Si/Ti ratios and different pH. For the samples with decreasing Si/Ti ratios in the second set of entries, the gold content increased from 0.009 to 0.02 and 0.10 wt% and the propylene conversion increased from 1.2 to 2.3 and 2.4%. The selectivity to PO for these samples again followed an opposite trend, decreasing from 99.6 and 91.9 to 70.2%. For the samples

Table 1
Properties of TS-1 supports with different Si/Ti ratios.

Sample	Ti content (wt%)	BET area ($m^2\ g^{-1}$)
TS-1 (Si/Ti = 35)	2.2	430
TS-1 (Si/Ti = 170)	0.46	390
TS-1 (Si/Ti = 500)	0.16	380

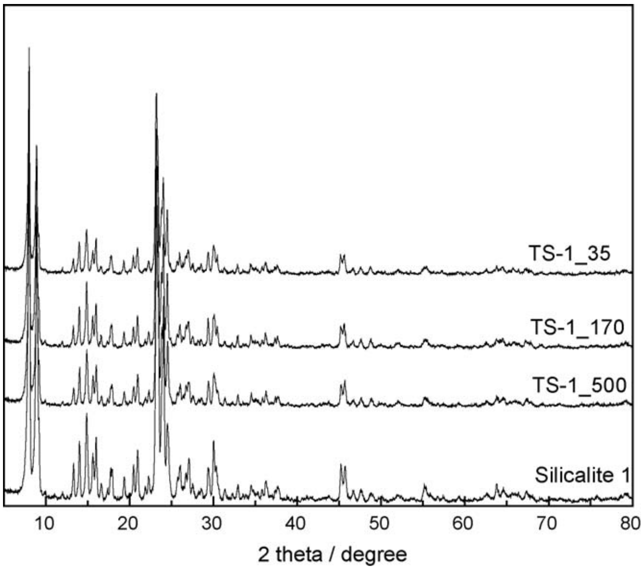

Fig. 1. XRD patterns of TS-1 supports with different Si/Ti ratios.

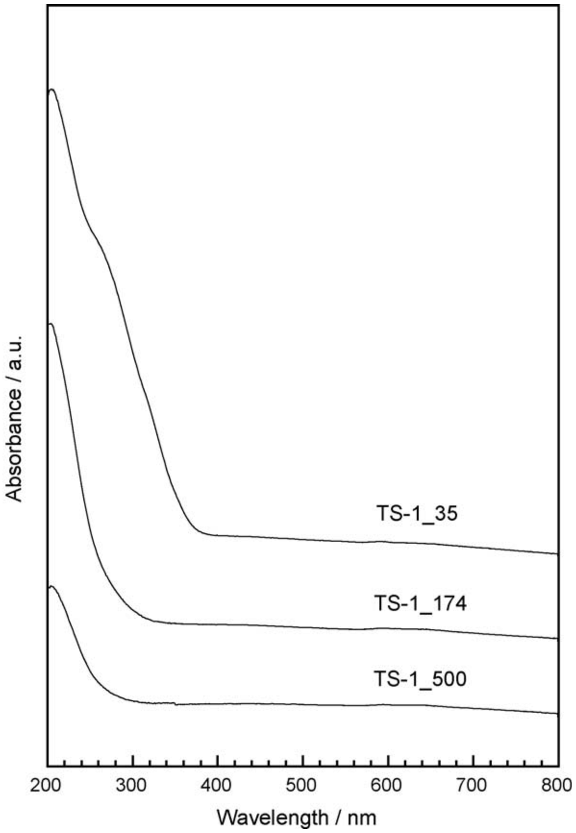

Fig. 2. UV–vis spectra of TS-1 supports with different Si/Ti ratios.

Table 2
Propylene epoxidation over Au/TS-1 catalysts prepared under various conditions.

Catalyst	$HAuCl_4 \cdot 4H_2O$ ($mg\ cm^{-3}$)	Au (wt%)	pH	Conversion (%)		Selectivity (%)						PO formation rate ($gPO\ h^{-1}\ kg_{cat}^{-1}$)
				C_3H_6	H_2	PO	PA	Ac	An	CO_2	H_2	
Effect of $HAuCl_4$ concentration												
0.005 Au/TS-1_170	0.33	0.005	7.0	0.3	0.3	98.4	0	0	0	1.6	>99	4.8
0.02 Au/TS-1_170	1.0	0.02	7.0	2.3	8.7	91.9	0.7	0	0.8	6.6	24.4	38
0.09 Au/TS-1_170	3.0	0.09	7.0	6.7	63.8	78.1	2.6	1.6	2.8	14.9	8.2	95
0.23 Au/TS-1_170	5.0	0.23	7.0	4.7	45.6	75.6	3.2	1.4	2.9	16.9	7.8	63
Effect of Si/Ti ratio												
0.009 Au/TS-1_500	1.0	0.009	7.0	1.2	3.2	99.6	0	0	0	0.4	37.2	22
0.02 Au/TS-1_170	1.0	0.02	7.0	2.3	8.7	91.9	0.7	0	0.8	6.6	24.4	38
0.10 Au/TS-1_35	1.0	0.10	7.0	2.4	23.4	70.2	9.1	2.1	1.2	17.4	7.2	31
Effect of pH												
0Au/TS-1_170	1.0	0	10	0	0	0	0	0	0	0	0	0
0.02 Au/TS-1_170	1.0	0.02	7.0	2.3	8.7	91.9	0.7	0	0.8	6.6	24.4	38
0.07 Au/TS-1_170	1.0	0.07	4.0	1.3	11.9	64.1	16.1	3.5	3.9	12.4	7.0	15

Reaction conditions: $C_3H_6/H_2/O_2/Ar = 3.5/3.5/3.5/24.5\ cm^3\ min^{-1}$, space velocity = 7000 $cm^3\ g_{cat}^{-1}\ h^{-1}$, reaction temperature = 473 K, pressure = 0.1 MPa. PO: propylene oxide; PA: propionaldehyde; Ac: acetone; and An: acrolein.

prepared at decreasing pH in the third set of entries, the gold content increased from 0 to 0.02 and 0.07 wt% and the propylene conversion increased from 0 to 2.3%, although it then declined to 1.3%. The selectivity to PO was zero for the sample with no conversion and was then 91.9 and 64.1%.

Fig. 4 presents the catalytic performance of Au/TS-1 catalysts with different Si/Ti ratios. The catalyst with the highest Si/Ti ratio (TS-1_500) contained the lowest amount of Au (0.009%) and gave the lowest propylene conversion, however, the highest PO selectivity and H_2 efficiency. Furthermore, the catalyst shows the most stable performance. The catalyst with intermediate Si/Ti ratio (TS-1_170) had intermediate Au loading (0.02%) and gave intermediate propylene conversion, PO selectivity, and H_2 efficiency. It should be noted that the catalyst suffered a slight deactivation at the beginning, before reaching steady-state in about 6 h. The catalyst with the lowest Si/Ti ratio (TS-1_35) had the highest Au loading (0.10%) and gave the highest propylene conversion, however, the lowest PO selectivity and H_2 efficiency. The catalyst suffered more severe deactivation as can be seen from the figure, dropping from a moderate propylene conversion (3.3%) initially to a lower level (2.4%) at steady-state after 16 h. For the H_2 selectivity, the 0.009 Au/TS-1_500 gave the highest H_2 selectivity while the 0.10 Au/TS-1_35 gave the lowest.

TEM images of the fresh and spent 0.16 Au/TS-1_120, 0.25 Au-Mg/TS-1_120, and 1.6 Au-Ba/TS-1_120 catalysts were obtained (Supplementary Information). It could be seen that for the 0.16 Au/TS-1_120 and 0.25 Au-Mg/TS-1_120 catalysts, both the fresh and the spent samples gave uniformly dispersed Au particles with mean diameters of 2–5 nm. For the 1.6 Au-Ba/TS-1_120 sample, the Au particles were a little larger, 4–6 nm, and more numerous.

Table 3 summarizes the catalytic performances of the catalysts promoted with various Groups 1 and 2 metal salts. It can be seen that the unpromoted catalyst, 0.16 Au/TS-1_120, contained 0.16% of Au, while the catalysts promoted with Group 1 alkali metals such as K and Cs contained similar or even lower Au loading. For the catalysts promoted with Group 2 alkaline earth metals, the situation was different. With the same moles of Group 2 metal ions in the solution (0.038 mmol), the amount of metal deposited on the catalyst followed the order of increasing metal atomic weight. For the series of alkaline earths the metal loadings (in mmol = mass weight/atomic weight × 1000) increased from 4.2×10^{-3} mmol (1×10^{-4} g) for Mg to 1.70×10^{-2} mmol (7×10^{-4} g) for Ca, 1.75×10^{-2} mmol (1.5×10^{-3} g) for Sr, and 0.026 mmol (3.5×10^{-3} g) for Ba. In parallel with this increase, the Au loading on these catalysts grew from 0.25 wt% for Mg to 0.86 wt% for Ca, 1.0 wt% for Sr, and 1.6 wt% for Ba.

As for the unpromoted catalysts, these samples also generally have low propylene conversions but high PO selectivities. Within this limitation, the reactivities of the promoted catalysts were markedly enhanced (Table 3). For example, at steady-state at 443 K, the unpromoted 0.16 Au/TS-1_120 catalyst gave a propylene conversion of 3.5%, while the K and Cs promoted catalysts gave a conversion of 5.2% each, and the Mg sample gave 5.7%, while at 423 K the Ca, Sr, and Ba promoted samples gave conversions of 6.6, 6.0, and 6.1%, showing enhancements of around 49–88%. Accompanying the increase in propylene conversion, H_2 conversions on the promoted catalysts also increased. The yields of reaction ($gPO\ h^{-1}\ kg_{cat}^{-1}$) tracked the conversions. The turnover frequencies (TOFs) were for PO production based on the gold surface atoms determined from the particle size as obtained from estimates from the X-ray absorption fine structure of the coordination number in the gold. The particle sizes of all the samples were similar, and the TOFs again tracked the conversions and selectivity.

One phenomenon that should be noted is that for the high Au loading samples such as the Ca, Sr, and Ba promoted catalysts, when reaction temperature exceeded 413 K, the H_2 combustion reaction occurred predominantly and a large amount of H_2O was produced. At the same time, by-products such as propionaldehyde, acetone, acrolein, and CO_2 were largely produced, leading to a decline in the PO selectivity. For example, at 413 K the Sr-promoted catalyst 1.0 Au-Sr/Au-TS-1_120 gave 89% PO selectivity and 30.7% H_2 conversion, while at 423 K, the PO selectivity was only 48.4% and the H_2 conversion was 83.7%.

Fig. 5 presents reactivity results for the promoted Au/TS-1. All the catalysts suffered a slight loss of activity in the initial period and reached steady-state after about 6 h. The 0.25 Au-Mg/TS-1_120 catalyst gave the highest initial propylene conversion and its activity decreased about 30% when it reached steady-state. The K and Cs promoted catalysts gave similar propylene conversion and the activity decreased about 20% when they reached steady-state. On the unpromoted catalyst, deactivation was comparable to that of the promoted catalysts given its smaller initial conversion. As for the PO selectivity, the highest PO selectivity was obtained on the unpromoted 0.16 Au/TS-1_120 and the 0.09 Au-Cs/TS-1_120 catalysts, while the 0.25 Au-Mg/TS-1_120 had the lowest PO selectivity.

Fig. 6 presents ammonia temperature-programmed desorption traces for the various promoted catalysts. The different

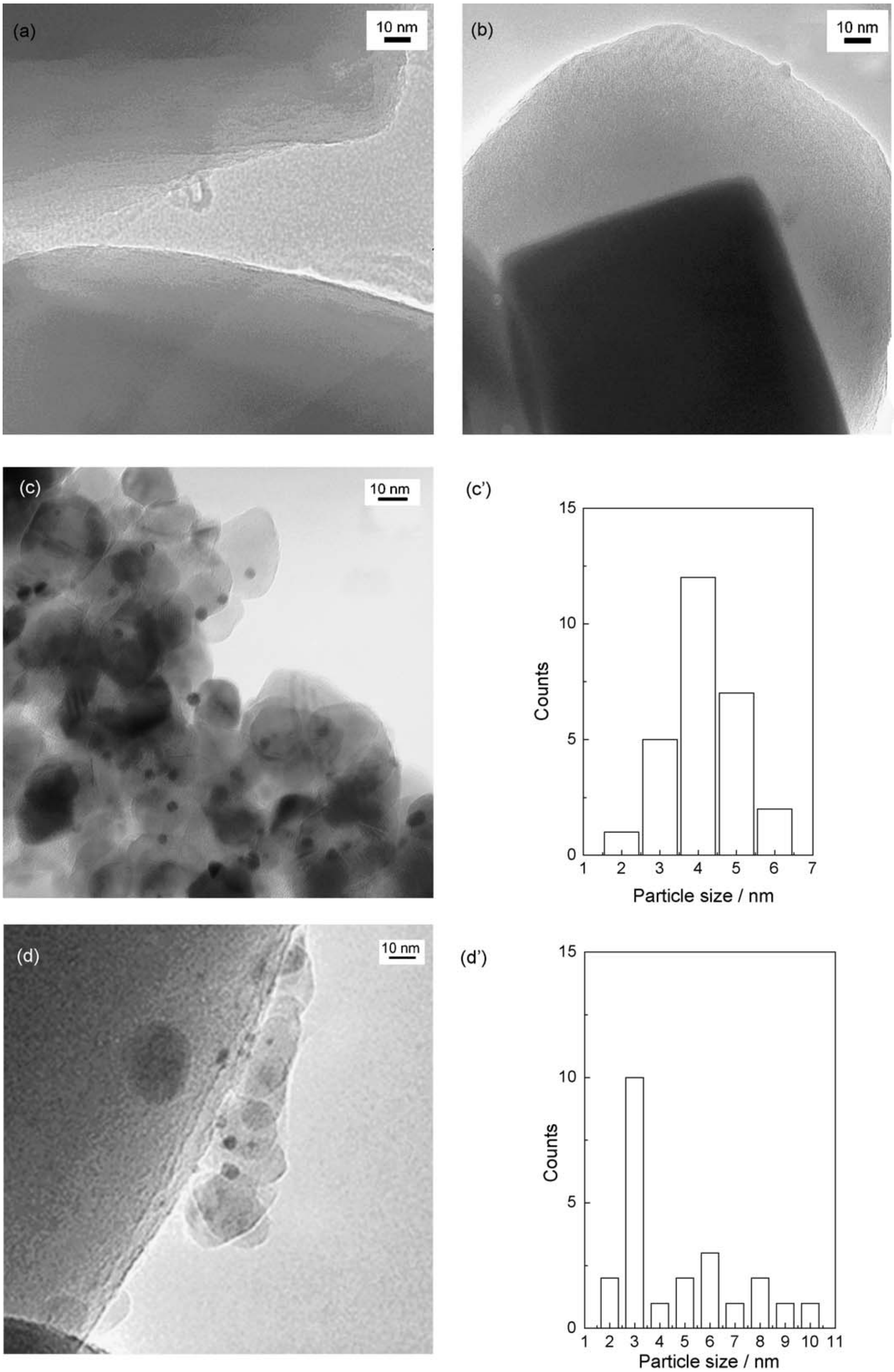

Fig. 3. TEM images and particle distributions of the Au/TS-1 catalysts. (a) 0.005 Au/TS-1_170; (b) 0.02 Au/TS-1_170; (c) 0.09 Au/TS-1_170; (c') particle distribution of the fresh 0.09 Au/TS-1_170; (d) the spent 0.09 Au/TS-1_170; and (d') particle distribution of the spent 0.09 Au/TS-1_170.

samples show similar features, with a maximum in desorption temperature at 418 ± 5 K and a moderate tail at higher temperature. The amounts desorbed were similar and tended to increase slightly with atomic number for the samples with alkaline earth promoters.

Fig. 7 shows FTIR background-subtracted spectra of the fresh and the spent 0.16 Au/TS-1_120 catalyst. The fresh catalyst does not show any bands in the region of C–H stretches, but the spent catalyst shows distinctive bands at 2884, 2939, and 2980 cm^{-1} that are characteristic of an adsorbed bidentate propoxy species [25].

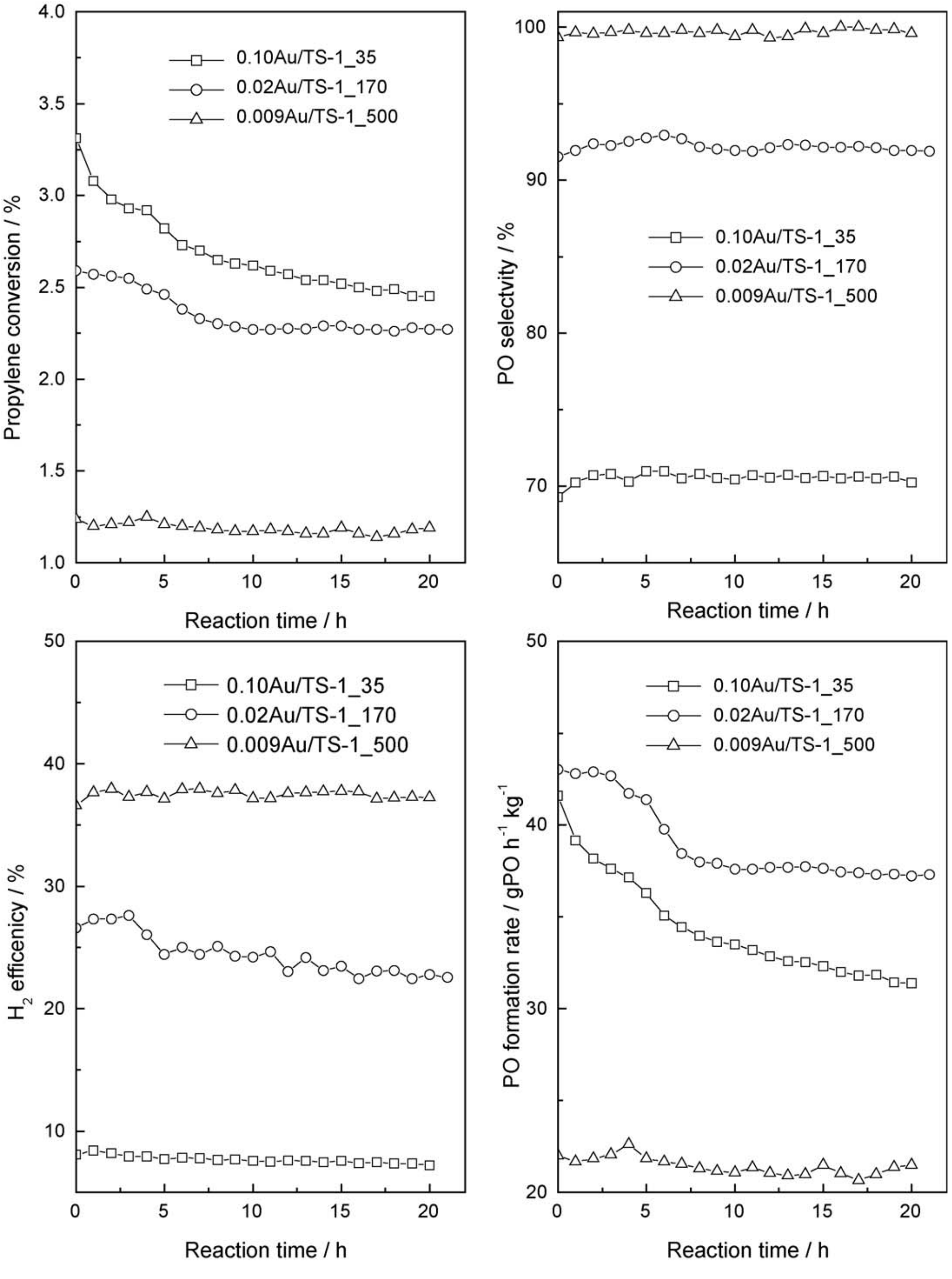

Fig. 4. Propylene epoxidation over different Au catalysts. Reaction conditions: $C_3H_6/H_2/O_2/Ar$ = 3.5/3.5/3.5/24.5 $cm^3\ min^{-1}$, space velocity = 7000 $cm^3\ g_{cat}^{-1}\ h^{-1}$, reaction temperature = 473 K, pressure = 0.1 MPa.

4. Discussion

A series of gold catalysts were prepared by deposition–precipitation on titanium silicalite-1 of different Si/Ti ratios (35, 170, and 500) with surface area of about 400 $m^2\ g^{-1}$ (Table 1) and external particle size of 100–200 nm. The MFI structure of the TS-1 supports was confirmed by XRD (Fig. 1). UV–vis characterization of the supports show that they contain Ti(IV). The strong signal at 210 nm is characteristic of isolated tetrahedral Ti(IV) [26,27]. However, due to the high Ti content in the TS-1_35 sample, a shoulder at around 280 nm was present, which indicated that some of the Ti was in octahedral coordination. Furthermore, a tail in the 320–340 nm region indicated that anatase phase TiO_2 was likely present in the TS-1_35.

The Ti(IV) species in tetrahedral coordination have been indicated to be beneficial for the direct propylene epoxidation with H_2 and O_2 [11]. It is believed that H_2 and O_2 react on the gold or the interface between gold and Ti atoms to form H_2O_2, which then migrates to the tetrahedral Ti sites to form hydroperoxide species responsible for epoxidation of propylene [17,20].

A series of Au/TS-1 catalysts were prepared at various conditions using the deposition–precipitation method. The Au

Table 3
Propylene epoxidation over Au/TS-1 catalysts prepared with different promoters.

Catalyst[a]	Loading (wt%)		Au capture efficiency (%)	D_{Au}[b] (nm)	*T* (K)	Conversion (%)		Selectivity (%)						PO formation rate	
	Au	Metal				C_3H_6	H_2	PO	PA	Ac	An	CO_2	H_2	gPO h^{-1} kg_{cat}^{-1}	TOF (s^{-1})[c]
0.16 Au/TS-1_120	0.16	0	1.1	2.6	413	2.5	14.2	95.0	2.2	0	0	2.8	16.7	43	0.050
					443	3.5	26.1	90.2	1.0	0.9	1.1	6.8	12.1	57	0.066
					473	4.6	46.1	80.1	2.4	1.6	2.6	13.1	8.0	67	0.078
0.15 Au-K/TS-1_120	0.15	0.10	1.0	–	443	5.2	34.8	88.9	1.5	0.9	1.4	6.7	13.3	84	–
0.09 Au-Cs/TS-1_120	0.09	0.11	0.6	3.0	443	5.2	28.4	89.7	1.0	0.6	0.9	5.3	16.4	85	0.20
0.25 Au-Mg/TS-1_120	0.25	0.01	1.7	2.5	413	3.9	31.1	90.9	1.0	1.0	1.1	5.7	11.4	65	0.047
					443	5.7	54.3	85.8	1.9	1.3	1.5	9.2	9.0	88	0.064
0.86 Au-Ca/TS-1_120	0.86	0.07	6.0	2.5	413	3.7	30.7	91.4	0.7	1.5	0.7	5.6	11.0	61	0.013
					423	6.6	89.2	46.6	3.0	4.1	9.0	37.1	3.1	56	0.012
1.0 Au-Sr/TS-1_120	1.0	0.15	7.0	3.3	413	3.9	42.4	89.2	0	1.2	1.1	7.2	8.2	62	0.014
					423	6.0	83.7	48.4	1.9	2.9	8.5	38.1	3.1	53	0.012
1.6 Au-Ba/TS-1_120	1.6	0.35	11.2	2.5	413	2.7	31.6	90.2	1.6	1.3	0	6.5	7.7	44	0.0049
					423	6.1	91.5	38.2	2.6	3.9	1.4	53.9	1.1	42	0.0048

Reaction conditions: $C_3H_6/H_2/O_2/Ar = 3.5/3.5/3.5/24.5$ cm^3 min^{-1}, space velocity = 7000 cm^3 g_{cat}^{-1} h^{-1}, pressure = 0.1 MPa. PO: propylene oxide; PA: propionaldehyde; Ac: acetone; and An: acrolein.

[a] The $HAuCl_4$ $4H_2O$ concentration in the DP solution is 3 mg cm^{-3}.

[b] Determined by EXAFS fitting (Supplementary Information).

[c] TOF = mol_{PO} s^{-1} $mol_{Ausurface}^{-1}$.

loadings increased with lower Si/Ti ratios (Table 2). This is related to the isoelectric point of the support, and has been discussed by Haruta et al. in connection with the preparation of gold catalysts by the DP method [28]. Since the IEP value of the silicious TS-1 support is about 2–3 [29], high pH results in negative charges on the support surface, which repulse the $Au[(OH)_3Cl]^-$ or $Au(OH)_4^-$ anions from the surface of the support, preventing their adsorption. Supports with low Si/Ti ratio (high Ti content) attract more gold than supports with high Si/Ti ratio at the same pH because the IEP of TiO_2 is about 4–5 [29] and produces less negative charge on the surface. Thus, high Ti content leads to higher gold adsorption. Similar effects of the Si/Ti ratio on gold content were found earlier [14], but were unexplained.

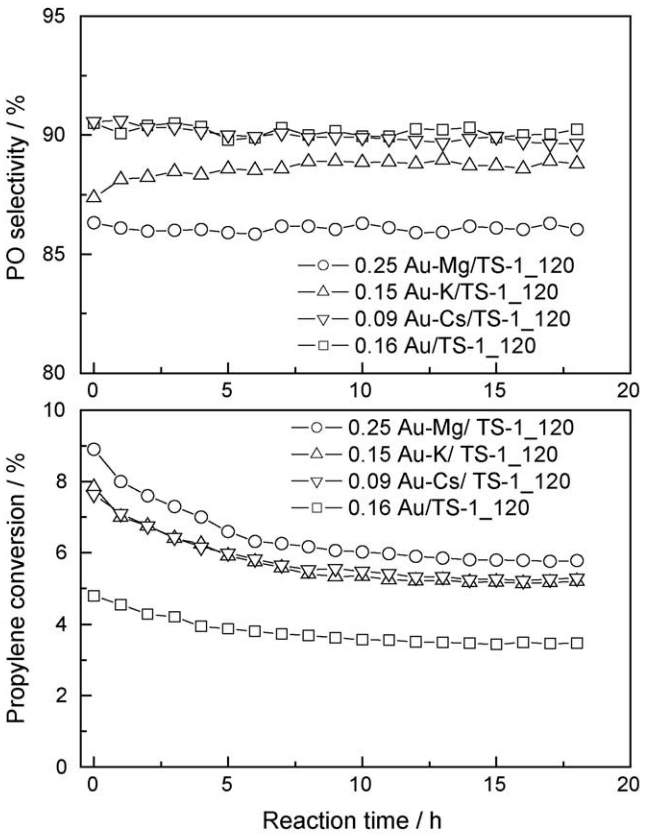

Fig. 5. Propylene epoxidation over various promoted Au/TS-1 catalysts. Reaction conditions: $C_3H_6/H_2/O_2/Ar = 3.5/3.5/3.5/24.5$ cm^3 min^{-1}, space velocity = 7000 cm^3 g_{cat}^{-1} h^{-1}, reaction temperature = 473 K, pressure = 0.1 MPa.

The Au loadings also tracked the preparation pH (Table 2), with lower pH values favoring higher gold deposition on the support. This again can be rationalized from the IEP of the support, as lower pH decreases the negative charge on the surface. However, these results are different from those presented by the group of Delgass and coworkers [11], who reported that the gold loading on their TS-1 support increased with pH. This may be related to the use in the previous study of different samples of TS-1 with a low Si/Ti ratio reported to range from 35 to 48, the use of different amounts of washing solution reported to range from 6 to 18 cm^3 g_{cat}^{-1}, or the use of a different precipitating agent in the DP process ($NaCO_3$ instead of NaOH). In the present study, the synthesis parameters were all carefully controlled so that pH was the only variable.

The 0.005 Au/TS-1_170 and the 0.02 Au/TS-1_170 catalysts show no visible gold particles due to the extremely low gold

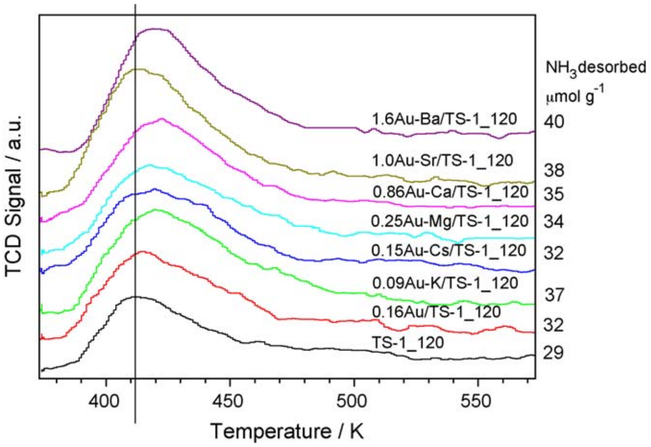

Fig. 6. Ammonia temperature-programmed desorption from various promoted Au/TS-1 catalysts. Pretreatment: 2 h at 573 K in He.

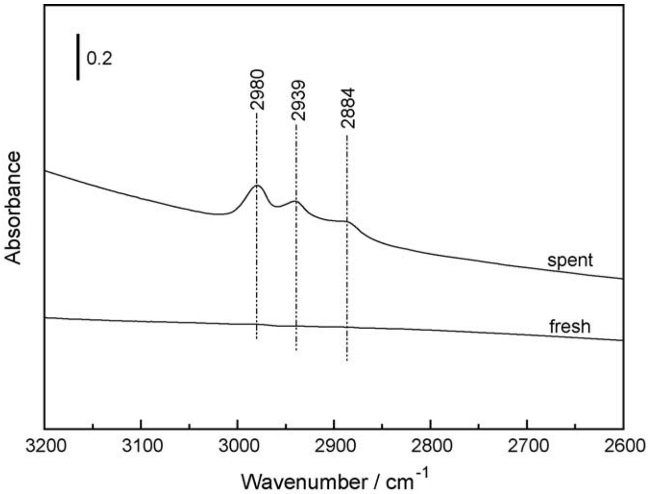

Fig. 7. FTIR spectra of the fresh and the spent 0.16 Au/TS-1_120 catalyst.

loading (Fig. 4). In these samples the gold may form small clusters which reside in the pores of the TS-1 in close proximity to the Ti centers. For the 0.09 Au/TS-1_170 catalyst with relatively high gold content, uniform gold particles with diameter of 2–5 nm were observed. The size of these gold particles precludes their localization inside the TS-1 pores, and they must be found in their outer surface.

The catalytic performance of these Au/TS-1 catalysts differs due to different gold loading, Si/Ti ratio, and pH during the DP process. For the same support TS-1_170, the amount of gold deposited at pH 7 increases with gold concentration in the DP solution, but the activity first increases then decreases with gold loading, indicating that the active catalyst for epoxidation is formed by a fine interplay between the amounts of gold and titanium. At first activity increases because of the larger content of gold, but then decreases because of growth in the particle size. This was noted in the aforementioned study from the group of Delgass and coworkers [11], and also observed for propane oxidation on Au/TiO_2 catalysts [30]. For the catalysts prepared at different pH values, although pH 4 leads to higher gold loading (0.07 Au/TS-1_170) than pH 7 (0.02 Au/TS-1_170), the 0.07 Au/TS-1_170 gave lower propylene conversion and much lower PO selectivity. Another possibility is that at low pH, more chlorine might remain in the catalyst as expected from gold complexes containing chlorine (e.g., $AuCl_4^-$, $AuCl_3(OH)^-$, $AuCl_3(H_2O)$, and $AuCl_2(OH)_2^-$) present in equilibrium at pH 4 [31], which is reported to be detrimental to the epoxidation [6]. In the present study chlorine content was undetected, but traces may have remained.

Stability is an important issue for propylene epoxidation over gold catalysts. For gold supported on TiO_2 [6], Ti-MCM-41 [32], Ti-MCM-48 [33], and Ti containing 3D mesoporous material [8,9], deactivation was often observed. In the Au/TS-1 system, the study from the group of Delgass and coworkers [11] suggested that the deactivation of their 0.52 Au/TS-1_48 catalyst was due to aggregation of the small Au particles. In the present work, diluted Au and Ti systems (0.009 Au/TS-1_500) produce stable and active Au/TS-1 catalysts, while high Au and Ti loading catalysts (0.10 Au/TS-1_35) suffer from deactivation (Fig. 4). The deactivation is probably caused by two factors, one is the aggregation of Au particles; the other is the existence of crystalline TiO_2. The first possibility seems not so substantial since the 0.09 Au/TS-1_170 with similar gold loading did not show obvious aggregation after the reaction, as shown in Fig. 3d. Compared to the catalyst (0.52 Au/TS-1_48) reported by Delgass and coworkers our catalyst contains much less gold, therefore, the propensity of gold aggregation is quite limited. On the other hand, the UV–vis spectrum (Fig. 2) clearly shows the presence of some crystalline TiO_2, which has been associated with deactivation of the catalyst because of the formation of a polymer-like product on the catalyst surface [25]. Therefore, it can be concluded that the deactivation of the 0.10 Au/TS-1_35 is mainly due to the bulk TiO_2. An earlier study suggested that this was associated with Ti connectivity, with greater connectivity producing less stable catalysts [13]. This will be discussed later.

Another interesting result is that in the very dilute Au and Ti system (0.009 Au/TS-1_500), H_2 selectivity is much higher than in the concentrated Au and Ti system (0.10 Au/TS-1_35) (Fig. 4), which is in accordance with the findings in our previous work [17]. We found that a gold catalyst supported on a mesoporous titanium silicate Ti-TUD with high gold loading (2.7 Au-Ba/Ti-TUD (7)) had much higher H_2 conversion and much lower H_2 selectivity than a 0.16 Au-Ba/Ti-TUD (9) catalyst, due to the fact that that there are sites on larger gold particles that carry out hydrogen oxidation to H_2O or hydrogen peroxide decomposition. In the current case, it is very likely that the 0.009 Au/TS-1_500 catalyst contains very small Au particles while the 0.10 Au/TS-1_35 contains large Au particles. One explanation would be that there are more highly coordinated surface gold atoms on the large particles that are not in the periphery (lower coordination atoms) of the particles close to the Ti atoms in the support, while smaller gold particles would have smaller proportions of these nonperiphery Au sites and therefore less propensity to combust hydrogen. This can be observed more clearly in Fig. 8 which shows the atom fraction at corners, edges, and crystal faces in a model gold particle as a function of the particle diameter [34].

Promotion of Au catalysts for enhancement of activity has been previously reported. Haruta and coworkers [8,9] found that addition of $Ba(NO_3)_2$ to the Au supported on 3D mesoporous titanium silicate could enhance the activity and H_2 efficiency, and they attributed this to a reduction in the number of acidic sites on the catalyst. However, in our previous work [17] it was concluded that the positive effect of the addition of $Ba(NO_3)_2$ was not due to the neutralization of acidic sites, as unpromoted and promoted catalysts adsorbed similar amount of NH_3, but was rather a result of higher gold capture by the catalyst. Cumaranatunge and Delgass [12] post-treated the TS-1 support with NH_4NO_3 and found

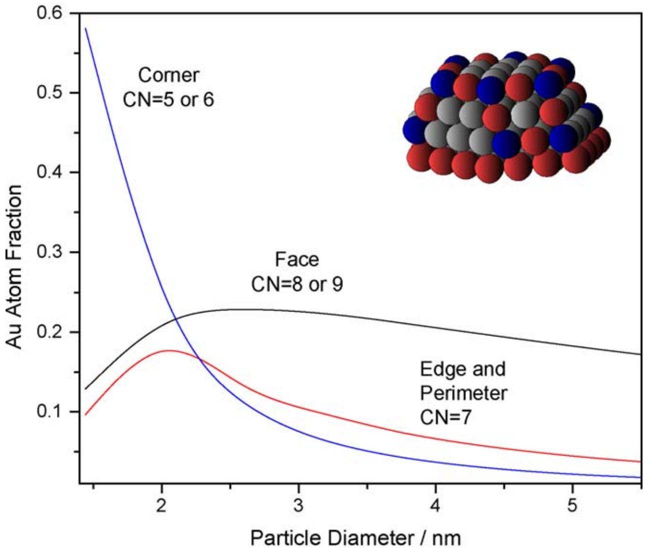

Fig. 8. Fraction of atoms at corners, edges, and crystal faces in a gold particle consisting of the top slice of a truncated octahedron as a function of the particle diameter [34].

that the treated sample could enhance the Au capture efficiency by fourfold compared to the unpromoted sample. They attributed the enhancement to the formation of a Au–amine complex.

In the present work, it was found that addition of Group 1 cations (K, Cs) did not enhance the gold loading, while the addition of Group 2 cations (Mg, Ca, Sr, Ba) did increase the gold loading (Table 3). Although the same number of moles of the Group 2 nitrates was added, the resulting Group 2 metal loadings were different. The gold that was captured by the catalyst tracked the Group 2 metal loading and a possible explanation is presented in Fig. 9. At pH 7, the surface of the TS-1 support should be negative charged, and should thus repulse the Au anions, as shown in Fig. 9a. The addition of Group 1 metal cations (M^+), probably results in M^+ attraction by the surface charge. However, since there is no spare positive charge in the M^+, the effect is that Au anions are not adsorbed on the support surface. With the addition of Group 2 metal cations (M^{2+}), the extra positive charge could attract the Au anions.

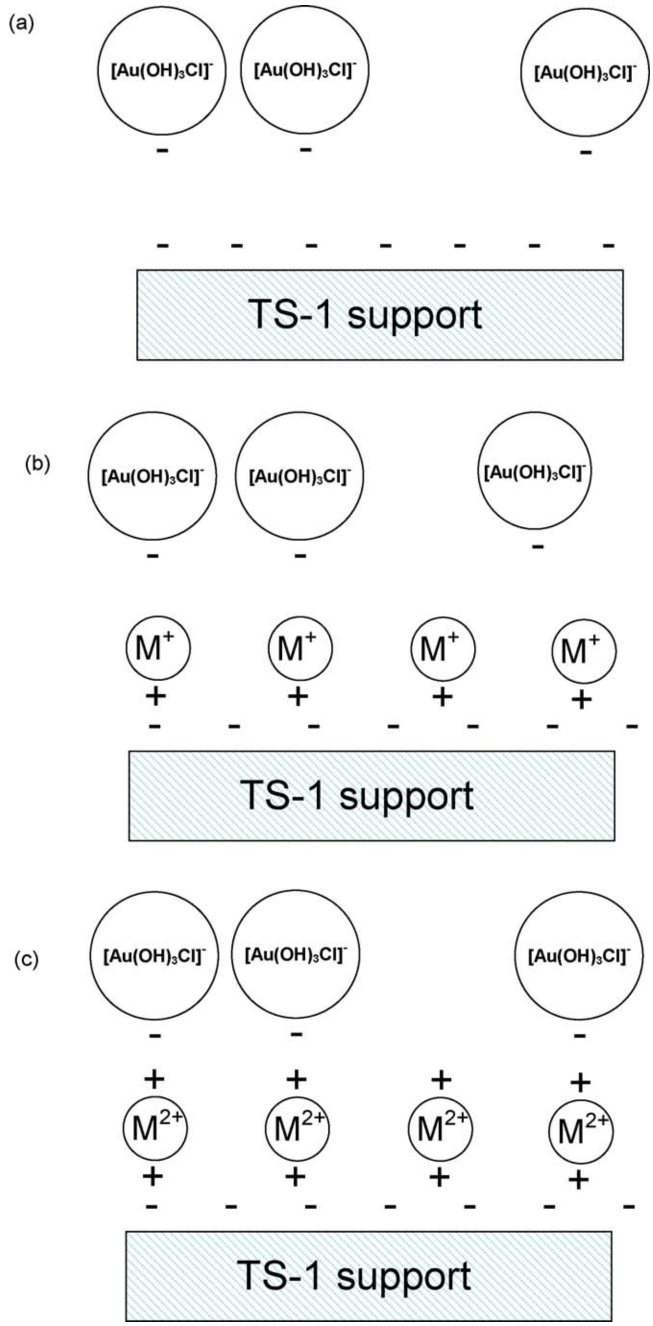

Fig. 9. Possible mechanism of adsorption of Au anion by promoters. (a) Unpromoted Au/TS-1 catalyst; (b) the IA metal promoted Au/TS-1 catalyst; and (c) the IIA metal promoted Au/TS-1 catalyst.

The catalytic activity of these catalysts is strongly dependent on the gold loading, except for the K and Cs promoted catalysts (Table 3). It should be noted that the 0.15 Au-K/TS-1_120 and the 0.09 Au-Cs/TS-1_120 catalysts show higher activity compared to the unpromoted 0.16 Au/TS-1_120 catalyst, with similar or even lower Au loading. Although EXAFS results indicated that the 0.09 Au-Cs/TS-1_120 has similar average Au particle size (3.0 nm) as the unpromoted 0.16 Au/TS-1_120 catalyst (2.6 nm), Yap et al. [11] concluded that in their Au/TS-1 catalysts a part of the gold loading was not accounted for in the Au particles large enough to be observed using TEM, particularly in those with low Au loadings. The situation in the current case could be quite similar, so that the enhancement of catalytic performance is probably due to the better dispersion of Au particles caused by the "uncounted" Au in these promoted catalysts (0.15 Au-K/TS-1_120 and 0.09 Au-Cs/TS-1_120), which results in more active sites, although the average particles size of these catalysts are close. For the Mg, Ca, Sr, and Ba promoted catalysts, generally higher activity was obtained compared to the unpromoted catalyst. However, on these catalysts, H_2 conversion was much higher than for the unpromoted catalyst. It is likely that the high gold loading results in large gold clusters, which consist of periphery atoms (close to Ti centers) and nonperiphery atoms (highly coordinated on-top sites away from the edges). These nonperiphery surface Au atoms, as found in well-developed surfaces, have been suggested to be involved in the decomposition of H_2O_2 [35].

The promoted catalysts showed deactivation during the reaction (Fig. 6). Delgass and coworkers [11] suggested that, the instability of the high gold loading samples was due to the aggregation of small gold particles. A comparison of TEM images of the fresh and spent catalysts (Supplementary Information) surprisingly revealed that even for the highest gold loading sample 1.6 Au-Ba/TS-1, there was no obvious aggregation of the gold particles after reaction. Therefore, there must be another explanation for the catalyst deactivation.

In order to explain the loss in activity, FTIR measurements were carried out to investigate the surface species during the reaction, as shown in Fig. 7. Bands arising at 2980, 2939, and 2880 cm^{-1} are assigned to the C–H stretching vibrations of bidentate propoxy species, which can result from PO adsorption on adjacent Ti sites [25]. Mul et al. [25] studied the propylene epoxidation reaction using $C_3H_6/H_2/O_2/He$ gas mixture and the adsorption of PO on Au/TiO_2 and Au/TiO_2 (1.6 wt%)/SiO_2 catalysts. These authors observed that PO adsorbed irreversibly on both catalysts resulting in the formation of bidentate propoxy moieties similar to those obtained in the present study on the 0.16 Au/TS-1_120 catalyst (Fig. 7). The strong adsorption of the propylene oxide product on adjacent Ti sites to form a bidentate species results in the eventual occupation of the sites responsible for epoxidation [18]. When the Ti sites are isolated, as in the case of the TS-1 samples of low Ti content, this manner of deactivation does not occur. The results here show that the bidentate intermediate and the organic fragments detected by FTIR during the gas-phase epoxidation of propylene on the 0.16 Au/TS-1_120 catalyst tracked with the initial deactivation of the catalyst (Fig. 5).

In summary, the origin of high activity and stability in Au/TS-1 catalysts can be attributed to several factors. First, the preparation of catalysts by the DP method using relatively low pH (close to 7) forms a surface with an isoelectric point that enhances the capture of anionic gold species. Second, promotion by alkaline earth elements assist in the deposition of gold by making the surface less negatively charged. Third, the use of catalysts with high Si/Ti ratios produce isolated Ti centers that do not form bidentate species, yet have sufficient Ti to form hydroperoxide species.

5. Conclusions

In conclusion, a series of Au/TS-1 catalysts were prepared and tested for direct propylene epoxidation. It was found that the gold loading was highly dependent on the preparation conditions such as initial Au concentration in the deposition–precipitation solution, the neutralizing pH, and the Si/Ti ratio of the TS-1 support. Addition of Group 2 metals in the catalyst could promote the activity by enhancing the Au capture efficiency. These variables could be associated with a single property, an optimal charged state of the surface to create conditions to enhance the deposition of anionic gold species during the DP process. Since the Au capture efficiency is generally low for the hydrophobic TS-1 material, the use of alkaline earth promoters opens an opportunity for the preparation of active Au/TS-1 catalysts using very dilute Au DP solutions.

Acknowledgements

The authors are grateful for financial support from the Ministry of Economy, Trade and Industry (METI, Minimum energy chemistry project) and the National Science Foundation (CBET 0651238). J.J.B.-S. and S.T.O. acknowledge financial support from the Japan Society for the Promotion of Science (JSPS) through the postdoctoral fellowship for foreign researcher program (No. P05627) and the invited fellow program. J.Q.L. and X.M.Z. acknowledge financial support from the National Science Foundation of China (Grant No. 20703039). The authors thank K.K. Bando for help with EXAFS analysis of the gold samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2008.09.005.

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