



## Research Note

Enhanced reactivity of direct propylene epoxidation with H<sub>2</sub> and O<sub>2</sub> over Ge-modified Au/TS-1 catalystsTong Liu<sup>a</sup>, Pelin Hacırlıoğlu<sup>b</sup>, S. Ted Oyama<sup>b,\*</sup>, Meng-Fei Luo<sup>a</sup>, Xiao-Rong Pan<sup>a</sup>, Ji-Qing Lu<sup>a,\*</sup><sup>a</sup> Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China<sup>b</sup> Environmental Catalysis and Nanomaterials Laboratory, Department of Chemical Engineering (0211), Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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## ABSTRACT

The epoxidation of propylene with H<sub>2</sub>–O<sub>2</sub> mixtures was studied over a gold catalyst supported on a Ge-modified TS-1 catalyst at 170 °C. Shifts of X-ray diffraction lines to lower angle showed that the Ge was incorporated into the structure of the TS-1. The presence of Ge more than doubled the conversion from 1.6% to 4% while increasing selectivity from 87% to 91%. Density functional theory calculations indicated that the origin of the enhanced activity was a ligand effect of Ge on Ti, which lowered the activation energy for the critical epoxidation step.

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## 1. Introduction

The direct propylene epoxidation to propylene oxide (PO) with H<sub>2</sub> and O<sub>2</sub> over gold catalysts supported on Ti-containing materials has attracted much attention [1] since it was first reported by the group of Haruta in 1998 [2]. Catalysts that have been investigated include gold supported on titania [2,3] and on various titanosilicates, including Ti-MCM-41, Ti-MCM-48, TS-2, and Ti-β [4–9]. However, these catalysts usually give propylene conversion less than 2% and suffer serious deactivation, because of the deposition of products on the catalyst surface. The group of Delgass found that Au supported on a microporous titanium silicalite-1 (TS-1) gave active, stable catalysts [10–13], as did our group for Au on Ti-TUD [14–16].

In order to enhance the reactivity, much attention has been paid on the modification of the support. Sinha et al. [17] prepared a gold catalyst deposited on a silylated three-dimensional mesoporous titanosilicate and found that it gave very high propylene conversion, although it experienced deactivation. Chowdhury et al. [18] found that adding trimethylamine in the reaction stream improved catalyst stability and H<sub>2</sub> efficiency, which they ascribed to the elimination of surface acidic sites. For the TS-1 support, Cumarantunge and Delgass [11] reported that treating TS-1 with NH<sub>4</sub>NO<sub>3</sub> improved the reactivity, probably due to increases in gold content. The same group [19] found further improvements in rate by intro-

ducing mesoporous scale defects through the addition of carbon pearls during the TS-1 synthesis. Lu et al. [20] found that a Mg-promoted catalyst gave a 50% enhancement of activity, due to increased Au capture efficiency and dispersion.

Theoretical calculations suggest that defects in TS-1 play an important role in the reactivity of propylene epoxidation. Wells et al. [21] carried out a density functional theory (DFT) study of hydroperoxy (OOH) intermediates and found that Ti sites located adjacent to Si vacancies in the TS-1 lattice are more reactive than fully coordinated Ti sites, which were inactive.

All the above-mentioned findings suggest that improvements of the Au catalyst for propylene epoxidation may lie in the modification of the support. The current work was inspired by the findings of Oldroyd et al. who modified MCM-41 materials with Ge(IV) species prior to the grafting of tetracoordinated Ti(IV) and found that the resulting catalyst was more active for cyclohexene epoxidation with H<sub>2</sub>O<sub>2</sub> compared to unmodified Ti-MCM-41 [22]. In this work, we demonstrate that modification of TS-1 by Ge(IV) species, gives enhanced reactivity for propylene epoxidation with H<sub>2</sub> and O<sub>2</sub>. A possible role of Ge is discussed, based on the theoretical calculation results.

## 2. Experimental

## 2.1. Synthesis of TS-1 and Ge-modified TS-1

For a typical synthesis of TS-1, 173 mmol of tetraethylorthosilicate (TEOS, 98%) was added to an aqueous solution of HCl

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(0.05 M), then a solution of 1.7 mmol of titanium (IV) tetrabutoxide (TBOT, 99%) dissolved in 20 cm<sup>3</sup> of isopropanol (99.5%) was added dropwise. After stirring for 15 min, 8 g of tetrapropylammonium hydroxide (TPAOH, 20% solution) was added dropwise to form a transparent gel, which was aged for 2 h at room temperature (RT), dried at 100 °C overnight, and finely ground. A quantity of TPAOH two times the weight of the solid was added and the mixture was crystallized in a Teflon autoclave at 448 K for 24 h. The solid was collected via centrifugation, washed thoroughly with deionized water, dried in vacuum at RT, and calcined at 773 K for 5 h (ramp of 3 °C min<sup>-1</sup>).

The Ge-modified TS-1 was synthesized in a similar manner, except that the addition of TBOT in the TS-1 synthesis was replaced by the addition of a mixture of TBOT and tetra-*n*-butylgermanium. For the nomenclature a sample designated as 0.02Ge-TS-1(100) indicates a molar ratio of Ge/Ti of 0.02 and of Si/Ti of 100.

## 2.2. Preparation of supported Au catalysts

Supported Au catalysts were prepared using the deposition-precipitation method. A 100 cm<sup>3</sup> solution of HAuCl<sub>4</sub> · 4H<sub>2</sub>O (2 mg cm<sup>-3</sup>) was heated to 343 K under vigorous stirring. After adjusting the pH of the solution to 7 using a 0.1 M NaOH solution, 1 g of support (TS-1 or Ge-TS-1) was added, and the suspension was aged at 343 K for 1 h. After cooling to RT, the solids were collected via centrifugation, washed with 50 cm<sup>3</sup> of deionized water, centrifuged again, and vacuum dried at RT overnight. The resulting solid was not calcined further. Actual Au, Ti, and Ge contents in the catalysts were determined by inductively coupled plasma (ICP) measurements. In the description of the catalysts, a catalyst designated as 0.22Au/0.02Ge-TS-1(100) indicates that the Au loading in the catalyst was 0.22 wt% and that the support was TS-1 with a Si/Ti ratio of 170 and a Ge/Ti ratio of 0.02.

## 2.3. Characterization and theoretical calculations

BET areas were obtained on a Quantachrome Autosorb-1 apparatus. X-ray diffraction (XRD) measurements were carried out with a PANalytical X'Pert PRO powder diffractometer using Cu K $\alpha$  radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images were obtained on a JEM2010 microscope (200 kV). The geometries of the compounds were obtained by energy minimization of the structures using a DFT method in Gaussian 98. The optimizations were conducted using the Becke3lyp hybrid functional with a 6-311G (2d, *p*)-polarized basis set.

## 2.4. Catalytic testing

Epoxidation of propylene was carried out in a quartz tubular microreactor of 8 mm diameter and 180 mm length equipped with an axial quartz-sheathed thermocouple, using 0.3 g catalyst of 100–140 mesh size without dilution. The catalyst was heated in a reaction gas mixture (C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> = 1/1/1/7 with flow rates of 3.5/3.5/3.5/24.5 cm<sup>3</sup> min<sup>-1</sup>, controlled by mass flow meters) from RT to reaction temperature in 6 h. The products were analyzed online using a gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector and a thermal conductivity detector, attached, respectively, to a FFAP capillary column (0.32 mm × 60 m) and a Porapak Q compact column (3 mm × 3 m). The FFAP and Porapak Q were used to detect oxygenates (acetaldehyde, PO, acetone, propionaldehyde, acrolein, acetic acid, and isopropanol) and H<sub>2</sub>O and CO<sub>2</sub>, respectively. The following definitions were used.

Propylene conversion = moles of (oxygenates + CO<sub>2</sub>/3)/moles of propylene in feed.

PO selectivity = moles of PO/moles of (oxygenates + CO<sub>2</sub>/3).

## 3. Results and discussion

The XRD patterns show the structure of the TS-1 support [23], which is almost unperturbed with Ge substitution or gold loading (Fig. 1a). Close examination shows that there is a small trend for decreasing angle with Ge content (Fig. 1b). This corresponds to an increase of unit cell size, which is consistent with the larger size of Ge over Si and indicates incorporation of Ge in the TS-1 structure. The TEM characterization shows that the Au particles are similar in size and distribution in all samples (Fig. 2). The sizes range from 2 to 4 nm, a range expected to give good selectivity to PO [15].

The PO activity of the various Au catalysts was obtained at steady state, after 5 h reaction (Table 1). The 0.13Au/TS-1(100) catalyst gives a propylene conversion of 1.6% and a PO selectivity of 87%, which are comparable to the results in the literature [20]. The Ge-modified TS-1 supports give higher conversions. The most reactive catalyst, 0.14Au/0.04Ge-TS-1(100), gave a propylene conversion of 4.0% and a PO selectivity of 91%, corresponding to a PO formation rate of 66 g<sub>PO</sub> h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>. This is a greater than 2-fold enhancement compared to the unmodified 0.13Au/TS-1(100) catalyst (25 g<sub>PO</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). The turnover frequency (TOF) based on Ti was 0.76 × 10<sup>-3</sup> s<sup>-1</sup> for the 0.13Au/TS-1(100) catalyst which is slightly lower than 1.17 × 10<sup>-3</sup> s<sup>-1</sup> for a 0.52Au/TS-1 catalyst<sub>48-162</sub> reported by Yap et al. [10] at similar reaction conditions, but higher

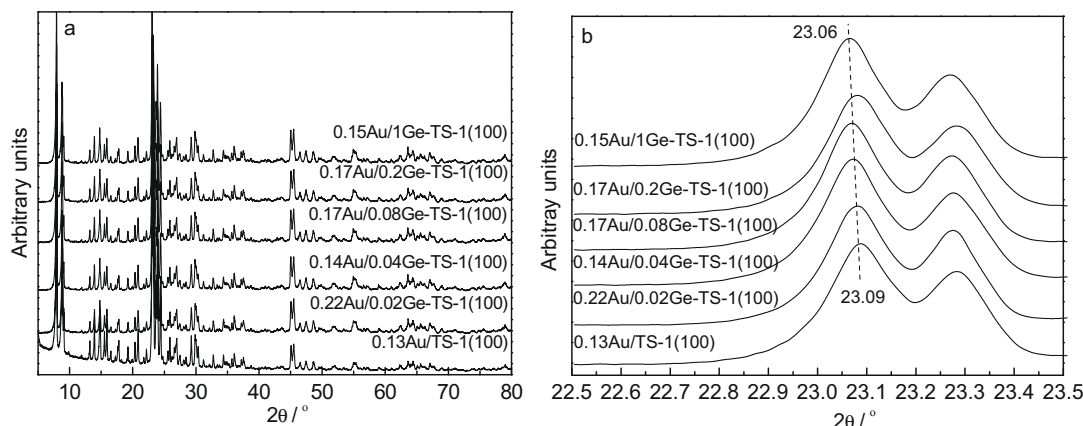


Fig. 1. XRD patterns of various Au/TS-1(100) catalysts.

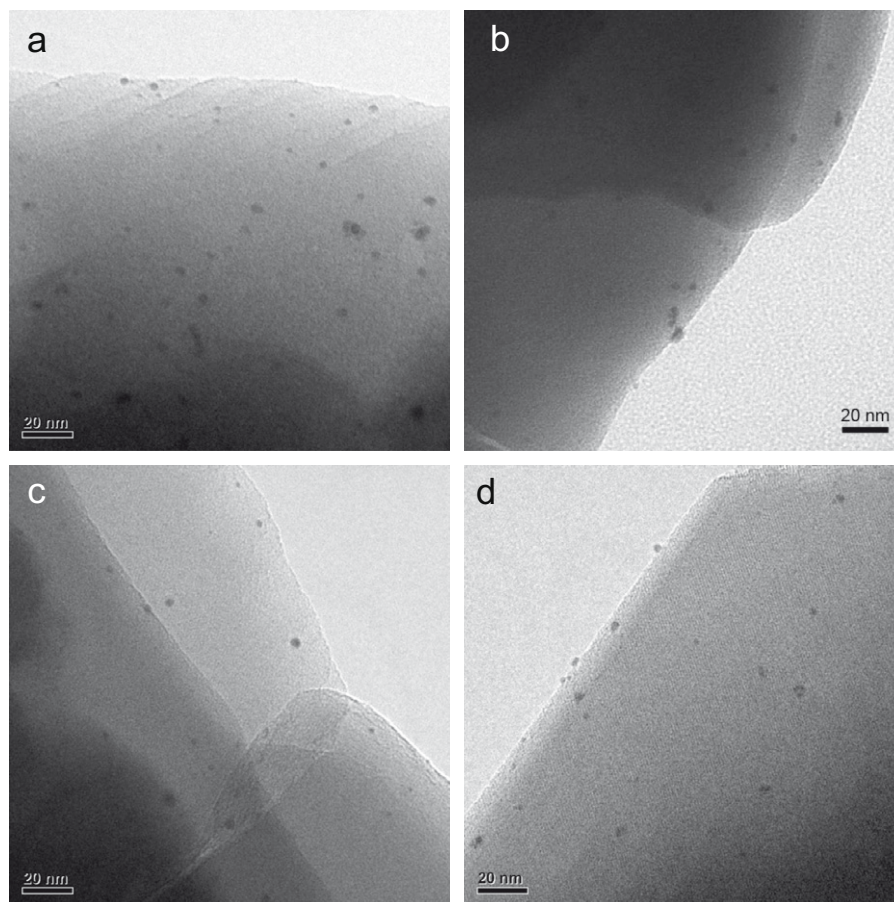


Fig. 2. TEM images of (a) 0.13Au/TS-1(100), (b) 0.14Au/0.04Ge-TS-1(100), (c) 0.17Au/0.08Ge-TS-1(100), and (d) 0.17Au/0.2Ge-TS-1(100).

**Table 1**  
Epoxidation of propylene on various Au/TS-1(100) catalysts.

Catalyst	$X_{C_3H_6}/\%$	$S_{PO}/\%$	PO formation rate/ $g_{PO} h^{-1} kg_{cat}^{-1}$	Turnover frequency ( $\times 10^{-3} s^{-1}$ ) <sup>a</sup>
0.13Au/TS-1(100)	1.6	87	25	0.76
0.22Au/0.02Ge-TS-1(100)	2.7	91	45	1.3
0.14Au/0.04Ge-TS-1(100)	4.0	91	66	2.0
0.17Au/0.08Ge-TS-1(100)	3.1	90	51	1.5
0.17Au/0.2Ge-TS-1(100)	3.0	89	48	1.5
0.15Au/1Ge-TS-1(100)	2.8	90	46	1.4

Reaction conditions: 170 °C, 0.1 MPa,  $C_3H_6$ :  $O_2$ :  $H_2$ :  $N_2 = 1:1:1:7$  ( $35 cm^3 min^{-1}$ ),  $GHSV = 7000 cm^3 h^{-1} g_{cat}^{-1}$ .

<sup>a</sup> Calculated based on Ti sites in the catalyst ( $160 \mu mol g_{cat}^{-1}$ ).

than  $0.25 \times 10^{-3} s^{-1}$  over a Au–Ba/Ti–TUD catalyst reported by Bravo-Suárez et al. [24]. The higher TOF obtained on the 0.13Au/TS-1(100) catalyst compared to that on the Au–Ba/Ti–TUD catalyst indicates that the Ti site in the MFI framework of TS-1 is more active than that in the three-dimensional mesoporous Ti–TUD, probably due to a different coordination environment of Ti in the  $SiO_2$  matrix. For the Ge-modified catalysts, the TOFs are all higher compared to that of the 0.13Au/TS-1(100) catalyst, among which the highest TOF of  $2.0 \times 10^{-3} s^{-1}$  is obtained on the 0.14Au/0.04Ge-

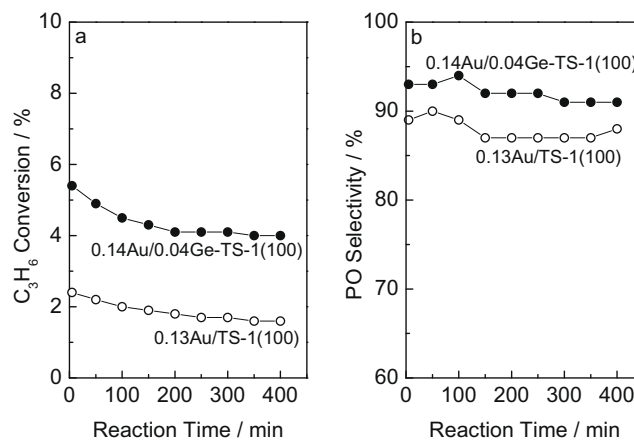
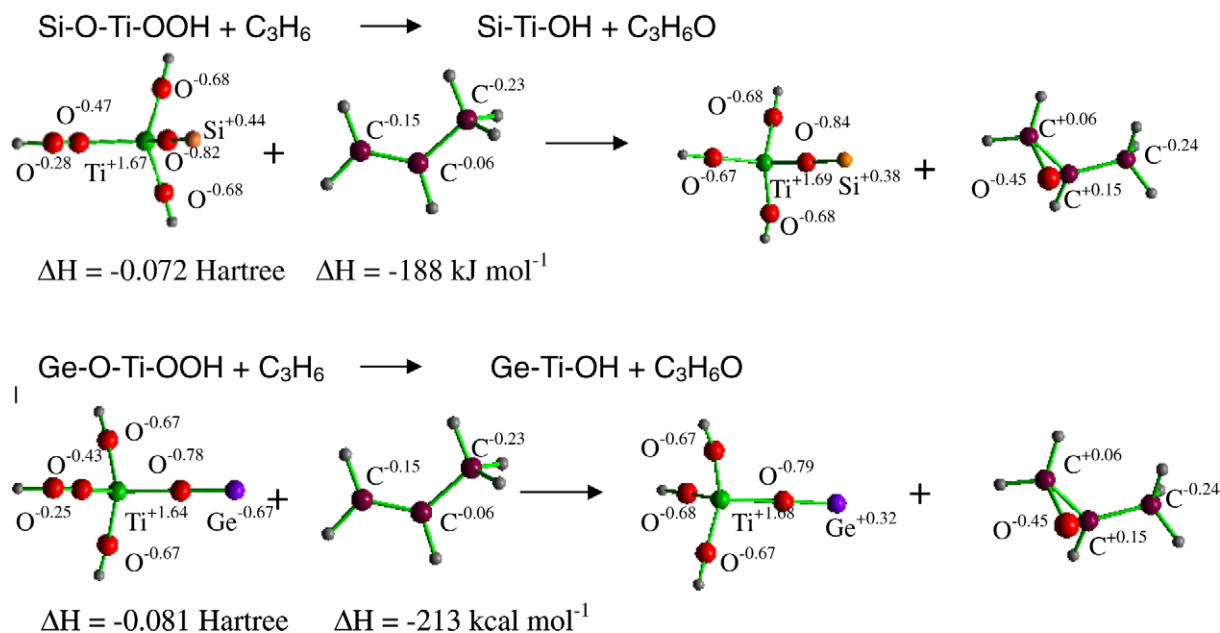


Fig. 3. Epoxidation of propylene on 0.13Au/TS-1(100) and 0.14Au/0.04Ge-TS-1(100) catalysts with time on stream. Reaction conditions: 170 °C, 0.1 MPa,  $C_3H_6$ :  $O_2$ :  $H_2$ :  $N_2 = 1:1:1:7$  ( $35 cm^3 min^{-1}$ ),  $GHSV = 7000 cm^3 h^{-1} g_{cat}^{-1}$ .

TS-1(100) catalyst. This demonstrates that the introduction of Ge into the TS-1 increases the reactivity of the catalyst. Activation energies of the 0.13Au/TS-1 and 0.14Au/0.04Ge-TS-1 catalysts were 31 and 24 kJ/mol, respectively. The activation energy of the 0.13Au/TS-1 catalyst is close to that previously reported [14,25]. The lower activation energy of the 0.14Au/0.04Ge-TS-1 catalyst compared to that of the 0.13Au/TS-1 catalyst implies that the enhancement of reactivity by Ge is due to an electronic promotion of the Ti center (ligand effect).



**Fig. 4.** Energetics of the Epoxidation Reaction for Ge- and Si-substituted Ti. (Red = Oxygen, Green = Titanium, Grey = Hydrogen, Purple = Germanium, Orange = Silicon, Brown = Carbon) Atomic charges in units of  $e = 1.602 \times 10^{-19}$  Coulomb are indicated. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

In order to investigate the stability of the Au/TS-1 catalyst, the reactivity as a function of reaction time was carried out on the 0.13Au/TS-1(100) catalyst and the 0.14Au/0.04Ge-TS-1(100) catalyst (Fig. 3). For the 0.13Au/TS-1(100) catalyst, the initial propylene conversion is 2.5%, and declines to 1.7% at the steady state, while for the 0.14Au/0.04Ge-TS-1(100) catalyst, the propylene conversion starts at 5.5%, and falls to 4.0% at the steady state. The PO selectivities on both catalysts remain unchanged during the reaction, with the 0.14Au/0.04Ge-TS-1(100) catalyst having a slightly higher PO selectivity (91–93%) than the 0.13Au/TS-1(100) (87–90%) catalyst. Deactivation of supported Au catalysts is frequently observed, due to the deposition of products on the catalyst surface, which may be polymeric species or bidentate propoxy species [26]. In our case the deactivation is slight, and this is because the Ti sites are isolated.

The epoxidation of propylene over gold-titanosilicate catalysts is believed to occur in several steps. First, oxygen interacts with metallic gold particles to form adsorbed oxygen species. These have been observed by electron paramagnetic resonance studies [18]. Then, in steps resembling those involved in the combustion reaction, hydrogen reacts with the adsorbed oxygen to form hydrogen peroxide [27]. The  $\text{H}_2\text{O}_2$  migrates to neighboring Ti-OH sites to form a hydroperoxide (TiOOH) species, which interacts with propylene to form a complex which then rearranges to form propylene oxide by a simple shift of the bonds [24]. Desorption of propylene and adsorbed water regenerate the active site. The TiOOH was shown to be a true reactive intermediate by in situ X-ray absorption near-edge spectroscopy measurements taken in a transient mode, which showed that it reacted at the same rate as the overall TOF [24]. Recent work shows that propylene can also adsorb on the gold [28]. This decreases the overall formation of hydrogen peroxide but should have no other effect on the reaction, as PO formation is likely to be the rate-determining step.

In order to derive insight on the enhanced reactivity of the Ge system over the Si system, theoretical calculations using DFT were carried out. To model the system the simplest structure, a tetrahedral Ti unit terminated by OH groups, was used. The unit was modified by the addition of a hydroperoxide group (OOH) and an

attached Si-O or Ge-O moiety (each in turn terminated by OH groups). The overall structure was Si-O-Ti(OOH)(OH)<sub>2</sub> or Ge-O-Ti(OOH)(OH)<sub>2</sub>. Since the epoxidation step is believed to be the rate-determining step of the process [24], the energetics of this reaction were studied (4). The results show that the heat of reaction for the Si complex was  $-188 \text{ kJ mol}^{-1}$ , while that for the Ge complex was  $-213 \text{ kJ mol}^{-1}$ . Although, a full transition state analysis of the reaction pathway is beyond the scope of this work, the activation energy trend can be deduced from the Polanyi-Horiuti relation ( $\Delta E = E^0 - \alpha|\Delta H|$ ), where  $E^0$  is a parameter and  $\alpha$  is a transfer coefficient ( $0 < \alpha < 1$ ). The greater exothermicity of the Ge reaction indicates that the activation energy will be lower, resulting in higher rates, as observed. The role of the Ge then is to improve the energetics of the system. This is likely due to modification of the electronic properties of the Ti centers by the attached Ge groups (ligand effect). A Mulliken population analysis shows that the Ti with Ge is slightly more negatively charged than the Ti with Si. In turn the proximal oxygen, which is the peroxide oxygen next to Ti that is transferred to propylene [1], is slightly more positively charged in the Ge complex ( $-0.43$ ) vs. the Si complex ( $-0.47$ ), and this likely facilitates its transfer to the double bond.

In a broader context, other elements can be envisaged to modify the TS-1 composition and affect the reactivity of the Ti component. From the results here more electron-donating elements are probably desirable.

#### 4. Conclusions

- The X-ray diffraction lines of a TS-1 support modified by Ge showed shifts to lower angle indicating incorporation of the element in the TS-1 structure.
- The TS-1 support modified with Ge gave higher conversions than the Si analog for the gold-catalyzed epoxidation of propylene with  $\text{H}_2\text{-O}_2$  mixtures.
- The origin of the activity increase is likely due to a ligand effect of the Ge on the Ti center which results in a lower activation energy of reaction.

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