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Gas-phase radical generation by Ti oxide clusters supported on silica: application to the direct epoxidation of propylene to propylene oxide using molecular oxygen as an oxidant

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A new catalytic system consisting of titanium oxide clusters supported on silica was found for radical production at relatively low temperature (~573 K). The clusters give rise to selective oxidation products, such as propylene oxide, through gas-phase chain reactions.

KEY WORDS: selective oxidation; propene oxide (PO); radical generation; titanium oxide; XAFS; UV-visible.

1. Introduction

There are only a few examples in the literature dealing with surface-initiate gas-phase reaction. The best known case is that of methane coupling with basic catalysts such as Li(MgO) or Sm_2O_3, which proceeds by the reaction of methane with surface centers to produce methyl radicals [1]. The methane activation step is slow and requires high temperatures (>873 K), therefore the productivity and selectivity of the reaction are limited, and the process has not been commercialized.

This paper presents results with a new system which produces radicals at relatively low temperatures (~573 K) from only propylene and oxygen, and gives rise to selective oxidation products through gas-phase chain reactions without deactivation for the tested period (>500 min). The system consists of Ti clusters supported on silica, and is applied to the oxidation of propylene. Contrary to expectations, the main product is propylene oxide (PO) rather than the allylic oxidation product acrolein. Because the conditions are mild, good selectivities to partial oxidation products are obtained.

Propylene oxide is an important commodity product [2] currently manufactured by several indirect methods, such as the chlorohydrin process, which uses Cl_2 and H_2O, or variations of the Halcon process, which use organic hydroperoxides. Compared with the indirect methods, a process for direct epoxidation ($C_3H_6 + 1/2O_2 = PO$) would be simpler and less expensive and there have been considerable efforts in the development of new catalysts for this reaction [3–8].

2. Experimental section

The Ti-oxide catalysts were prepared by wet impregnation of a silica support (Cariact Q-30, 120 $m^2\ g^{-1}$, Fuji Silisia Chemical Ltd.) with a Ti dimer precursor complex ($(NH_4)_8[Ti_2(C_6H_4O_7)_2(O_2)_2]_2 \cdot 8H_2O$, Furuuchi Chemical). Comparison was made to a Ti monomer catalyst prepared using a Ti iso-propoxide monomer precursor [6,7]. Following impregnation, catalysts were vacuum dried at 343–353 K and calcined at 873 K. The catalytic reactions were carried out in a stainless steel down-flow reactor with an inner quartz liner at 3.5 atm and 568–573 K with a feed consisting of $C_3H6/O_2 = 10/10$ (mL min^{-1}) (table 1) or $He/C_3H_6/O_2 = 5/5/10$ (mL min^{-1}) (figure 1). The reactor had a volume section (25 mL) following the catalyst bed that could be empty or could be filled with quartz chips. The X-ray absorption fine structure spectra (XANES and EXAFS) were obtained by the fluorescence method at the BL-7C beam line of the Photon Factory (High Energy Accelerator Research Organization, Ibaraki, Japan). The spectra were analyzed with REX 2000 (Rigaku, Tokyo, Japan) software (fitting range, 4–11 $Å^{-1}$, R-range, 0.98–3.38 Å. The backscattering amplitude and phase shift functions were estimated by using the spectrum of anatase-type TiO_2 as a standard material). A sample of the dimer precursor was also calcined at 873 K to form a reference sample.

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Table 1
Initial activities of TiO_2/SiO_2 catalysts

No.	Catalyst	C_3H_6 Conv. (%)	Select (%)			
			PO	AA	CO_x	Other
1	TiO^{a}_2 (2.0%)/SiO_2	9.2	35	20	39	5.9
2	TiO^{b}_2 (2.0%)/SiO_2	4.4	27	23	43	7.5
3	TiO^{a}_2 (6.7%)/SiO_2	11	28	19	45	7.9
4	TiO^{a}_2 (15%)/SiO_2	22	21	12	63	5.2
5	TiO^{c}_2	2.2	22	19	56	3.4
6	SiO_2	0.2	36	42	20	2.8
7	TiO^{d}_2 (2.0%)/SiO_2	1.9	1.6	18	50	30

$T = 568$ K; $P = 3.5$ atm; Feed gas C_3H_6: 10 mL min^{-1}, O_2: 10 mL min^{-1}.
Catalyst weight, 1.0 g + quartz sand 3.0 g, 25–60 min.
$T = 573$ K. AA = Acetaldehyde, CO_x = CO, CO_2.
[a] prepared from Ti_2 complex.
[b] prepared from Ti(iso-PrO)$_4$.
[c] decomposed unsupported Ti_2 complex.
[d] post-catalytic-bed volume of the reactor filled with quartz sand.

In situ UV-vis diffuse reflectance spectra were collected using a Cary 5000 Varian spectrometer equipped with a Harrick Scientific reaction chamber (Model HVC-DRP) in conjunction with the praying mantis diffuse reflectance attachment (DRP-XXX). Catalysts and reference (SiO_2 Q-30) spectra were recorded under the same pretreatment and reaction conditions (different gases, temperatures and 0.35 MPa of total pressure) over the range 200–800 nm. Spectra are collected after treatment of the samples under He at 298 K, 0.35 MPa and 30 min, O_2/He at 573 K, 0.35 MPa and 15 min, C_3H_6/He at 573 K, 0.35 MPa and 15 min, C_3H_6/O_2/He at 573 K, 0.35 MPa and 60 min, and He at 298 K, 0.35 MPa and 30 min. Diffuse reflectance spectra were analyzed using the Kubelka–Munk function, $F(R_\alpha)$, calculated from absorbance data.

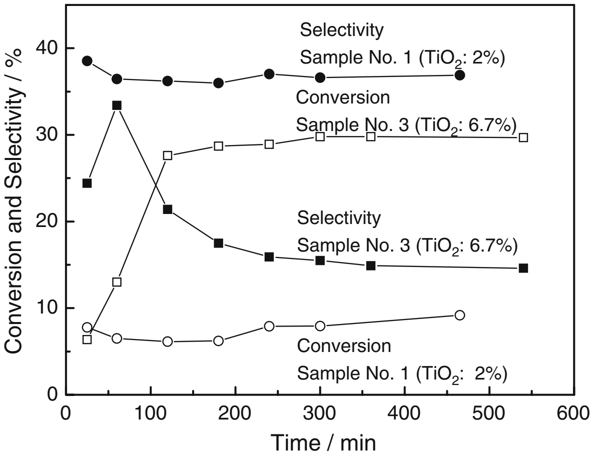


Figure 1. Time course of PO formation using TiO_2/SiO_2 catalysts.

3. Results and discussion

Two types of TiO_2/SiO_2 catalysts of different structure are compared in this study. One was prepared from a dimer precursor and according to EXAFS analysis retained Ti–Ti interactions. The other was prepared from a monomer complex and did not display Ti–Ti nearest-neighbor distances. Reactivity testing was carried out in a flow system with a reactor possessing a volume section after the catalyst bed that could be empty to allow propagation of radical chain reactions or filled with quartz chips to quench homogeneous reactions.

Table 1 compares the activities of the TiO_2/SiO_2 catalysts, obtained mostly with an empty post-catalytic-bed volume. Sample No. 1, prepared from the Ti dimer complex precursor, shows good conversion and PO selectivity compared to Sample No. 2, prepared from Ti isopropoxide (Ti monomer). The major side product in both cases was acetaldehyde. Samples with higher Ti loadings (Nos. 1, 3, 4) gave higher propylene conversions, but slightly lower PO and acetaldehyde selectivites. Reference samples of the calcined titanium dimer precursor (unsupported) and the silica supported duly gave low conversion (Nos. 5, 6). The high conversions of the supported sample suggest that the titanium oxide species are highly dispersed on the SiO_2 support. A sample of the low loading (2%) Ti dimer catalyst in which the post-catalytic-bed volume was filled with quartz sand (No. 7) gave low conversion. Comparison to Sample No. 2 indicates that the post-catalytic volume is essential for PO production using this type of catalyst.

Figure 1 shows that the Ti oxide dimer catalysts has good stability in the tested period in contrast with previously studied direct PO catalysts [5,6]. An induction period was observed for the Ti (6.7%) catalyst. The cause may be related to the generation of radical species whose formation and disappearance need to be balanced gradually as they involve the establishment of radical branching steps. Induction periods are generally observed in radical oxidation reactions [9]. The induction period does not appear with the Ti (2%) catalyst. The reason may be that because of its lower activity the rate of formation of radicals was lower and reached a balance with the consumption of radicals in a short time.

Figures 2 and 3 show the XAFS spectra of the TiO_2/SiO_2 catalysts and Table 2 shows the curve fitting results. From the XANES pre-edge peaks, it can be deduced that the structures of the Ti oxide species on the SiO_2 support (Samples No. 1 and 2) are different from those of rutile and anatase type TiO_2. There have been many studies of Ti XANES spectra [10,11]. Sankar *et al.* have shown that the exact position of the pre-edge peak can be correlated to the Ti coordination [12]. Based on this work and the energy of the pre-edge peak of TS-1, a 4-coordinate standard material, the Ti species on the SiO_2 support (Samples No. 1 and 2) are assigned to be close to 5-coordinate (figure 2 (right)). Also, the pre-edge energy of the Ti_2-complex indicates that the Ti is between 5 and 6-coordinate. This is in agreement with an X-ray crystal structure analysis [13] of the complex that indicates that the Ti are 5-coordinate. In the EXAFS spectra of Samples 1 (dimer precursor) and 2 (monomer precursor), the first peak at 0.15 nm in both spectra are assigned to Ti–O bonds. In Sample 1, a second peak at 0.27 nm is clearly observed, and this is assigned to a Ti–Ti distance in a Ti–O–Ti structure. According to curve fitting results (table 2), the Ti-oxide species in Sample 1 are deduced to have a cluster structure consisting of a few Ti atoms (2 or 3) bonded through bridging oxygen atoms. In contrast, the Ti monomer does not form a cluster structure, and the Ti species are isolated on the SiO_2 surface. This contrasts with an earlier report that Ti isopropoxide forms dimers on the silica [14], but the complexes in that work were not calcined and retained isopropyl ligands. When calcined the complexes probably decompose into monomers.

UV-vis spectroscopy is useful for assessing the nuclearity of oxide clusters and was employed to give further insight on the structure of the Ti species. Figure 3 shows absorbance in Kubelka–Munk units versus E plots. Sample No. 1 shows a clear shoulder on the low-energy side, and the signal was deconvoluted using two Gaussian curves. The low energy curve with a maximum at 4.4 eV is assigned to dimers, while the high energy curve with a maximum at 5.4 eV is assigned to monomers. This is consistent with previously reported UV-vis spectra [15,16]. The sample, thus, is composed of a mixture of monomers and dimers with relative areas of 82% and 18%, respectively. Since the extinction coefficients are unknown, the absolute amounts of each species cannot be determined, but clearly there is a correlation between the catalytic performance and the presence of dimers. Sample No. 2 shows a spectrum that can be fit by a single Gaussian, with a peak at 5.1 eV, corresponding to monomers.

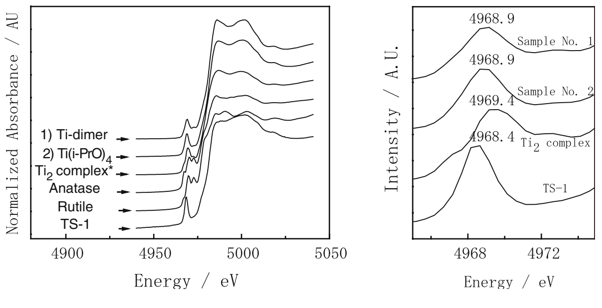


Figure 2. Ti–K edge XANES and FT-EXAFS spectra of TiO_2/SiO_2 catalysts and structure of titanium oxide species from XAFS analysis. Sample No. 1, prepared from titanium dimer complex; sample No. 2, prepared from Ti(iso-PrO)$_4$; *titanium source of catalyst A, untreated.

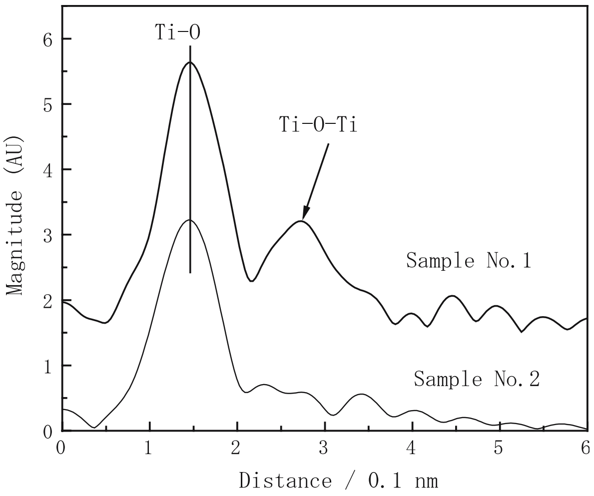
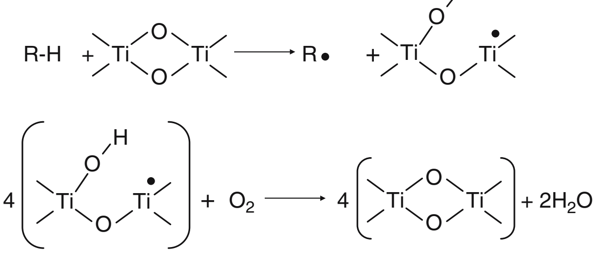


Figure 3. FT-EXAFS spectra TiO_2/SiO_2 catalysts.

Formation of activated oxygen species on Ti centers from oxidants such as H_2O_2 in the liquid-phase epoxidation of alkenes using catalysts [17] like TS-1 is well-known. The radical generation function of the Ti cluster in this study is likely to be different. A possible reaction mechanism in which the Ti cluster is effective in generating radicals by stabilizing a Ti^{3+} state is presented in scheme 1. Although we have no evidence in this work for the formation of the Ti^{3+} species, isolated tetrahedral Ti oxide species have been shown to produce Ti^{3+}



Scheme 1. Radical formation on the titanium oxide dimer.

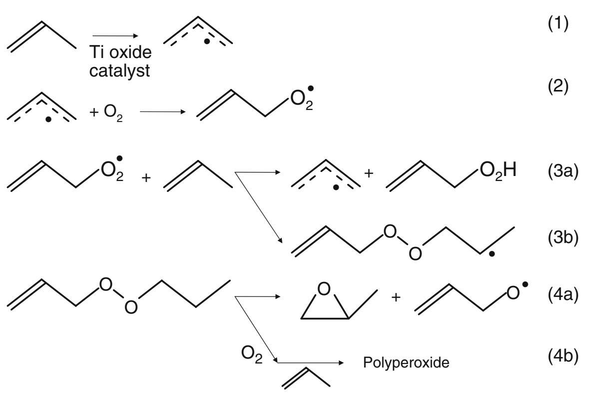
Table 2
Ti K-edge EXAFS results of Ti-oxide/SiO_2 catalysts

Sample	Shell	CN	R (nm)	σ nm	*R*-factor (%)
Sample No. 1	Ti–O	5.5	0.188	0.0089	3.2
(from Ti_2 complex)	Ti–Ti	1.5	0.284	0.0042	
Sample No. 2	Ti–O	3.8	0.183	0.0076	3.7
(from $Ti(OC_3H_6)_4$)					

in photocatalysts by UV radiation [18], or by reduction in H_2 at 773 K [19].

After radical formation other oxygenates may be formed in the post-catalytic volume by well-known gas-phase radical reactions as shown in scheme 2 [20]. The nature of the reaction products gives insight as to the chemistry involved. The first species generated are likely to be allyl radicals which then interact with molecular O_2 to form peroxy radicals that lead to the formation of peroxodimers or hydroperoxides. The hydroperoxides epoxidize propylene to PO and the peroxodimers decompose to form PO. Acetaldehyde is formed from a scission process.

Surface-initiated gas-phase radical generation has been known for a long time. Lunsford [21] cites the work of Langmuir [22] in which hydrogen radicals were generated by incandescent tungsten wires (> 1300 K). Other example include the formation of gas-phase methylallyl radicals during the oxidation of 1-butene and isobutylene over bismuth oxide at 723 K [23], the generation of radicals during the oxidative dehydrogenation of propane over a V-MgO catalyst at 829 and 843 K [24], and the desorption of hydroxyl radicals during the catalytic reactions of water or hydrogen with oxygen over basic metal oxides (MgO, CaO, SrO, BaO) in the temperature range 1100–1300 K [25]. In the case of propylene, Chelliah and Keulks report surface-initiated homogeneous reactions that produce propylene oxide over a bismuth molybdate catalyst operating at 698 K [26]. Our work can be distinguished from these previous studies by the remarkably low temperatures (~573 K) at which the radicals are generated. This is probably a consequence of the unique properties of the Ti dimer complex which has a suitable structure for generating the radical.



Scheme 2. Formation of propylene oxide.

4. Conclusions

A catalyst containing Ti oxide dimers supported on SiO_2 was prepared from a Ti dimer complex and was found to be effective for direct PO production. The catalyst was produced by simple impregnation and thermal decomposition, and its dimer structure was confirmed by EXAFS analysis. The production of PO likely occurred by a gas-phase radical chain reaction mechanism as deduced from the effect of the post-catalytic-bed volume.

Acknowledgments

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