Production of Propene Oxide by a Homogeneous Chain Reaction Initiated by Surface Radical Generation*

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Effective Ti catalysts were found for the vapor phase synthesis of propylene oxide, one of the most challenging reactions in heterogeneous catalysis. The observation that the reaction was enhanced by the presence of a post-catalytic bed volume indicated that the reaction occurred through a homogeneous chain reaction, likely initiated by surface radical generation. EXAFS analysis of the SiO₂-supported catalysts indicated that active samples had Ti oxide clusters on the support. The catalytic activity was stable for 500-600 min, and indicated a promising catalytic system. [DOI: 10.1380/ejsnt.2006.74]

Keywords: Extended X-ray absorption fine structure (EXAFS); Catalysis; Titanium oxide; Alkenes; Oxygen; Epoxidation; Radical generation

I. INTRODUCTION

Surface-initiated gas-phase reactions have been discussed only infrequently in the literature. One example is that of methane coupling with basic catalysts such as Li(MgO) or Sm₂O₃, which proceeds by the reaction of methane with surface centers to produce methyl radicals [1]. The methane activation step is slow and the high temperatures (> 873 K) required for a significant reaction rate limit the selectivity, so the process has not been commercialized.

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

Propylene oxide (PO) is an important industrial product [2] currently manufactured by several indirect methods, such as the chlorohydrin process, which uses Cl₂ and H₂O, or variations of the Halcon process, which use or-

ganic hydroperoxides. Compared with the indirect methods, a process for direct epoxidation (C₃H₆+1/2O₂=PO) would be simpler and less expensive. However, the direct reaction is difficult because of the high reactivity of the hydrogens in the allylic position which on standard catalysts leads to products such as acrolein [3].

There has been considerable effort in the development of new catalysts and systems for the direct PO synthesis reaction. Examples are (1) silver-based catalysts [4], (2) gold nano-particle catalysts [5], (3) Ti-oxide catalysts [6-8], (4) molten salt catalysts [9], and (5) gas phase homogeneous reaction system [10]. These systems suffer from low selectivities and short lives. For example, gold nano-particle catalysts have high selectivity (> 98%), but unfortunately short lives (< 6 h). Similarly, Ti-oxide catalysts have high conversion (> 20%) but also have short lives (< 5 h).

This paper reports results with a new system consisting of Ti-oxide clusters supported on silica which produces PO at relatively low temperatures (~573 K) from only propene and oxygen. The clusters have a stable conversion over the course of the experiments.

II. EXPERIMENTAL

The Ti-oxide catalysts were prepared by impregnation of a silica support (Cariact Q-30, 120 m²g⁻¹, Fuji Silisia Chemical Ltd.) with Ti precursors. Two precursors were compared, a Ti dimer precursor complex [11] ((NH₄)₈[Ti₂(C₆H₄O₇)₂(O₂)₂]-8H₂O, Furuuchi Chemi-

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TABLE I: Initial activities of $\text{TiO}_2/\text{SiO}_2$ catalysts prepared from Ti_2 complex. $T = 568 \text{ K}$, $P = 3.5 \text{ atm}$, Feed gas, C_3H_6 , $10 \text{ mL}\cdot\text{min}^{-1}$, O_2 , $10 \text{ mL}\cdot\text{min}^{-1}$. Catalyst weight, $1.0 \text{ g} + \text{quartz sand } 3.0 \text{ g}$, $25\text{-}60 \text{ min}$. ^a post catalytic-bed volume, ^b prepared from Ti_2 complex, ^c prepared from $\text{Ti}(\text{iso-PrO})_4$, ^d decomposed unsupported Ti_2 complex, ^e Post catalytic bed volume of the reactor filled with quartz sand. $T = 573 \text{ K}$. $\text{CO}_x = \text{CO}, \text{CO}_2$.

No.	Catalyst	PCBV ^a (mL)	Precursor	Conversion of C_3H_6 (%)	Selectivity (%)			
					PO	Acetaldehyde	CO_x	Other
1	TiO_2^b (2.0%) / SiO_2	25	Dimer	9.2	34.7	20.2	39.2	5.9
2	TiO_2^c (2.0%) / SiO_2	25	Monomer	4.4	26.7	23.2	42.6	7.5
3	TiO_2^b (6.7%) / SiO_2	25	Dimer	11.1	28.1	19.0	45.0	7.9
4	TiO_2^b (15%) / SiO_2	25	Dimer	21.5	20.6	11.5	62.7	5.2
5	TiO_2^d	25	Dimer	2.2	21.5	18.9	56.2	3.4
6	SiO_2	25	-	0.2	35.5	41.7	20.0	2.8
7 ^e	TiO_2 (2.0%) / SiO_2	None	Dimer	1.9	1.6	18.4	49.6	30.4

FIG. 1: Time course of PO formation using $\text{TiO}_2/\text{SiO}_2$ catalysts $T = 566 \text{ K}$, $P = 3.5 \text{ atm}$, Feed gas: $\text{He}/\text{C}_3\text{H}_6/\text{O}_2 = 5/5/10$ ($\text{mL}\cdot\text{min}^{-1}$).

cal), and a Ti monomer precursor [6] (Ti iso-propoxide). Following impregnation the catalysts were vacuum dried at $343\text{-}353 \text{ K}$ 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 $568\text{-}573 \text{ K}$ with a feed consisting of $\text{C}_3\text{H}_6/\text{O}_2 = 10/10$ ($\text{mL}\cdot\text{min}^{-1}$) (Table 1) or $\text{He}/\text{C}_3\text{H}_6/\text{O}_2 = 5/5/10$ ($\text{mL}\cdot\text{min}^{-1}$) (Fig. 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 products were analyzed by two on-line gas chromatographs (Shimadzu, Model GC-14A, Kyoto, Japan) equipped with FID and TCD detectors (4 ch). The columns employed were TC-FFAP, Porapack-Q, Gasukuro-pack-54, and Molecular sieve-5A. Product mass balances closed to $100\% \pm 5\%$. 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, $4\text{-}11 \text{ \AA}^{-1}$, R-range, $0.98\text{-}3.38 \text{ \AA}$. The backscat-

tering 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.

III. RESULTS AND DISCUSSION

Table 1 compares the activities of the $\text{TiO}_2/\text{SiO}_2$ 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 selectivities. Reference samples of the calcined titanium dimer precursor (unsupported) and the silica support duly gave low conversions (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. A blank experiment with no catalyst did not give any conversion. Comparison to Sample No. 2 indicates that the post-catalytic volume is essential for PO production using this type of catalyst. This is a strong indication that the reaction is occurring in the gas-phase through radical chain reactions. We speculate that the role of the Ti dimer catalyst is to generate radicals which initiate the reactions. We are currently designing an apparatus that will enable us to trap radical intermediates and to verify their existence with electron spin resonance spectroscopy.

The Ti oxide dimer catalysts showed good stability in the tested period (Fig. 1) 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 have been reported in radical oxidation reactions [12]. The induction period does not appear with the Ti (2%) catalyst. The reason may be that be-

FIG. 2: Ti-K edge XANES spectra of $\text{TiO}_2/\text{SiO}_2$ catalysts. Sample No. 1, prepared from titanium dimer complex. Sample No. 2, prepared from $\text{Ti}(\text{i-PrO})_4$. * Titanium source of catalyst No. 1, untreated.

FIG. 3: FT-EXAFS spectra of $\text{TiO}_2/\text{SiO}_2$ catalysts.

cause 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 $\text{TiO}_2/\text{SiO}_2$ catalysts. 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 . 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. The Ti-oxide species in Sample 1 might be 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 with Ti-O-Ti bond, and the Ti species might be isolated on the SiO_2 surface.

Formation of activated oxygen species on Ti centers from oxidants such as H_2O_2 in the liquid-phase epoxidation of alkenes using catalysts [13] like TS-1 is well-known. The radical generation function of the Ti cluster in this study is likely to be different. Although we do not have direct evidence, we hypothesize that the Ti oxide cluster with Ti-O-Ti structure could be effective in radical generation by stabilizing a Ti^{3+} state. Isolated tetrahedral Ti oxide species have been shown to produce Ti^{3+} in photocatalysts by UV radiation [14], or by reduction in H_2 at 773 K [15]. After radical formation other oxygenates may be formed in the post-catalytic-volume by well-known gas-phase radical reactions [16–19]. 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.

Surface-initiated gas-phase radical generation has been known for a long time. Lunsford [20] cites the work of Langmuir [21] in which hydrogen radicals were generated by incandescent tungsten wires (> 1300 K). Other examples include the formation of gas-phase methylallyl radicals during the oxidation of 1-butene and isobutylene over bismuth oxide at 723 K [22], the generation of radicals during the oxidative dehydrogenation of propane over a V-MgO catalyst at 829 and 843 K [23], 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 [24]. 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 [25]. 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.

IV. CONCLUSION

In conclusion 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 from a Ti dimer precursor by simple impregnation and thermal decomposition, and its structure was determined 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.

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