催 化 学 报

2010 Chinese Journal of Catalysis Vol. 31 No. 10

文章编号: 0253-9837(2010)10-1195-05 **国际版 DOI**: 10.1016/S1872-2067(10)60111-8 **研究快讯:** 1195~1199

基于H_2/O_2等离子体和钛硅沸石的丙烯气相环氧化方法

苏 际[1], 周军成[1,2], 刘春燕[1], 王祥生[1], 郭洪臣[1]

[1]大连理工大学催化化学与工程系精细化工国家重点实验室, 辽宁大连 116012

[2]中国船舶重工集团公司第七一八研究所, 河北邯郸 056027

摘要: 将H_2/O_2非平衡等离子体现场产生的气态H_2O_2和丙烯与耦合反应器中钛硅沸石 TS-1 直接接触, 实现了丙烯气相环氧化反应. 结果表明, 非平衡等离子体生成气态H_2O_2的速率由介质阻挡放电的输入功率决定, 环氧丙烷的生成速率和选择性取决于钛硅沸石催化剂和反应条件. 在H_2和O_2进料流量分别为 170 和 8 ml/min, 介质阻挡放电输入功率为 3.5 W, 环氧化反应温度为 110 °C, 丙烯进料量为 18 ml/min, 催化剂用量为 0.8 g 的条件下, 生成环氧丙烷产率达 246.9 g/(kg·h)、环氧丙烷选择性和H_2O_2有效利用率分别为 95.4% 和 36.1%, 反应 36 h 内未见催化剂失活.

关键词: 等离子体; 过氧化氢; 钛硅分子筛; 气相丙烯环氧化; 环氧丙烷

中图分类号: O643 **文献标识码:** A

Gas Phase Epoxidation of Propylene with TS-1 and in Situ H_2O_2 Produced by a H_2/O_2 Plasma

SU Ji[1], ZHOU Juncheng[1,2], LIU Chunyan[1], WANG Xiangsheng[1], GUO Hongchen[1,*]

[1]*State Key Laboratory of Fine Chemicals, Department of Catalytic Chemistry and Engineering, Dalian University of Technology, Dalian 116012, Liaoning, China*

[2]*718th Research Institute of China Shipbuilding Industry Corporation, Handan 056027, Hebei, China*

Abstract: Gas phase epoxidation of propylene was performed by directly contacting propylene and gaseous H_2O_2 on the surface of TS-1 catalyst in an integrated reactor. The gaseous H_2O_2 was produced in situ by a H_2/O_2 plasma. The H_2O_2 formation rate can be enhanced by increasing the power density of the H_2/O_2 plasma reactor. The yield and selectivity for propylene oxide (PO) can be increased by optimizing the reaction conditions and using suitable TS-1 catalysts. With a power injection of 3.5 W, flow rates of H_2, O_2, and propylene of 170, 8, and 18 ml/min, respectively, catalyst loading of 0.8 g, and epoxidation temperature of 110 °C, the yield and selectivity for PO and the utilization rate of H_2O_2 were 246.9 g/(kg·h), 95.4%, and 36.1%, respectively. During the gas phase reaction, no decline of TS-1 activity was observed.

Key words: plasma; hydrogen peroxide; titanium silicalite-1; gas-phase epoxidation of propylene; propylene oxide

环氧丙烷 (PO) 是重要的基本有机化工中间体. 目前, PO 生产方法主要有氯醇法和共氧化法, 然而这两种方法分别存在环境污染和联产品等问题, 所以自 20 世纪 80 年代以来, 人们一直致力于开发以H_2O_2为氧化剂、钛硅沸石 (TS-1) 为催化剂的丙烯环氧化技术[1,2]. 目前, 基于H_2O_2和 TS-1 的丙烯液相环氧化技术已在比利时、韩国和泰国等地工业化[3]. 但该技术尚存在原料H_2O_2成本昂贵和溶剂甲醇使用量过多等问题[4,5].

近年来, Haruta 等[6~9]以及 Cumaranatunge 等[10]以负载 Au 的含 Ti 材料 (TiO_2, TS-1, Ti-MCM-41 和 Ti-MCM-48) 为催化剂, H_2和O_2为原料原位获得活性氧物种 (一般认为与H_2O_2有关), 并在不使用任何溶剂的条件下进行丙烯气相环氧化反应. 最近, Klemm 等[11]以气化的工业H_2O_2为原料, 采用微通道反应器技术研究了 TS-1 催化剂上丙烯直接气相环

收稿日期: 2010-06-24.

联系人: 郭洪臣. Tel: (0411)39893913; Fax: (0411)84786992; E-mail: hongchenguo@163.com

基金来源: 国家自然科学基金(20233050).

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版(http://www.sciencedirect.com/science/journal/18722067).

氧化反应. 上述方法因不使用溶剂, 工艺十分简单, 同时以 H_2 和 O_2 为起始原料还可克服直接使用工业 H_2O_2 带来的成本问题. 但是,用微反应器合成大宗化学品实用性不大. 目前在负载 Au 催化剂上原位产生环氧化活性氧物种的效率还非常低[4].

我们在 H_2/O_2 非平衡等离子体直接合成 H_2O_2 的研究基础上[12], 建立了一种新的丙烯气相环氧化方法, 如图 1 所示. 该法采用等离子体和钛硅沸石固定床耦合反应器, 即反应器上段是自冷式介质阻挡放电反应器 (适宜工作温度范围是 2~30 °C), 用于将 H_2-O_2 混合气在常温常压下直接转化为 H_2O_2 [13]; 下段是装填 TS-1 的固定床反应器 (常压, 适宜工作温度范围 50~200 °C), 这样上段产生的 H_2O_2 在此进行丙烯环氧化反应. 可见, H_2O_2 合成和丙烯气相环氧化分段进行, 便于优化各自反应条件, 另外用非平衡等离子体直接合成 H_2O_2 不仅选择性和产率高, 而且不需气化, 可直接用于气相环氧化反应.

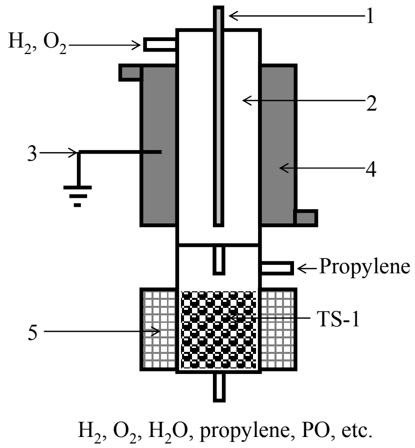

图 1 丙烯气相环氧化耦合反应器示意图

Fig. 1. Integrated reactor for gas-phase epoxidation of propylene. 1—High voltage electrode; 2—DBD (dielectric barrier discharge) plasma chamber; 3—Grounding electrode; 4—Circulating cooling water; 5—Electric heater. PO— Propylene oxide.

本文采用两种自合成的 TS-1 催化剂, 其中 TS-1[1] 按文献[14]合成, 晶粒度约为 150 nm, Si/Ti 比为 33; TS-1[2] 按文献[15]合成, 晶粒度为 5~10 μm, Si/Ti 比为 150. X 射线粉末衍射 (XRD)、漫反射紫外-可见吸收光谱 (UV-Vis) 以及骨架振动红外吸收光谱 (FT-IR) 等表征结果表明, 所用 TS-1 样品均属于典型的 MFI 结构, 且基本不含非骨架 Ti. 环氧化反应在上述耦合反应器中进行, 产物用两个串联的 GC 7890 型气相色谱仪 (分别使用 TCD 检测器和 FID 检测器) 在线分析.

表 1 为在耦合反应器中进行丙烯气相环氧化反应结果. 由表可见, 当介质阻挡放电输入功率从 2.4 W 提高到 3.5 W 时, H_2O_2 时空产率由 2.1 g/(L·h) 增至 5.7 g/(L·h); 相应地 PO 产率由 62.9 g/(kg·h) 增至 157.3 g/(kg·h), 但 H_2O_2 有效利用率略有下降, 这可能与丙烯和 H_2O_2 的比例变化有关. 保持输入功率不变, 即 H_2O_2 产率不变, 当反应温度从 50 °C 提高到 110 °C, PO 产率由 80.4 g/(kg·h) 增至 157.3 g/(kg·h), H_2O_2 有效利用率也由 11.7% 提高到 23.0%. 当反应温度升至 140 °C 时, PO 产率下降到 150.3 g/(kg·h), 且 PO 选择性和 H_2O_2 有效利用率均有所下降. 当以 TS-1[2] 代替 TS-1[1] 时, 在相同反应条件下, PO 产率可达 246.9 g/(kg·h), 明显优于 Cumaranatunge 等[10]和 Huang 等[7]报道的气相环氧化最好结果 (分别为 134 和 137 g/(kg·h)). 另外, 本文气相环氧化生成 PO 选择性较高, 一般超过 95% (副产物主要有 CO_2、乙醛、丙醛、丙酮、丙烯醛和丙二醇等). 这可能与等离子体合成的 H_2O_2 纯度高和避免因使用溶剂而发生副反应等因素有关.

综上可见, 非平衡等离子体生成气态 H_2O_2 的速

表 1 氢气、氧气和丙烯在介质阻挡放电等离子体和 TS-1 固定床耦合反应器中气相环氧化结果

Table 1 Gas-phase epoxidation of hydrogen, oxygen, and propylene in an integrated reactor composed of DBD plasma and TS-1 fixed bed units

PI (W)	Y_{H2O2}/(g/(L·h))	Catalyst	T/°C	Y_{PO}/(g/(kg·h))	S_{PO}/%	U_{H2O2}/%
2.4	2.1	TS-1[1]	110	62.9	95.5	24.2
3.0	3.7	TS-1[1]	110	104.9	95.5	23.7
3.5	5.7	TS-1[1]	110	157.3	95.6	23.0
3.5	5.7	TS-1[1]	50	80.4	96.5	11.7
3.5	5.7	TS-1[1]	80	122.3	96.6	17.9
3.5	5.7	TS-1[1]	140	150.3	92.2	21.9
3.5	5.7	TS-1[2]	110	246.9	95.4	36.1

PI—Power injected into the H_2/O_2 DBD plasma chamber.

U_{H2O2} = (PO produced in TS-1 bed)/(H_2O_2 produced in DBD plasma chamber), in molar unit.

率由介质阻挡放电输入功率决定, 而PO的生成速率、选择性以及H_2O_2有效利用率则取决于TS-1本身性质和反应温度.

能否在不使用溶剂和反应温度较高的气相环氧化反应条件下尽可能提高H_2O_2有效利用率, 是该领域的主要挑战. 为了研究H_2O_2在TS-1催化剂上的分解规律, 本文设计了预吸附H_2O_2的TS-1样品吹扫实验, 具体过程为: 首先在室温用30% H_2O_2溶液浸泡TS-1^{1}样品, 经抽滤得到含H_2O_2的TS-1^{1}湿样品, 然后在与气相环氧化相似的进料条件($H_2/C_3 = 170/18$)下, 于不同温度吹扫TS-1^{1}湿样品, 同时用四级质谱检测吹扫尾气中的O_2和PO浓度变化. 所得结果见图2. 由图可见, 在50 °C的较低温度下, 用含丙烯的气体吹扫样品时就有PO生成, 同时H_2O_2分解生成O_2. 随着吹扫温度的提高, O_2和PO的瞬时最大浓度逐渐增加. 这说明H_2O_2的分解和环氧化是一对竞争反应, 且均随温度的升高而加快. 还可以看出, 当吹扫温度低于80 °C时, 提高吹扫温度相对有利于PO生成; 而当吹扫温度高于80 °C时(如110 °C), 提高吹扫温度则对生成O_2相对有利. 这说明选取适当温度可提高H_2O_2的有效利用率. 由表1也可见, 在耦合反应器中进行的气相环氧化反应中确实存在环氧化反应的最佳温度, 为110 °C, 高于图2中得出的适宜温度. 这可能是由于吹扫实验中TS-1样品微孔内凝聚了大量液体H_2O_2, 在吹扫过程中其与丙烯接触机会少而更易发生分解. 总之, 选择适宜的环氧化反应温度能够提高H_2O_2的有效利用率.

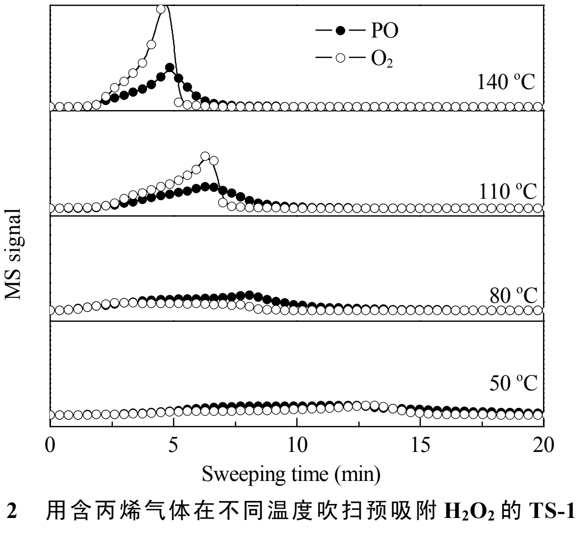

图2　用含丙烯气体在不同温度吹扫预吸附H_2O_2的TS-1^{1}样品时在线质谱监测结果

Fig. 2.　On-line MS analysis of the vent gas when a propylene-containing gas flowed over TS-1^1 adsorbed with H_2O_2.

据文献[6,16]报道, 在负载型Au催化剂上发生的气相环氧化反应失活很快, 这被认为是具有双齿结构的烯烃氧化物种强吸附在含Ti载体的Ti-O-Ti结构上所致. 在本文中, 当耦合反应器中环氧化反应温度为50 °C时, 2 h后就出现失活. 经调变反应温度(未示出)发现, 这是由于反应过程中生成的水润湿了催化剂表面, 堵塞了其孔道所致. 在80 °C以上进行环氧化反应可以避免这种失活. 图3为在110 °C下环氧化反应稳定性实验结果. 可以看出, 反应36 h内, 环氧化反应未见失活. PO产率和选择性以及H_2O_2有效利用率分别维持在246.9 g/(kg·h), 95.4%和36.1%左右. 这可能有两方面原因: (1)本文采用的TS-1催化剂中Ti原子基本上都是以孤立的骨架Ti形式存在, 基本不含Ti-O-Ti结构的非骨架钛物种, 因而可避免由双齿结构的丙烯氧化物种强吸附引起的结焦失活; (2)本文所用的气态过氧化氢在较高的环氧化温度下可能具有自清洁作用[17], 即H_2O_2的氧化可能及时清除了催化剂表面的强吸附物种, 从而避免了催化剂结焦失活.

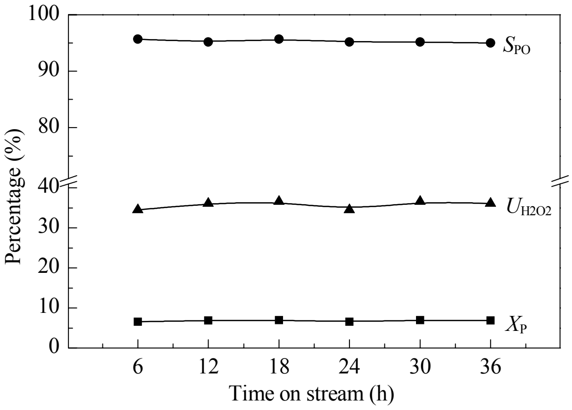

图3　在耦合反应器中进行的丙烯环氧化反应的稳定性

Fig. 3.　Stability of the propylene epoxidation conducted in the integrated reactor.

综上所述, 本文提出了一种以H_2、O_2和丙烯为原料的丙烯气相环氧化制备PO的新方法. 它利用H_2/O_2等离子体现场合成H_2O_2, 提高了H_2O_2的生成效率, 避免了负载Au催化剂制备困难等问题. 同时, 现场生成的H_2O_2是气态, 不用气化即可直接用于反应, 简化了反应流程. 在优化反应条件的基础上制备适合于气相环氧化反应的TS-1催化剂, 可望解决过氧化氢利用率低等问题.

参考文献

1 Clerici M G, Bellussi G, Romano U. *J Catal*, 1991, **129**: 159

2 成卫国, 王祥生, 李钢, 郭新闻, 催化学报 (Cheng W G, Wang X Sh, Li G, Guo X W. *Chin J Catal*), 2004, **25**: 513

3 蔡杰, 吴丽娜, 中国氯碱 (Cai J, Wu L N. *China Chlor-Alkali*), 2009, (5): 1

4 Nijhuis T A, Makkee M, Moulijn J A, Weckhuysen B M. *Ind Eng Chem Res*, 2006, **45**: 3447

5 Danciu T, Beckman E J, Hancu D, Cochran R N, Grey R, Hajnik D M, Jewson J. *Angew Chem, Int Ed*, 2003, **42**: 1140

6 Hayashi T, Tanaka K, Haruta M. *J Catal*, 1998, **178**: 566

7 Huang J H, Taker T, Akita T, Ohashi H, Haruta M. *Appl Catal B*, 2010, **95**: 430

8 Uphade B S, Yamada Y, Akita T, Nakamura T, Haruta M. *Appl Catal A*, 2001, **215**: 137

9 Uphade B S, Akita T, Nakamura T, Haruta M. *J Catal*, 2002, **209**: 331

10 Cumaranatunge L, Delgass W N. *J Catal*, 2005, **232**: 38

11 Klemm E, Dietzsch E, Schwarz T, Kruppa T, de Oliveira A L, Becker F, Markowz G, Schirrmeister S, Schütte R, Caspary K J, Schüth F, Hönicke D. *Ind Eng Chem Res*, 2008, **47**: 2086

12 Zhou J C, Guo H C, Wang X S, Guo M X, Zhao J L, Chen L X, Gong W M. *Chem Commun*, 2005: 1631

13 郭洪臣, 周军成, 王祥生, 郭明星, 赵剑利, 宫为民(Guo H Ch, Zhou J Ch, Wang X Sh, Guo M X, Zhao J L, Gong W M). CN 1 546 368. 2004

14 Taramasso M, Perego G, Notari B. US 4 410 501. 1983

15 Li G, Guo X W, Wang X Sh, Zhao Q, Bao X H, Han X W, Lin L W. *Appl Catal A*, 1999, **185**: 11

16 Mul G, Zwijnenburg A, Vander Linden B, Makkee M, Moulijn J A. *J Catal*, 2001, **201**: 128

17 Liu X W, Wang X Sh, Guo X W, Li G, Yan H Sh. *Catal Lett*, 2004, **97**: 223

英译文

English Text

Propylene oxide (PO) is an important intermediate for the production of a variety of chemicals. Commercially, PO is produced by the chlorohydrin process and hydroperoxide process. These commercial processes face the problems of by-product management and co-product marketing. The development of alternative processes that solve one or more of these issues is ongoing. The epoxidation of propylene with dilute H_2O_2 is a highly desired green chemistry reaction for PO production [1,2]. Currently, this process (HPPO) has been commercialized in Belgium, Korea, and Thailand [3]. Compared with conventional PO process technologies, the HPPO process offers the benefits of economics, environmental friendliness, and opportunities for future growth. However, the high H_2O_2 cost (production and transportation) and solvent problems (PO solvolysis, mass transfer issue, reactants diffusion control) [4,5] are the Achilles heel of this process.

In recent years, Haruta et al. [6–9] and Cumaranatunge et al. [10] have studied the gas phase generation of PO from hydrogen, oxygen, and propylene over TiO_2, TS-1, Ti-MCM-41, and Ti-MCM-48 supported gold (Au) catalysts. Most recently, Klemm et al. [11] have reported the gas phase epoxidation of propylene with vaporized H_2O_2 in a microreactor. These gas phase epoxidation methods do not have the problem of a solvent. At the same time, the generation of H_2O_2 in situ from H_2 and O_2 offers the chance to lower the cost of H_2O_2. However, the low H_2O_2 (or hydroperoxide species) generation efficiency on metallic sites [4] and difficulty of the scale-up of microreactors are disadvantages of these gas phase epoxidation methods.

We had previously shown that high concentration gaseous H_2O_2 can be continuously generated by the reaction of a H_2/O_2 non-equilibrium plasma [12]. In this work, gas phase epoxidation of propylene was studied by directly contacting plasma generated gaseous H_2O_2 and propylene on the surface of a TS-1 catalyst. The investigation was carried out in a tubular Pyrex reactor which consisted of two tightly coupled reaction units (Fig. 1). The DBD plasma unit was used for H_2O_2 synthesis [13], and the fixed-bed unit, which was loaded with the TS-1 catalyst, was used for epoxidation. The most important feature of this integration was the utilization of gaseous H_2O_2, produced by the DBD plasma selectively and efficiently, for PO production.

The TS-1 samples (particle sizes of TS-1^1 and TS-1^2 were 150 nm and 5–10 μm, respectively; Si/Ti ratios were 33 and 150, respectively) used were synthesized according to literature [14,15]. The insertion of Ti atoms into the silicalite framework of these samples was confirmed by XRD and FT-IR spectroscopy. Non-framework Ti species were below the detection of the UV-Vis technique. The products of the epoxidation of propylene with gaseous H_2O_2 were determined by two online gas chromatographs (GC 7890, equipped with TCD and FID detector, respectively) in series.

The gas phase epoxidation results (Table 1) of O_2, H_2 and propylene in the integrated reactor showed that a high PO yield can be achieved by: (1) increasing the power injection (PI), (2) optimizing the reaction temperature, and (3) choosing a suitable TS-1 catalyst. High PI can increase the H_2O_2 formation rate in the H_2/O_2 DBD plasma unit, which was a major advantage in this study. The TS-1 catalyst was very important in determining PO yield and H_2O_2 utilization. As shown in Table 1, under optimum reaction conditions (PI = 3.5 W, 110 °C), H_2O_2 utilization was improved to 36.1% over the TS-1^2 catalyst. Meantime, PO yield was greatly improved to 246.9 g/(kg·h), which was much higher than the best results of 134 and 137 g/(kg·h) reported by Cumaranatunge et al. [10] and Huang et al. [7], respectively. More importantly, the PO selectivity in this study was generally maintained at over 95%. We believe that the gas phase epoxidation of propylene with high purity plasma gaseous H_2O_2 avoids the formation of many byproducts. Side reactions were promoted when solvent and commercial H_2O_2 (contains acidic stabilizer) were used.

H_2O_2 utilization is an important issue in the gas phase epoxidation process with an O_2 and H_2 mixture because it affects the economics of this method. The reduction of H_2O_2 decomposition is the key to improving H_2O_2 utilization. In order to investigate the effects of reaction temperature on H_2O_2 decomposition and epoxidation, a simulated epoxidation experiment was carried out. Online MS was used to analyze in real time the concentration changes of O_2 and PO in the vent gas when a propylene-containing gas (H_2/C_3 = 170/18) was flowed over TS-1^1 pre-adsorbed with H_2O_2. The samples of TS-1^1 pre-adsorbed with H_2O_2 were prepared by the impregnation-filtration method. Figure 2 shows that a lower reaction temperature (below 80 °C) favored epoxidation, and a higher temperature (above 80 °C) favored H_2O_2 decomposition. This implied that a relatively mild reaction temperature favored H_2O_2 utilization. However, the epoxidation of propylene and decomposition of H_2O_2 are competitive reactions over a broad temperature range. Attempts to improve H_2O_2 utilization in epoxidation by simply adjusting the reaction temperature will be inefficient. The simulated epoxidation experiment suggested that a suitable temperature was 80 °C. However, the fixed-bed reaction (Table 1) suggested that the best epoxidation reaction temperature should be 110 °C. The discrepancy may be due to the different state of H_2O_2 in simulated epoxidation and gas phase epoxidation. The capillary condensation of liquid H_2O_2 in the channels of TS-1 make the decomposition much easier at a higher temperature. Table 1 indicates that the choosing of a suitable TS-1 catalyst can solve low H_2O_2 utilization.

Figure 3 shows the stability of gas phase propylene epoxidation conducted in the integrated reactor during a 36 h operation. No deactivation was observed. This result is longer than the catalyst life (< 10 h) of a Au/TiO_2 catalyst in the gas phase epoxidation in the presence of H_2, O_2 and propylene. The yield and selectivity for PO were maintained at 246.9 g/(kg·h) and 95.4%, respectively. H_2O_2 utilization was maintained at 36.1%. We believe that the excellent stability of gas phase epoxidation of propylene and gaseous H_2O_2 can be attributed to both the TS-1 catalyst and the self-cleaning effect of H_2O_2. First, the TS-1^2 sample has high crystallinity and was free of Ti-O-Ti species. According to literature reports [6,16], on a Ti-O-Ti containing titania support, strongly adsorbed species, carbonates/carboxylates were easily formed that resulted in the deactivation of the epoxidation catalyst. On the other hand, coking deactivation can be prevented by cleaning the strongly adsorbed coking precursors with H_2O_2. This function of H_2O_2 can be inferred from the previous works of regenerating a spent TS-1 catalyst by H_2O_2 oxidation [17].

In summary, this study proposed a novel epoxidation method using H_2, O_2, and propylene. Compared with previous epoxidation methods, the advantages of this method are: better H_2O_2 formation rate from the use of the DBD plasma H_2O_2-synthesizing technique, a simpler technological process by directly using gaseous H_2O_2 in propylene epoxidation, and simple catalyst preparation with the use of only TS-1 catalysts. Future research will focus on the preparation of a more suitable TS-1 catalyst for the gas phase epoxidation of propylene.

Full-text paper available online at ScienceDirect
http://www.sciencedirect.com/science/journal/18722067