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*Synthesis, Characterization and
Catalytic Properties in Propylene
Epoxidation of Titanium Silicalites*

李 钢◇著



大连理工大学出版社

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Titanium Silicalites**

Li Gang

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序

教育是国家和民族振兴发展的根本事业。决定中国未来发展的关键在人才,基础在教育。大学是培育创新人才的高地,是新知识、新思想、新科技诞生的摇篮,是人类生存与发展的精神家园。改革开放三十多年,我们国家积累了强大的发展力量,取得了举世瞩目的各项成就,教育也因此迎来了前所未有的发展机遇。国内很多高校都因此趁势而上,高等教育在全国呈现出欣欣向荣的发展态势。

在这大好形势下,我校本着“海纳百川、自强不息、厚德笃学、知行合一”的精神,长期以来在培养精英人才、促进科技进步、传承优秀文化等方面进行着孜孜不倦的追求。特别是在人才培养方面,学校上下同心协力,下足功夫,坚持不懈地认真抓好培养质量工作,营造创新型人才成长环境,全面提高学生的创新能力、创新意识和创新思维,一批批优秀人才脱颖而出,其成果令人欣慰。

优秀的学术成果需要传播。出版社作为文化生产者,一直肩负着“传播知识,传承文明”的历史使命,积极推进大学文化建设和大学学术文化传播是出版社的责任。我非常高兴地看到,我校出版社能够始终抱有这种高度的使命感,积极挖掘学校的学术出版资源,以充分展示学校的学术活力和学术实力。

在我校研究生院的积极支持和配合下,出版社精心策划和编辑出版的“大连理工大学学术文库”即将付梓面市,该套丛书也获得了大连市政府的重点资助。第一批出版的是获得“全国百优博士论文”称号的6篇博士论文。这6篇论文体现了化工、土木、计算力学等几个专业的学术培养成果,有学术创新,反映出我校近几年博士生培养的水平。

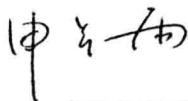
评选优秀学位论文是教育部贯彻落实《国家中长期教育改革和规划纲要》、实施辽宁省“研究生教育创新计划”的重要内

容,是提高研究生培养和学位授予质量,鼓励创新,促进高层次人才脱颖而出的重要举措。国务院学位办和省学位办从1999年开始首次评选,至今已开展14次。截至目前,我校已有7篇博士学位论文荣获全国优秀博士学位论文,30篇博士学位论文获全国优秀博士学位论文提名论文,82篇博士学位论文获辽宁省优秀博士学位论文。所有这些优秀博士论文都已经列入了“大连理工大学学术文库”出版工程之中,在不久的将来这些优秀论文会陆续面市。我相信,这些优秀论文的出版在传播学术文化和展示研究生培养成果的同时,一定会在全校范围内营造出一个在学术上争先创优的良好氛围,为进一步提高学校的人才培养质量做出重要贡献。

博士生是我们国家学术发展最重要的力量,在某种程度上代表了国家学术发展的未来。因此,这套丛书的出版必然会有助于孵化我校未来的学术精英,有效推动我校学术队伍的快速成长,意义极其深远。

高等学校承担着人才培养、科学研究、服务社会、文化传承创新四大职能任务,人才培养作为高等教育的根本使命一直是重中之重。2012年辽宁省又启动了“大连理工大学领军大学建设工程”,明确要求我们要大力实施“顶尖学科建设计划”和“高端人才支撑计划”,这给我校的人才培养提供了新的机遇。我相信,在校师生的共同努力下,立足于持续,立足于内涵,立足于创新,进一步凝心聚力,推动学校的内涵式发展;改革创新,攻坚克难,追求卓越,我校一定会迎来美好的学术明天。

大连理工大学校长



2013年10月

摘 要

随着新世纪的来临,人类环保意识日益增强,对环境保护的要求日益提高,要求化学加工技术减少副产品排放、发展“环境友好工艺”。分子筛催化在开发环境友好工艺、促进可持续发展中具有极大的潜力。特别是 1983 年 Taramasso 等首次报道的钛硅分子筛 TS-1,在以 H_2O_2 为氧化剂的低温氧化反应中具有特殊的催化性能,反应条件温和,反应选择性高,副产品为水,对环境无害。以 TS-1 为催化剂, H_2O_2 为氧化剂,近年开发出了苯酚羟基化制苯二酚、丙烯环氧化制环氧丙烷等一系列反应。但是,与钛硅分子筛的美好应用前景相比,其在工业推广中所迈出的步伐却很小。钛硅分子筛 TS-1 昂贵的生产成本和苛刻的合成条件,是其工业化应用的主要障碍。基础研究方面,钛硅分子筛合成过程和催化机理仍有许多问题没有搞清,使得钛硅分子筛的合成及应用研究主要在摸索中进行。

钛硅分子筛 TS-1 经典合成法采用不含碱金属离子的高纯 TPAOH 为模板剂,成本较高,而且合成条件苛刻、制备重复性差,工业化困难大。本书采用高分辨固体核磁共振技术、XRD、IR、UV-Vis、SEM、ESR 等多种技术手段,系统研究了钛硅分子筛合成中的模板剂作用、钛物种存在形式、晶化机理、晶化动力学等,在此基础上选择了以 TPABr 为模板剂的合成体系。

本书以 TPABr 为模板剂,采用氨水、正丁胺、TEAOH 等调节凝胶 pH 值,合成了钛硅分子筛 TS-1。系统研究了合成 TS-1 分子筛的规律和影响因素,开发出了适于进一步放大的钛硅分子筛合成体系,并实现了 100 L 规模放大。将合成的钛硅分子筛 TS-1 用于丙烯环氧化反应,系统研究了丙烯环氧化反应的影响因素、反应中的溶剂效应、介质酸碱效应、焙烧方式对分子筛性能的影响等,提出了丙烯环氧化机理。

从上述的系统研究工作中,得到了如下结果:

一、以 $^1\text{H} \rightarrow ^{13}\text{C}$ CP / MAS NMR 谱为主要工具,系统研究了钛硅分子筛合成中的模板作用。研究表明:在 TPABr-TBAOH 体系中,TPABr 和 TBAOH 可同时起模板作用;但在 TPABr-正丁胺、TPABr-TEAOH、TPABr-己二胺等其他体系,当 $n(\text{TPABr})/n(\text{SiO}_2) \geq 0.05$ 时,其他有机胺不起模板作用,只是作为调节凝胶碱度的碱源;当 $n(\text{TPABr})/n(\text{SiO}_2) < 0.05$ 时,TEAOH 或正丁胺可被包藏在沸石孔道中起模板作用;导向 Pentasil 结构的模板能力 $\text{TPA}^+ > \text{TBA}^+ > \text{TEA}^+ > \text{正丁胺}$ 等有机胺;包藏在沸石孔道中的 TEA^+ 、 TPA^+ 可能发生部分分解;模板分子的烷基链长与分子筛孔道长度的匹配对于其在分子筛合成中所能起的模板作用影响很大。

二、采用元素分析、XRD、 ^{29}Si MAS NMR、UV-Vis、ESR、UV-Raman 谱等为工具,对钛硅分子筛中钛的存在形式进行了系统研究。研究发现:钛硅分子筛中可能存在多种钛物种。采用不同制备方法,钛硅分子筛中钛的存在形式不同,各种钛物种的含量也不同。以 TPABr 为模板剂的钛硅分子筛合成法中,钛结合进入骨架的方式与经典法不同,因此随着钛含量的提高,晶胞膨胀不如经典法显著。但采用这两种合成方法,随着分子筛中钛含量的提高,均出现由单斜晶系向正交晶系的转变。骨架钛物种可与 H_2O_2 形成稳定性适中的 $\text{Ti}-\text{O}_2^-$ 结构,成为氧化反应的活性中心。以 TPABr 为模板剂合成钛硅分子筛 TS-1,合成中不易产生锐钛矿,但易产生部分缩合的六配位钛物种。此种物种在 UV-Vis 谱 270~280 nm 附近出现跃迁信号,也可和 H_2O_2 形成 $\text{Ti}-\text{O}_2^-$ 结构,但过于稳定,难以作为氧化反应的活性中心。因此,部分缩合的六配位钛物种在反应中表现出惰性。酸处理过程中此种物种容易被脱除,但脱除不影响钛硅分子筛催化活性。

三、采用 pH 计、 ^{13}C NMR、IR 等对钛硅分子筛的晶化过程进行了研究。母液 pH 先降后升,母液中 TPA^+ 逐渐被消耗,钛逐步进入分子筛骨架。这些均表明以 TPABr 为模板剂,钛硅分子筛的

形成遵从液相转变机理。TPABr-正丁胺体系钛硅分子筛TS-1晶化动力学研究表明:加入晶种可以明显缩短TS-1成核诱导期,并降低晶粒粒度;TPABr-正丁胺体系不加晶种时TS-1成核活化能、晶体生长活化能分别为 44.4 kJ/mol、75.7 kJ/mol;采用变温晶化可降低晶粒粒度。

四、以 TPABr 为模板剂,采用多种硅源、碱源和不同配料方式合成了钛硅分子筛TS-1,系统研究了合成中的规律和影响因素。钛硅分子筛TS-1的合成可以在较低模板剂用量 $[n(\text{TPABr})/n(\text{SiO}_2)=0.05]$ 、较宽硅钛比范围 $[n(\text{SiO}_2)/n(\text{TiO}_2)=8\sim\infty]$ 、较宽温度范围(413~473 K)内进行。与用经典法合成TS-1不同,在TPABr-氨水这样的弱碱体系中合成,TS-1晶化较慢,但晶化完全后不需要晶化调整期,可立即终止晶化、分离产品。研究发现合成中TPABr的最低用量在 $n(\text{TPABr})/n(\text{SiO}_2)=0.025\sim0.05$ 范围内。可以采用此最低用量进行合成,从而极大地降低了TS-1的成本。采用自制TPABr为模板剂,硅溶胶为硅源,TBOT为钛源,正丁胺为碱源,合成了钛硅分子筛TS-1,制备重复性良好,并实现了逐步放大。钛硅分子筛静止晶化放大合成中出现晶粒增大现象。采用搅拌可明显降低晶粒粒度,但过于剧烈的搅拌会导致晶格缺陷增多。100 L 规模放大合成TS-1,产率>95%,所得产品相对结晶度较高,无杂晶,晶粒大小为 $1.0\text{ }\mu\text{m}\times 2.0\text{ }\mu\text{m}\times 6.0\text{ }\mu\text{m}$,在丙烯环氧化反应中表现出良好的催化性能。使用间歇反应器,在温度333 K、 H_2O_2 用量0.741 mol/L、丙烯压力0.4 MPa、催化剂用量11.9 g/L、时间1.5 h、甲醇为溶剂的反应条件下,以100 L 规模合成的TS-1为催化剂,丙烯环氧化反应结果为 $X_{\text{H}_2\text{O}_2}=97.4\%$, $U_{\text{H}_2\text{O}_2}=94.6\%$, $S_{\text{PO}}=92.4\%$ 。

五、研究了钛硅分子筛TS-1的焙烧过程。研究发现:以TPABr为模板剂合成的钛硅分子筛TS-1,焙烧过程中TPABr在370~650 °C分步氧化分解,由热分析数据估算出沸石原粉中 $n(\text{TPABr})/n(\text{SiO}_2)=0.040\sim0.045$;采用在氮气下程序升温的方式焙烧分子筛原粉,所得催化剂性能较佳;将TS-1焙烧至>900 °C,

样品结晶度下降,催化活性降低;1 300 °C焙烧后,TS-1转化为方石英,彻底丧失催化活性。

六、系统研究了在釜式反应器中丙烯环氧化反应的规律,优化了反应条件,考察了不同结晶度、不同晶粒大小的TS-1分子筛的催化性能,研究了丙烯环氧化反应的介质效应。研究表明:反应温度对反应结果影响显著,随反应温度升高, H_2O_2 转化率提高,但环氧丙烷(PO)选择性降低。丙烯压力对反应结果无明显影响。随TS-1分子筛结晶度上升, H_2O_2 转化率和利用率均提高。无搅拌时,TS-1分子筛晶粒大小对丙烯环氧化反应影响显著;搅拌良好时,TS-1晶粒大小对反应影响不大。采用甲醇/水混合溶剂,随着溶剂中水含量增加,环氧丙烷(PO)选择性下降,丙二醇(PG)选择性升高;水含量超过一半时, H_2O_2 转化率明显降低。与甲醇做溶剂相比,采用乙醇、异丙醇、正丙醇或丙酮为溶剂时,反应效果均较差。反应介质pH对环氧化产物分布影响显著,碱性物质的加入可以明显提高PO选择性,抑制PO和溶剂发生的副反应。但过量碱性物质易造成钛硅分子筛失活,碱性物质造成的失活是可逆的;用碱金属盐处理钛硅分子筛,然后焙烧,可使骨架钛转变为稳定的非活性物种,再用酸处理可使钛硅分子筛恢复活性。多种证据表明,钛硅分子筛中骨架钛、 H_2O_2 与溶剂ROH形成了一种五元环活性中间体。

本书在进行理论研究的同时,建立了以TPABr为模板剂的钛硅分子筛合成体系,进行了系统研究并成功实现了100 L规模钛硅分子筛的合成,所得分子筛用于丙烯环氧化具有优良的性能,开发了具有工业应用前景的合成钛硅分子筛的新路线,解决了钛硅分子筛催化丙烯环氧化工艺实现工业化的首要问题。这些工作为进一步的理论研究和实现工业化奠定了良好基础。

Abstract

With the new century coming, people pay more attention to the environment and ask the chemical industry to reduce the pollution as possible as it could. Zeolite can take the important role in developing the clearer chemical technology. Taramasso et al. firstly reported the synthesis of titanium silicalite TS-1 in 1983 and it was found that TS-1 exhibited the unique catalytic performance in oxidation reaction involving H_2O_2 as the oxidant. Many reactions using TS-1 as the catalyst such as the hydroxylation of phenol and the epoxidation of propylene have been investigated recently. But the application of TS-1 in the industry was hindered seriously by many defects of the classical synthesis such as the high cost of the raw material and the severe preparation condition. Many problems in the synthetic procedures and the catalytic scheme were still unclear, which made the titanium silicalite was mainly synthesized according to experiences.

In the classical synthesis of TS-1 alkali free TPAOH is used as the template and TS-1 is produced at the severe condition and high cost, which makes the synthesis difficult to be industrialized. In this paper many techniques such as solid-state NMR, XRD, IR, UV-Vis, SEM and ESR were used to study the template effect, crystallization mechanism, crystallization kinetics and titanium species existing in titanium silicalite and the synthesis using TPABr as the template was selected according to the above work.

TS-1 was synthesized using TPABr as the template and ammonia, *n*-butylamine, TEAOH etc. were used to adjust the pH value of the gel. Effect of the synthesis parameters such as the crystallization time, $n(\text{TPABr})/n(\text{SiO}_2)$, $n(\text{SiO}_2)/n(\text{TiO}_2)$, base

amount etc. were systematically discussed. A better synthesis was selected and was enlarged in a 100 L autoclave. As-obtained TS-1 was used to catalyze propylene into propylene oxide (PO). Effect of the reaction parameters, the solvents and the pH value of the medium on the epoxidation result was investigated. At last, a catalytic scheme of propylene epoxidation was given.

From the systematical studies in this paper, the following results have been obtained.

1. Template effect was investigated systematically using $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS NMR. It has been shown that both TPABr and TBAOH serve as templating agent in TPABr + TBAOH system. But in other systems, when there is enough TPABr, other organic amines or ammoniums only work as the bases. TBAOH or *n*-butylamine can take the role of template when less TPABr is added. It indicates that the ability of organic amines or ammoniums to direct the Pentasil structure decreases as following: $\text{TPA}^+ > \text{TBA}^+ > \text{TEA}^+ > n\text{-butylamine}$ etc. Some TEA^+ , TPA^+ in the channel may decompose. It is important for the formation of the channels of zeolite that the sum of lengths of two neighboring alkyl chains matches with the distance of two consecutive cages in the channel.

2. Titanium species existing in titanium silicalite were investigated using chemical analysis, XRD, ^{29}Si MAS NMR, UV-Vis, ESR, UV-Raman. It has been observed that several kinds of titanium species may exist in titanium silicalite. There are different kinds and different amount of titanium species in TS-1 samples synthesized using different methods. The form that titanium atoms incorporate into the framework of titanium silicalite synthesized using TPABr as template differs from that using the classical method and the unit cell volume does not

significantly expand. But the symmetry changes from monoclinic to orthorhombic with the increase of titanium content in both methods. The $\text{Ti}-\text{O}_2^-$ originated from framework titanium and H_2O_2 has the moderate stability and may be active site in oxidation reaction. TS-1 synthesized using TPABr as template does not contain anatase, but contains a kind of partly condensed titanium species with six-fold coordination. The titanium species may correspond to 270 ~ 280 nm band in UV-Vis spectra and also can form $\text{Ti}-\text{O}_2^-$. But this kind of $\text{Ti}-\text{O}_2^-$ is very stable and can not be the catalytic active center. So the six-fold coordination titanium species may be inactive in both the oxidation reaction and the decomposition of H_2O_2 . The titanium species is easily washed off using acid and acid-treating will not influence the catalytic activity of TS-1.

3. The crystallization mechanism of titanium silicalite was investigated systematically using pH-meter, ^{13}C NMR, IR etc. The pH value of the mother liquid decreases at the beginning and then increases after a period. TPA^+ in the mother liquid is consumed gradually and the titanium atoms are introduced into the framework synchronously with the formation of the zeolite structure. All the above phenomena reveal the crystallization process follows the solution-mediated transformation mechanism. The crystallization kinetics of TS-1 was studied in the presence of TPABr and *n*-butylamine. It has been shown that the function of seeds is to afford the nuclei and cut off the nucleation period, thus reduce the crystal size of TS-1. The apparent activation energies for nucleation and crystal growth in this system are 44.4 kJ/mol and 75.7 kJ/mol, respectively. TS-1 with smaller crystal size can be obtained if it forms nuclei at lower temperature and then crystallizes at higher temperature.

4. TS-1 was synthesized using TPABr as the template. Different silica sources, bases and different procedures to prepare the gel were used. It has been observed that the crystallization rate is slower in the weak base systems such as TPABr-ammonia, but the crystallization can be terminated immediately when the crystallinity reaches the high point, as differs from the classical method. There is a threshold to the $n(\text{TPABr})/n(\text{SiO}_2)$ between 0.025 and 0.05. The TPABr amount can reduce to this threshold, which decreases the cost of TS-1 largely. The synthesis of titanium silicalite TS-1 using self-made TPABr as the template, silica colloidal as the silica source, *n*-butylamine as the base, TBOT as the titanium source was enlarged step by step. The crystal size of TS-1 increases with enlarging at static condition. This kind of phenomenon can be inhibited when using stirring, but defects in the crystal increases if stirring too vigorously. TS-1 was synthesized in a 100 L autoclave with high productivity and as-synthesized TS-1 exhibited high crystallinity and good performance in propylene epoxidation. (Reaction condition: temperature 333 K; time 1.5 h; H_2O_2 0.741 mol/L; propylene pressure 0.4 MPa; catalyst 11.9 g/L; solvent methanol. Reaction result: $X_{\text{H}_2\text{O}_2} = 97.4\%$, $U_{\text{H}_2\text{O}_2} = 94.6\%$, $S_{\text{PO}} = 92.4\%$.)

5. TS-1 was calcined on different conditions. It has been observed that the TPA^+ in TS-1 decomposes at the range of 370 ~ 650 °C. The ratio of $n(\text{TPABr})/n(\text{SiO}_2)$ can be calculated out from the thermal analysis result and it is 0.040 ~ 0.045 in as-synthesized zeolite. The calcining method—temperature programmed at nitrogen is preferred to obtain TS-1 catalyst. If the calcining temperature exceeds 900 °C, both the crystallinity and the catalytic activity of TS-1 decrease. TS-1 turns to the

crisobalite and loses its activity at 1 300 °C.

6. The titanium silicalite, which was synthesized using tetrapropylammonium bromide (TPABr) as template, was used to catalyze the synthesis of propylene oxide (PO) from propylene and hydrogen peroxide in an autoclave reactor. Effects of the reaction parameters, the property of the catalyst, the solvents and the pH value of the medium on the propylene epoxidation were investigated. It has been shown that pressure of propylene has no effect on propylene epoxidation, but the temperature has a significant effect. As the temperature rises, the H_2O_2 conversion rate increases and PO selectivity decreases. Both the rate H_2O_2 converts and the efficiency of H_2O_2 are improved with increasing the crystallinity of TS-1. The crystal size of TS-1 has significant effect on the propylene epoxidation, but this kind of effect weakens if stirring well. As the content of water in the mixed solvent of methanol and water rises, the PO selectivity decreases and propylene glycol selectivity increases. As the content of water reaches a half in the mixed solvent, the H_2O_2 conversion rate decreases. Compared with methanol, inferior results are obtained if ethanol, *n*-propylalcohol, *i*-propylalcohol or acetone is used as the solvent. The pH value of the medium influences the composition of the product remarkably. The PO selectivity increases significantly if a small amount of base is added in the medium. But a larger amount of base easily inhibits the activity of TS-1. The framework titanium can turn to a stable inactive species if TS-1 is treated with the base material such as Na_2CO_3 and Na_2SO_3 and then calcined. The deactivated catalyst can resume its activity after being treated using acids. The TS-1 catalyst synthesized using TPABr as template can be used more than twenty times still with better performance in propylene