学校编号：10348　　分类号　密级
学号：　B1999825012　　UDC

厦门大学理学博士学位论文

Ce-Ag-Mo-P-O 催化剂上丙烷选择氧化制丙烯醛反应研究

张昕

指导教师：万惠霖　教授

申请学位级别：博士　　专业名称：物理化学
论文提交日期　　论文答辩日期：
学位授予单位：厦门大学
答辩委员会主席
评阅人

The Ph.D Dissertation of Science in Xiamen University

Studies on Selective Oxidation of Propane to Acrolein over Modified Molybdenum-based Catalyst

Xin Zhang

Supervised by

Professor Huilin Wan

Department of Chemistry

Xiamen University

Aug. 2001

扩展式摘要

我国有着丰富的丙烷资源，由廉价的丙烷合成高附加值的丙烯醛的经济意义是不言而喻的。另外，丙烷选择氧化制丙烯醛反应中包含着如何促进中间体定向转化为目标产物和如何抑制稳定性较差的产物丙烯醛进一步氧化等重要的催化科学问题，所以，进行该反应的研究具有重要的理论意义。

迄今为止，丙烷选择氧化制丙烯醛催化剂的反应性能都不高，研制出的反应性能较好的催化剂对丙烯醛的收率一般在 10%左右，并且通常是在低丙烷转化率的情况下才能获得高丙烯醛选择性。丙烷选择氧化制丙烯醛的反应机理还不明确，两条可能的反应途径是丙烷经过中间产物丙烯生成丙烯醛，或经过正丙氧基（正丙醇）中间体生成丙烯醛。

丙烷选择氧化制丙烯醛的催化剂和催化反应中的许多问题尚待研究，如催化剂的结构和催化剂性能间的关系还不清楚，特别是反应条件下催化剂的（动态）结构和反应性能之间的关系；催化剂的氧化还原性和酸碱性对催化剂性能的影响还存在争论；对催化反应机理的研究较少，已有的研究还不够深入细致。

针对丙烷选择氧化制丙烯醛反应中的上述问题，本文研制了一种与类似的催化剂相比反应性能较好的丙烷选择氧化制丙烯醛 Ce-Ag-Mo-P-O 催化剂，在此基础上，用 XRD 技术测定了不同组成催化剂的结构，用 H_2-TPR，O_2-TPD，*in situ* LRS，EPR 及 XPS 技术考察了不同组成催化剂的氧化还原性，用 NH_3-DRIFT，异丙醇裂解反应表征了不同组成催化剂的酸碱性，讨论了催化剂的性质对可能反应中间体定向转化为丙烯醛的影响，即催化剂的性质和催化剂性能的关系。继之，采用 *in situ* LRS 并结合 XRD，XPS 和催化剂反应性能评价考察了催化剂的动态结构，讨论了催化剂动态结构的成因及其和反应性能的关系。最后，对 Ce-Ag-Mo-P-O 催化剂上丙烷选择氧化制丙烯醛的反应途径进行

了研究。为此，评价了丙烷和丙烷选择氧化制丙烯醛反应中间体（中间产物）或其探针分子如丙烯、正丙醇、异丙醇、溴代正丙烷、溴代异丙烷、丙醛、丙酮等在和丙烷选择氧化制丙烯醛相似反应条件下的反应性能；并采用共焦显微拉曼光谱技术考察了丙烷、丙烯、溴丙烯、烯丙醇、正丙醇、异丙醇、溴代正丙烷、溴代异丙烷、丙醛、丙酮、丙烯醛、甲酸、乙酸等在 Ce-Ag-Mo-P-O 催化剂上的活化和转化情况。综合上述实验结果，提出了在 Ce-Ag-Mo-P-O 催化剂上丙烷选择氧化制丙烯醛的可能反应途径。详细研究结果分述如下：

1. Ce-Ag-Mo-P-O 催化剂的研制和反应条件对催化剂性能的影响

受现有的有关丙烷选择氧化制丙烯醛催化剂的组成、结构和反应机理研究结果启发，选择 Mo 和 P 元素为催化剂的主要组分，并在 Mo-P-O 催化剂中添加助剂，研制成 Ce-Ag-Mo-P-O 催化剂。在较优的反应条件（500 ^{o}C，2400 ml/(g.cat).h^{-1}，$C_3H_8/O_2/N_2$=3/1/4）下，在 Ce-Ag-Mo-P-O（Ce/Ag/Mo/P=1/3/10/6）催化剂上进行丙烷选择氧化制丙烯醛反应，获得丙烷的转化率为 15.3%，丙烯醛选择性为 28.7%，丙烯醛收率为 4.4%的结果。与类似的催化剂相比，Ce-Ag-Mo-P-O 是一种催化性能较好的丙烷选择氧化制丙烯醛催化剂。

2. Ce-Ag-Mo-P-O 催化剂的性质对催化剂性能的影响

比较研究了 Ce-Ag-Mo-P-O 催化剂和 Ag-Mo-P-O 催化剂的结构、氧化还原性和酸碱性，讨论了催化剂的性质对中间体定向转化为丙烯醛的影响和对催化丙烷选择氧化制丙烯醛的影响。

研究发现，在催化剂中添加 Ce，提高了可能反应中间体丙烯和正丙氧基（正丙醇）定向转化为丙烯醛的能力和催化丙烷选择氧化制丙烯醛的反应性能。催化剂中存在最佳的 Ce 含量范围，在 Ce/Mo=0.1 的 Ce-Ag-Mo-P-O 催化剂上，

中间体或丙烷定向转化为丙烯醛的选择性较高。

随着催化剂中 Ce 含量的增加，催化剂的可还原性增强，催化剂中 Mo^{6+}/Mo^{5+} 比降低，催化剂表面钼中心酸性，特别是催化剂表面钼中心 L 酸性降低，这是因为：(1)催化剂中 Ce 和 Mo 发生了相互作用，形成 $Mo^{6+} + Ce^{3+} \Leftrightarrow Mo^{4+}$ (Mo^{5+}) + Ce^{4+} 氧化还原循环，(2)催化剂中各相结构较匹配，生成“一致性界面”，使相间界面能垒降低。由于这两种效应的共同作用，使得催化剂中电子和离子的传递变得容易，并促进催化剂中高价阳离子的还原过程，所以，催化剂的可还原性增强，催化剂中 Mo^{6+}/Mo^{5+} 比降低。Mo^{6+} 浓度降低，催化剂表面钼中心 L 酸性降低。

在催化剂中添加一定量的 Ce，降低 Mo^{6+}/Mo^{5+} 的比例及钼中心的 L 酸性，可以促进反应中间体（中间产物）丙烯和正丙氧基（正丙醇）定向转化为丙烯醛，从而提高催化剂对丙烷选择氧化制丙烯醛的能力。

3. Ce-Ag-Mo-P-O 催化剂中 Mo-O 物种（多钼酸根）的动态结构研究

催化剂的结构是影响催化剂性能的关键因素。因此，搞清楚催化剂的结构，特别是反应条件下催化剂的动态结构及其和催化剂性能的关系，对于准确揭示反应中催化剂的构-效关系，研制高性能的丙烷选择氧化制丙烯醛催化剂有着重要的意义。由于原位表征技术的限制和复合氧化物催化剂的复杂性，至今，对复合氧化物催化剂反应条件下的动态结构及其与催化剂性能之间的关系研究较少。本文采用原位共焦显微拉曼光谱以及 XRD、XPS 和催化剂反应性能评价方法，考察了 Ce-Ag-Mo-P-O 催化剂中 Mo-O 物种（多钼酸根）在丙烷选择氧化制丙烯醛反应中的动态结构，讨论了催化剂中该物种表现出动态结构的可能成因，及其与反应性能的关系。

研究表明，反应条件下，催化剂表面 MoO_3 和 Ce_2MoO_6 中 Mo-O 物种的结构转化为 $AgMoO_2PO_4$ 中 Mo-O 物种的结构，即催化剂的动态结构，这一过程

主要是由丙烷氧化反应诱导的。

MoO_3、Ce_2MoO_6和 $AgMoO_2PO_4$中 Mo-O 物种的结构特性决定了反应条件下 MoO_3和 Ce_2MoO_6中 Mo-O 物种的结构转化为 $AgMoO_2PO_4$中 Mo-O 物种的结构。MoO_3和 Ce_2MoO_6中的 Mo-O 物种是由畸变的、具有类似 O_h对称性的$[MoO_6]^{6-}$八面体相联构成的层状结构，该结构中部分氧离子容易脱除，容易发生扭曲。$AgMoO_2PO_4$ 中 Mo-O 物种的结构具有类似$[Mo_6O_{19}]^{2-}$的结构，组成$[Mo_6O_{19}]^{2-}$的$[MoO_6]^{6-}$八面体具有类似 C_{4v} 对称性。$[Mo_6O_{19}]^{2-}$中的$[MoO_6]^{6-}$八面体具有非键的 d 电子轨道（b_2），在动态情况下，非键 b_2 轨道可以接受一个电子，而体系的能量基本不改变。MoO_3和 Ce_2MoO_6中 Mo-O 物种的结构不具有这样的结构特性，在反应条件下易转化为 $AgMoO_2PO_4$中 Mo-O 物种的结构，该物种体系能量较低、结构更稳定，更适于完成 Mars van Kreleven Redox 循环，表现出较好的丙烷选择氧化制丙烯醛性能。$AgMoO_2PO_4$中 Mo-O 物种的结构可能是丙烷选择氧化为丙烯醛的活性动态结构之一。

4. Ce-Ag-Mo-P-O 催化剂上丙烷选择氧化制丙烯醛的反应机理

丙烷选择氧化合成丙烯醛反应机理比较复杂，反应中涉及到多种可能的基元步骤，故目前，对丙烷选择氧化制丙烯醛反应机理的研究还处在探索阶段。

本文考察了丙烷和丙烷选择氧化制丙烯醛反应中间体（中间产物）或其探针分子如丙烯、正丙醇、异丙醇、丙醛、丙酮、溴代正丙烷（正丙氧基探针分子）、溴代异丙烷（异丙氧基探针分子）在Ce-Ag-Mo-P-O催化剂上的反应性能。实验结果表明，丙烯是丙烷选择氧化制丙烯醛反应中的初级产物；在和丙烷选择氧化制丙烯醛相似的反应条件下，进料丙烯氧化主要生成丙烯醛；异丙氧基（异丙醇）氧化主要生成丙烯和丙酮；正丙氧基（正丙醇）氧化主要生成丙烯和丙醛；丙醛氧化主要生成丙烯醛。接着，采用共焦显微拉曼光谱技术考察了丙烯醛、乙酸、甲酸、烯丙醇（σ-氧烯丙基探针分子）、溴丙烯（烯丙基探针

分子)、丙烯、正丙醇、异丙醇、丙醛、丙酮、溴代正丙烷、溴代异丙烷、丙烷等在Ce-Ag-Mo-P-O催化剂上的活化和转化行为。结合反应中间体及其探针分子的反应性能和它们在催化剂上的活化和转化行为，我们提出了Ce-Ag-Mo-P-O催化剂上丙烷选择氧化制丙烯醛反应的可能机理：在Ce-Ag-Mo-P-O催化剂上，丙烷选择氧化制丙烯醛存在两条可能的反应途径，(1）丙烷在催化剂表面以丙烯为中间体（中间产物），接着经过π-烯丙基物种、σ-氧烯丙基物种（-O-CH_2-CH=CH_2）生成丙烯醛；(2）丙烷在催化剂表面活化生成正丙氧基（正丙醇)，正丙氧基（正丙醇）或以丙烯为中间体生成丙烯醛，或以丙醛为中间体经过丙烯基醇盐物种（-O-CH=CH-CH_3）生成丙烯醛。虽然丙烯很可能是丙烷选择氧化制丙烯醛反应中的初级产物，但其相对选择性较高，所以还不能断言反应途径（1）和反应途径（2）中的第一种途径是Ce-Ag-Mo-P-O催化剂上丙烷选择氧化制丙烯醛反应的主要途径。

关键词：丙烷，选择氧化，丙烯醛，Ce-Ag-Mo-P-O 催化剂，氧化还原性，酸碱性，催化剂动态结构，催化反应机理

Extended Abstract

Propane is an important composition in the natural gas, coal-bed gas and oil well gas, especially the amount of propane is about 60% in the oil well gas. To this day, propane is widely used as fuel. Recently, transformation of propane to high valuable chemical, such as propene, acrolein and acrylic acid by means of selective oxidation has become more and more attractive because of the great economical attraction and fundamental theoretical interesting

It is important that the selective oxidation of propane to acrolin reaction is studied in detail. A great deal of work has been done on the catalysts preparation, catalyst characterization and reaction mechanism in the past years.

All kinds of catalyst for selective oxidation of propane have been developed. We try to divide these catalysts for selective oxidation of propane to acrolein to six kinds, (1) mutli-composition oxide catalyst, (2) catalyst doped by halogen or halid, (3) VPO-based catalyst and phosphate catalyst, (4) heteropoly acid catalyst, (5) supported catalyst, (6) two-layer catalyst. The best yield of acrolein generally acknowledged is about 10%, and the higher selectivity of acrolein is often obtained with the lower conversion of propane. The best catalyst for selective oxidation of propane to acrolein is $Ag_{0.01}Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ reported by Kim in 1989.

The previous research results show that the optimal reaction conditions of obtaining high acrolein selectivity are different on the different catalysts for selective oxidation of propane to acrolein. The effects of acid-base properties, redox properties and active site on the catalytic performance are complicated.

As far as the reaction mechanism of selective oxidation of propane to acrolein is concerned, generally speaking, the formation of acrolein from propane might undergo two possible routes. One is propene/π-allyl as an intermediate of the formation of acrolein, the other is 1-propoxy/1-propanol as intermediate. It is possible that the two routes exit simultaneously in the selective oxidation of propane to acrolein.

Although a lot of research works on the selective oxidation of propane to acrolein have been done, many questions should be answered for better understanding of catalysis and reaction mechanism and for designing an efficient catalyst. In this dissertation, selective oxidation of propane is selected as an aim reaction, we investigated the dynamic structure of catalyst under reaction conditions, the acid-base properties, the redox properties, the ratio of Mo^{6+}/Mo^{5+} in catalyst, and the reaction mechanism by means of testing catalytic performance, XRD, UV-*vis*, *in situ* LRS, XPS, NH_3-DRIFT, Decomposition of iso-propanol, TPR, TPD, ESR techniques. A many of questions, such as the relationship between structure and catalytic performance, the effect of acid-base properties, redox properties and active site properties on the catalytic performance and on the direction transformation of intermediates to acrolein, the model of activation of propane, and the reaction pathways etc., were discussed.

1. The Develop of Catalyst for Selective Oxidation of Propane to Acrolein

Mo and P were selected as main composition of catalyst. The role of promoter (Fe、Co、Ni、Cu、Ag、Zn、Sn、Mn、W、La、Ce、Pr、Nd、Sm、Te、Zr、Ce、V、Bi), the effect of blending ratio of composition in the catalyst and the effect of reaction conditions (temperature, space velocity and C_3H_8/O_2) on the catalytic performance were investigated.

The Ce-Ag-Mo-P-O (Ce/Ag/Mo/P=1/3/10/6) catalyst showed the highest catalytic performance of selective oxidation of propane to acrolein among these investigated catalysts. 28.7% selectivity of acrolein with 15.3% conversion of propane was obtained under $C_3H_8/O_2/N_2$ (3/1/4) flow with the space velocity of 2400 ml/(g.cat).h^{-1} at 500 ^oC. Compared with the reported same kind of catalyst, the Ce-Ag-Mo-P-O catalyst opposed good catalytic performance of selective oxidation of propane to acrolein.

2. The Relationship between Structure and Catalytic Performance

In order to design an efficient catalyst for selective oxidation of propane to acrolein, it is necessary that the better understanding of the relationship between the structure and performance, particularly the relationship between dynamic structure and catalytic performance under the reaction conditions.

Up to date, few literatures have been contributed to this field on the dynamic structure of oxide catalyst under reaction conditions because of the limitation of *in situ* characterization techniques. By means of *in situ* LRS, UV-*vis*, XRD, XPS and testing catalytic performance, the dynamic structure of Ce-Ag-Mo-P-O catalyst was investigated. The reasons of dynamic structure and the relationship between dynamic structure and catalytic performance were discussed.

Under the reaction conditions, MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species transformed to $[Mo_6O_{19}]^{2-}$ -like species on Ce-Ag-Mo-P-O catalyst surface. This process might be induced by the reaction of propane oxidation and the reaction temperature. Propane oxidation on the catalyst enhanced the transformation of MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species to $[Mo_6O_{19}]^{2-}$ -like species. On the other hand, the reaction temperature led to the reversible transformation of MoO_3 to the $[Mo_6O_{19}]^{2-}$ -like species, and the reaction of propane oxidation resulted in the irreversible process of transformation of MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species to the $[Mo_6O_{19}]^{2-}$ -like species.

The reason of the transformation of MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species to the $[Mo_6O_{19}]^{2-}$ -like species was that MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species takes on special structure. MoO_3 is a complicate layer and zigzag rows structure, which is built up by rather distorted MoO_6 octahedron. In *c* axis direction, there are holes in MoO_3 layer structure. This structure makes the transformation of MoO_3 easily under the reaction conditions.

The transformation of MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species to $[Mo_6O_{19}]^{2-}$ species adapted to going on selective oxidation of propane to acrolein on energy and structure. The MoO_6 octahedron in MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species possesses two *cis*-terminal oxygen elements and O_h symmetry. The MoO_6 octahedron in $[Mo_6O_{19}]^{2-}$ species has single terminal oxygen element and C_{4v} symmetry. Under the reaction

conditions, MoO_3 could distort and the d orbit of MoO_6 octahedron (O_h) in MoO_3 could split to MoO_6 (C_{4v}) in $[Mo_6O_{19}]^{2-}$ species. So the system energy of surface Mo species reduced.

According to the molecular orbit diagram, the MoO_6 octahedron (C_{4v}) in $[Mo_6O_{19}]^{2-}$ species has b_2 non-bonding orbit. If Mo^{6+} (Mo^{5+}) is reduced (oxidized) to Mo^{5+} (Mo^{6+}) ($d^0 \Leftrightarrow d^1$), the electron input or output b_2 non-binding orbit, which hardly influence the total energy of species, that is, $[Mo_6O_{19}]^{2-}$ species has low redox potential. Therefore, the $[Mo_6O_{19}]^{2-}$ species is easily to be redox and its structure changes slightly. As far as MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species are concerned, they have no such special nature. MoO_3 and $[Mo_7O_{24}]^{6-}$ -like species have lower redox ability than the $[Mo_6O_{19}]^{2-}$ species.

$[Mo_6O_{19}]^{2-}$ species has higher redox capability, so it can effectively transfer lattice oxygen, the active oxygen species, to the activated propane or intermediates to form acrolein. It is possible reason that high selectivity and yield of acrolein was obtained at 500 ^oC under $C_3H_8/O_2/N_2$ (3/1/4) flow.

3. The effect of the acid-base properties, the redox properties and the active site properties on the catalytic performance

One of the possible reasons of low selectivity of acrolein in selective oxidation of propane is the low degree of transformation of intermediates to acrolein under reactions. The acid-base properties, the redox properties and the Mo^{6+}/Mo^{5+} ratio have great effect on the directional transformation of intermediates to acrolein. The selectivity of acrolein could be improved by modifying the acid-base properties and the redox properties as well as the Mo^{6+}/Mo^{5+} ratio of catalyst.

The acid-base properties, the redox properties and the Mo^{6+}/Mo^{5+} ratio of the catalysts with different Ce/Mo ratio were characterized by NH_3-DRIFT, Decomposition of *iso*-propanol , TPR, TPD, *in situ* LRS, ESR and XPS techniques. The results show the addition of Ce in the catalyst influenced the acid-base properties, the redox properties and the Mo^{6+}/Mo^{5+} ratio, and the above properties influence the catalytic performance of selective oxidation of propane to acrolein and the capability of transformation of intermediates to acrolein.

The addition of Ce in the catalyst improved the selectivity of acrolein during selective oxidation of propane, and the highest selectivity of acrolein was obtained on the catalyst with Ce/Mo=0.1.

The promoter Ce also enhanced propene and 1-propanol as intermediates to transform to acrolein, similarly, the highest selectivity of acrolein was obtained in both propene oxidation and 1-propanol oxidation on the Ce-Ag-Mo-P-O (Ce/Mo=0.1) catalyst.

The amount of Ce in the catalyst influenced the acid-base properties, the redox properties and the Mo^{6+}/Mo^{5+} ratio of the catalysts. With the increase of Ce amount in the catalyst, the acid property reduced, especially the Lewis acid, and the basic property enhanced, on the other hand, the redox properties of catalyst improved and the Mo^{6+}/Mo^{5+} ratio decreased.

The reasons that the addition of Ce in the catalyst influenced on the acid-base properties and the redox properties and the Mo^{6+}/Mo^{5+} ratio are as following. First, Ce and Mo interacted to form the redox cycle as $Mo^{6+} + Ce^{3+} \Leftrightarrow Mo^{4+}$ (Mo^{5+}) + Ce^{3+}. Second, the “coherent interface” formed among phases. The two effects enhance the transformation of electron and the diffusion of oxygen species. So, the catalyst showed the higher redox properties and the lower Mo^{6+}/Mo^{5+} ratio with increasing the Ce amount in the catalyst. The high oxidation state metal ions supply the Lewis acid site of catalyst. The reduction of Mo^{6+} made Lewis acid property weak. On the other hand, the high capability of redox and more reduced Mo as active site for activatiopn of molecular oxygen resulted in the increase of the concentration of O^{2-}on the catalyst under the reaction conditions, which is responsible for the improvement of the base property.

The O^{2-} species is active oxygen species for transformation propene and 1-propane to acrolein on the catalyst. The increase of the concentration of O^{2-} and the improvement of the capability of diffusion of O^{2-} species are in favor of the directional transformation of intermediates to acrolein. However, the O^{2-} species is also responsible for the deep oxidation of intermediates and propane, so the deep oxidation products become main product when the Ce/Mo ratio is more than 0.1.

These results show appropriate modification of acid-base properties, redox properties and the ratio of Mo^{6+}/Mo^{5+} could improve the transformation of intermediates to acrolein and the selectivity of acroelin in selective oxidation of propane.

4. Reaction Mechanism

The reaction mechanism of selective oxidation of propane to acrolein was investigated by testing catalytic performance of intermediate/probe molecular of intermediates and by LRS study on the activation and transformation of intermediate/probe molecular of intermediates on the Ce-Ag-Mo-P-O catalyst.

According to previous research works, propene, 1-propanol, 2-propanol, allylic alcohol, propionaldehyde, acetone, acrolein, acetic acid, formic acid, 1-bromopropane, 2-bromopropane, 3-bromopropene, iso-butane and propane were selected as possible intermediates or the probe molecular of intermediates.

The main activation model of propane on the Ce-Ag-Mo-P-O catalyst was that propane dehydrogenated H from CH_2, and then coordinated with lattice oxygen to form 2-propoxy on the catalyst surface.

There are two possible routes undergo which acrolein formed from propane. (1) propane was activated to 2-propoxy. The 2-propoxy transformed to acrolein though π-allyl and σ-ally consequently. π-allyl could transformed reversibly to propene and it desorbed to gas phase. This route was main route of the formation of acrolein on the catalyst for the selective oxidation of propane to acrolein.

The second route of the formation of acrolein was 1-propoxy/1-propanol as intermediate. There were two possible routes for the transformation of 1-propoxy/1-propanol. One route was that 1-propoxy/1-propanol could transform to acrolein through propene intermediates. The other route was that 1-propoxy/1-propanol dehydrogenated H to propionaldehyde-like species, the latter isomerized to enolate species by acid-base step. The enolate species transformed to acrolein by reduction step.

目录

第一章 绪论----------1
第一节 丙烷选择氧化制丙烯醛和丙烯酸反应研究进展----------1
1.1. 丙烷选择氧化制丙烯醛和丙烯酸的研究意义----------1
1.1.1.丙烷选择氧化制丙烯醛和丙烯酸研究的经济意义----------2
1.1.2.丙烷选择氧化制丙烯醛和丙烯酸研究的理论意义·----------2
1.2. 反应简单热化学和动力学分析----------3
1.3. 丙烷选择氧化制丙烯醛和丙烯酸催化剂 ----------4
1.3.1. 多组分复合氧化物催化剂 ----------7
1.3.2. 含卤素的催化剂----------10
1.3.3. 杂多酸催化剂----------14
1.3.4. VPO 基催化剂和磷酸盐催化剂----------17
1.3.5. 担载型催化剂----------21
1.3.6、两段式催化剂----------23
1.4. 催化剂氧化还原性和酸碱性对催化剂性能的影响----------26
1.5. 催化剂的动态结构----------28
1.6. 丙烷选择氧化制丙烯醛和丙烯酸反应机理----------33
1.6.1. 丙烯是反应中间体(中间产物) ----------34
1.6.2、正丙氧基（正丙醇)、异丙氧基（异丙醇）为中间体（中间产物）
----------38
1.7. 结语----------42
第二节 课题的研究目的和设计·----------44
参考文献----------46

第二章 实验部分----------52
第一节. 催化剂的制备----------52
第二节. 催化剂反应性能评价----------53
第三节. 催化剂的表征----------56

第三章 Ce-Ag-Mo-P-O 催化剂的研制和反应条件对催化剂性能的影响-------60
第一节 结果与讨论----------61
1.1. 丙烷气相氧化反应----------62
1.2. 催化剂的组成和配比对丙烷选择氧化制丙烯醛反应性能的影响----------63
1.2.1. P/Mo 比对催化剂性能的影响----------63
1.2.2. 第三组分对催化剂反应性能的影响----------65
1.2.3. Ag/Mo 比对催化剂性能的影响----------67
1.2.4. 第四组分对催化剂性能的影响----------68
1.2.5. Ce/Mo 比对催化剂性能的影响----------69
1.3. 反应条件对催化剂性能的影响----------71
1.3.1. 反应温度对催化剂性能的影响----------72
1.3.2. 反应气空速对催化剂性能的影响----------73
1.3.3. 反应气 C_3H_8/O_2 对催化剂性能的影响----------74
1.4. 丙烷选择氧化制丙烯醛催化剂性能比较----------76
第二节 本章小结----------78
参考文献----------80

第三章 Ce-Ag-Mo-P-O 催化剂和 Ag-Mo-P-O 催化剂
性质和结构的比较研究----------81
第一节 实验结果----------82

1.1. Ce-Ag-Mo-P-O 催化剂和 Ag-Mo-P-O 催化剂的相结构表征----------82
1.2. Ce-Ag-Mo-P-O 催化剂和 Ag-Mo-P-O 催化剂氧化还原性表征----------84
1.2.1. 催化剂的 H_2-TPR 和 O_2-TPD 表征----------87
1.2.2. 催化剂的原位共焦显微拉曼光谱表征----------89
1.2.3. 催化剂的 XPS 表征----------91
1.2.4. 催化剂的 EPR 表征----------94
1.3. Ce-Ag-Mo-P-O 催化剂和 Ag-Mo-P-O 催化剂酸碱性表征----------96
1.3.1. 催化剂异丙醇分解反应性能----------97
1.3.2. 催化剂 NH_3-DRIFT 表征----------98
1.4. 助剂 Ce 对可能中间体定向转化为丙烯醛的影响----------100
第二节 讨论----------103
2.1. 助剂 Ce 影响催化剂性质的原因----------103
2.2. 催化剂的性质对催化剂丙烷选择氧化制丙烯醛反应性能的影响 -- 104
第三节 本章小结----------106
参考文献----------107

第五章 Ce-Ag-Mo-P-O 催化剂中 Mo-O 物种（多钼酸根）的动态结构研究
----------110
第一节 实验结果----------111
1.1. Ce-Ag-Mo-P-O 催化剂的原位共焦显微拉曼光谱表征----------111
1.1.1.催化剂在 $C_3H_8/O_2/N_2$ 气氛中不同温度下的原位共焦显微拉曼光谱 111
1.1.2.催化剂在 C_3H_8 气氛中不同温度下的原位共焦显微拉曼光谱-------- 115
1.1.3.催化剂在 O_2 气氛中不同温度下的原位共焦显微拉曼光谱---------- 116
1.1.4.催化剂在 N_2 气氛中不同温度下的原位共焦显微拉曼光谱---------- 117
1.1.5.催化剂在 500 ^oC、不同气氛中的原位共焦显微拉曼光谱---------- 118
1.2 反应前后 Ce-Ag-Mo-P-O 催化剂的 XRD 表征---------- 120