环境和绿色催化(Environment & Green Catalysis)

1、催化加氢脱硫(Catalytic Hydrodesulfurization)

催化加氢脱硫（HDS）部分简介

在现有加氢脱硫过程的基础上对催化剂进行了改进，研制出具有更高脱硫活性或脱硫选择性的新型催化剂，以满足环境法规对于柴油中硫含量越来越严格的要求，实现对柴油的超深度脱硫。我组设计制备了新型的担载型过渡金属磷化物催化剂（MoP/SiO_2、Ni_2P/SiO_2、$Ni\text{-}Mo\text{-}P/SiO_2$），并通过了红外光谱技术对催化剂进行了表征，发现他们对于 DBT 的 HDS 反应活性是 Ni_2P/SiO_2 > $Ni\text{-}Mo\text{-}P/SiO_2$ > MoP/SiO_2，HDS 反应主要通过直接脱硫途径进行，降低了脱硫过程中的氢耗，并且表现出较强的抗硫中毒性能。另外，我组还设计制备了新型的非担载型多金属硫化物催化剂 Ni-Mo-W-S，在对于柴油的 HDS 反应中其表现出了极高的活性。对于这些新型催化剂的研究，为我们在现有的设备上实现柴油的超深度脱硫指明了未来的发展方向。

Introduction of Hydrodesulfurization (HDS)

In recent years, stringent environmental regulations for the sulfur content in diesel fuels have been enacted throughout the world. So several of new HDS catalysts had been designed and prepared by us to achieve ultra-deep desurfurization of diesel. We developed various transition metal phosphides, such as MoP/SiO_2, Ni_2P/SiO_2 and $Ni\text{-}Mo\text{-}P/SiO_2$ and characterized the catalysts by infrared spectroscopy (IR). The HDS activities of the phosphides catalysts follow the order Ni_2P/SiO_2 > $Ni\text{-}Mo\text{-}P/SiO_2$ > MoP/SiO_2. The HDS of DBT mainly occurs through direct desulfurization (DDS) pathway. Further more, we also developed a novel unsupported NEBULA-like Ni-Mo-W sulfide catalyst which exhibited an excellent HDS activity in HDS of diesel. The ultra low sulfur-content diesel (ULSD) could be obtained by this catalyst. Our research results suggested that these new kinds of HDS catalysts are potentially a promising catalyst for hydrodesulfurization processing and deserve to a deep-going research.

2、燃料油乳液催化脱硫（Desulfurization for Fuel Oil in Emulsion Catalysis System）

在最近几十年里，由于环境法规的日益严格，很多关注点都集中在深度燃料油的深度脱

硫方面。虽然加氢脱硫对除去硫醇、硫化物、二硫化物极其有效，但其难以除去二苯并噻吩（DBT）和其一些衍生物，特别是 4、6—二甲基苯并噻吩（4.6-DBT）而达到一个超深度脱硫的效果。将油品的含硫量降低到 0—50ppm 对加氢脱硫是一个挑战。因此发展非加氢脱硫的方法成为需要。在非加氢脱硫中，氧化和萃取的联合使用被认为是一个最有前途的方法。在我们之前的工作中，我们发现了 Q3[PW12O40]和 Q4[H2NaPW10O36]组装在柴油和双氧水中可以选择的氧化含硫的物质生成砜类物质，对双氧水的消耗也只是计量而已。
对于汽油，其主要含硫物质为噻吩，它很难用我们以前的催化剂高效脱除。所以我们正在寻找和设计新的催化剂以实现汽油的氧化脱硫。

In the last decade, much attention has been paid to the deep desulfurization of fuel oils due to more stringent environmental regulations. Although hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides, and disulfides, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethydibenzothiophene (4,6-DMDBT), to an ultra-low level. It is a challenge to reduce the sulfur to 0-50 ppm level to HDS. Therefore, it is highly desirable to develop non-HDS methods to meet the demands of producing clean diesel1 with an extremely low concentration of sulfur-containing compounds. Among them, oxidative desulfurization combined with extraction is considered to be one of the most promising processes. Our previous work found that amphiphilic catalysts, Q3[PW12O40] and Q4[H2NaPW10O36], assembled in an emulsion in diesel, could selectively oxidize sulfur-containing compounds into their corresponding sulfones by using an approximately stoichiometric amount of H2O2 as the oxidant.
To gasoline which mainly contain thiophenes, it can not efficiently be desulfurized by our precious catalyst. So we are going to search and design new catalyst for desulfurizaition of gasoline.

3、光催化氧化脱硫(Photocatalytic Oxidation of sulfur-containing organic molecules)

寻找新的高效光催化剂和溶剂的组合，在光的激发下，将油品中的含硫分子如苯并噻吩或二苯并噻吩氧化成的砜，进一步氧化成为 SO2 或者 H2SO4,这样一方面避免了传统工艺中最后液-液萃取除去产物的步骤，同时也减少了油品的损失。

Upon illumination with light, try to find more efficient combination of photocatalyst/sensitizer and solvent to oxidize sulphone to produce SO2/H2SO4 eventually, which can be gained from oxidation of sulfur-containing molecules in oil such as benzothiophene, dibenzothiophene and so on. In this way, the liquid-liquid extraction used for removing the final products in conventional technics could be avoided, on the other hand the loss of oil could be reduced.

4、吸附超深度脱硫 (Ultra-deep Adsorptive Desulfurization)

由于加氢脱硫方法对于噻吩及其衍生物的脱除并非很有效，为了生产超净燃料油，吸附脱硫的方法是一个不错的选择。利用物理吸附或者化学吸附作用将有机含硫化合物固定在吸附剂上从而将其除去，我们小组已经研究出一些脱硫性能优异的吸附剂，如：改性活性炭，Ni/ZnO 金属氧化物系列以及金属交换改性的分子筛等等。

Because Hydrodesulfurization(HDS) is less effective for aromatic thiophenes and thiophene

derivatives,Adsorptive Desulfurization(ADS) is a good alternative way to produce ultraclean (near zero sulfur) fuel oil. Based on physical or chemical adsorption of organosulfur compounds on the solid sorbent surface,our group have invented some new adsorbents with good desulfurization performance such as modified activated carbon,Ni/ZnO metal oxide system and metal exchanged zeolites etc.