

学 位 論 文 の 要 旨

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学位論文題目	Synthesis of novel manganese-based oxide catalysts for combustion of volatile organic compounds (揮発性有機化合物燃焼用新規マンガン系酸化物触媒の合成)		
学位論文要旨			
<p>Volatile organic compounds (VOCs) released from various chemical industrial processes, transporting sections, necessities manufacturing and human daily activities are severely harmful to environment, animals and plants due to their contributions to air pollution, e.g., photochemical smog, inhalable particles and tropospheric ozone. Among various VOCs purification technologies that have been developed such as catalytic oxidation, incineration, biodegradation, adsorption, wet scrubbing, plasma process and photocatalysis methods, catalytic combustion of VOCs has attracted wide attention owing to its high efficiency, low cost, non-secondary pollution and easy operation. Supported noble metal and non-noble metal oxides are two common catalysts for the catalytic VOCs combustion. However, the former's high price and unsatisfactory stability properties have long been motivating the search and development of the latter. Among non-noble metal oxide catalysts, Mn-based ones have been widely explored due to their tunable multiple valences and excellent redox capacity. However, traditional catalyst synthesis routes are needed to improve and modify in order to adapt to the advanced concepts of high efficiency, environmental protection and innovation advocated by today's society. Therefore, after reviewing the VOCs catalytic oxidation mechanisms and the construction strategies as well as advantages of microscopic heterogeneous structures that seriously affect catalyst performances, this work developed three novel and highly efficient Mn-based catalysts and applied them to the catalytic toluene combustion.</p> <p>Firstly, a novel green pectin-driven sol-gel with an auto-combustion route was successfully applied for the synthesis of manganese oxide catalysts, which exhibited superior catalytic performance for low-temperature combustion of toluene compared to those cases using manganese oxide catalysts synthesized by traditional citric acid and glycine-driven sol-gel routes. The characterization results showed that the MnO<sub>x</sub>-P catalyst synthesized by the present method exhibited a unique hierarchical mesoporous structure with lower crystallinity and smaller grain size, leading to abundant active species and defect structures. Comparing with the catalysts synthesized by those traditional sol-gel methods, the MnO<sub>x</sub>-P catalyst had excellent low-temperature reducible performance and better oxygen mobility, which is considered to be resulted from the specific interaction of chelation and calcination processes. In addition, the MnO<sub>x</sub>-P catalyst exhibited satisfactory long-term stability and water tolerance during catalytic toluene combustion process.</p>			

Secondly, for the first time, a nanosheet-state CoMnx mixed oxide with multifarious active regions was synthesized by oxidation-etching assembly of metal organic framework (MOF) precursor and applied for catalytic combustion of toluene at low temperatures. The obtained optimum catalyst denoted as CoMn6 showed excellent performance, which achieved 90% conversion of 1,000 ppm toluene under a weight hourly space velocity (WHSV) of  $60,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  at  $219^\circ\text{C}$ . While, it also exhibited long-term stability with strong water resistance property. The characterizations of physicochemical properties indicated that the oxidation-etching assembly process built an abundant mesoporous structure in the CoMnx catalyst, which greatly increased the specific surface area (SSA). Especially, potassium permanganate as oxidant and manganese source led to uniform dispersion and assembling of cobalt atoms, which caused the generation of low-crystallinity CoMnx mixed oxide with abundant dislocations, vacancies, phase interfaces and amorphous structures, resulting in excellent low-temperature reducibility, outstanding lattice oxygen mobility and abundant active species such as  $\text{Mn}^{3+}$ ,  $\text{Co}^{3+}$  and adsorbed oxygen species. Density functional theory (DFT) calculations demonstrated that gaseous oxygen with the longer bond length ( $1.406 \text{ \AA}$ ) and stronger adsorption energy ( $-4.443 \text{ eV}$ ) could be adsorbed and activated well on the  $\text{MnCo}_2\text{O}_{4.5}$  (311) plane, which is beneficial for the toluene oxidation. In situ diffuse reflectance infrared spectroscopy (DRIFTS) technique was applied to track the intermediates of toluene combustion under different atmospheres, which further deduced the contributions of different active regions and oxidation mechanism over the CoMnx catalyst. The present facile strategy of oxidation-etching assembly of the MOF precursor for the creating of novel catalyst with high performance could be applied in a wide variety of materials besides VOC combustion catalysts.

Finally, a nanoparticles-stacking MnCox oxide with multifarious active phases was successfully synthesized by a starch- paste assisted method, which achieved complete combustion of 1,000 ppm toluene at  $226^\circ\text{C}$ . The characterization results showed that by using this method, it resulted in not only the construction of the porous structure but also successful enrichment of active species such as trivalent manganese, trivalent cobalt and electrophilic oxygen species, thanks to the intensive interaction of Mn and Co species with the assistance of starch-paste. The special metal dispersibility and valence adjustment functions of starch contributed to the production of multifarious active phases with amazing reducibility as well as oxygen mobility at lower temperature. In situ DRIFTS experiments and DFT calculation results showed that the synergistic complementary regions provided vibrant lattice oxygen and the reproducible electrophilic oxygen species for toluene combustion, guaranteeing the continuous and efficient catalytic performance. This study provides a new viewpoint and idea for creating of novel catalysts with multiple active regions.