

学 位 論 文 の 要 旨

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学位論文題目	Synthesis novel catalysts with low crystallinity for effective elimination of volatile organic compounds (VOCs)（揮発性有機化合物（VOC）を効果的に除去するための低結晶化度の新規触媒の調製）		
<p>学位論文要旨</p> <p>Volatile organic compounds (VOCs), classified as major contributors to hazardous pollution, are harmful to human health as well as atmosphere. Therefore, it is highly desired to control the emissions of VOCs. So far, various processes such as biodegradation, adsorption and absorption, plasma-catalysis, photocatalytic oxidation, wet scrubbing and catalytic oxidation have been developed and applied for the VOC elimination. Among them, catalytic oxidation is considered as the most effective alternative because it has no harmful byproducts and can be operated at relatively low temperatures. However, the development of high-performance catalysts for the total VOCs oxidation plays the key role in the removal efficiency with low energy consumption. Due to the high cost and sintering of noble metal, transition metal oxide catalysts with high activity and low cost is necessary for the large-scale applications. Generally, transition metal oxide catalysts are limited owing to their higher operation temperature compared to the supported noble-metal ones. However, the catalytic activity can be tuned by adjusting morphology, specific surface area, oxygen species and so on. Therefore, it is important to design transition metal oxide catalysts for further promoting the catalytic performance. As we all known, oxygen vacancy defect (OVD) engineering has been recognized as an effective strategy to prepare high-performance catalysts for VOCs oxidation since the generated oxygen-deficient sites could lead to an unbalanced electronic structure, resulting in rapid electron transfer in the catalysts and thereby reducing the reaction temperature. Herein, a series of new effective strategies to prepare the oxide catalysts with low crystallinity were designed and applied for increasing the concentration of OVDs. Furthermore, in order to further improve the catalysts activity, the relationships between the correlating physiochemical properties and performance were explored to investigate the reaction mechanism and oxidation pathways.</p> <p>Firstly, a facile agar-gel method was successfully applied to prepare a series of homogenous Mn-Co mixed oxides for highly efficient catalysis of total toluene oxidation. The obtained Mn₂Co₁ mixed oxide exhibited a high catalytic activity with T_{50%} of 228 °C and T_{100%} of 238 °C as well as high tolerability even under 20 vol.% water vapor environments. It was found that the obtained optimum Mn₂Co₁ mixed oxide had high specific surface area, large amounts of Co³⁺, Mn³⁺, and Mn⁴⁺ species, abundant adsorbed oxygen species, rich lattice defects, high reducibility at low temperature, and excellent O₂ adsorption ability. Meanwhile, <i>in situ</i> DRIFTS spectra measurements confirmed the generated intermediates at different environments during the toluene oxidation and revealed that both adsorbed oxygen and lattice oxygen species could simultaneously participate in the toluene adsorption-oxidation process, especially the rate-controlling step should be the C=C breakage of aromatic ring. It is expected that the present</p>			

agar-gel method with low cost and convenient operation could be widely applied for the designing of novel mixed metal oxides catalysts for VOCs oxidation.

Secondly, in this study, a series of holmium (Ho)-doped octahedral molecular sieve (OMS-2) catalysts with abundant active oxygen species were successfully synthesized via a facile redox co-precipitation route for the oxidation of toluene. The introduction of trace Ho species during the OMS-2 synthesis process resulted in not only larger surface area and more amorphous phases formation but also abundant active oxygen species, especially oxygen vacancies in the final Ho-doped OMS-2 by the delamination of OMS-2. EPR and XPS analyses were applied to confirm the generated oxygen vacancies and the elemental valences related to the active oxygen species on the catalyst surface. As a result, the 0.5% Ho-OMS-2 showed much higher catalysis performance ($T_{100\%} = 228\text{ }^{\circ}\text{C}$ even under 5 vol.% H_2O vapor) than the OMS-2 for the toluene oxidation. Meanwhile, *in situ* DRIFTS analyses demonstrated that the oxidation of toluene was greatly facilitated on the 0.5% Ho-OMS-2 owing to the abundant active oxygen species on the surface, and benzyl, benzyl alcohol, benzaldehyde, benzoate, maleic anhydride, and carbonates were the main intermediates during oxidation of toluene at relatively low temperatures. Compared with the reported Mn-based catalysts, the as-prepared 0.5% Ho-OMS-2 exhibited lower 100% conversion temperature based on the excellent physiochemical properties. Therefore, in order to further decrease the conversion temperature, other transition metal oxide catalysts should be applied.

Finally, a series of samarium (Sm) doped cerium oxide ($x\%$ Sm/ CeO_2) catalysts were prepared by pyrolysis of Sm containing Ce-based metal organic framework (Sm/Ce-MOF) precursor and applied for catalytic oxidation of toluene. The obtained catalysts were characterized by SEM, TEM, XRD, BET, Raman, XPS, H_2 -TPR, O_2 -TPD, and their catalytic activities were evaluated by oxidation of toluene over them. It was found that doping of Sm increased the concentration of oxygen vacancy as well as the low temperature reducibility, thereby improved the catalytic performance. Moreover, among the prepared Sm doped CeO_2 catalysts, the 1% Sm/ CeO_2 catalyst showed the best performance for the oxidation of toluene with conversions of 50% and 100% at temperatures of 194 and 222 $^{\circ}\text{C}$ respectively under a WHSV of 60,000 mL/(g·h). In addition, the 1% Sm/ CeO_2 catalyst also exhibited excellent stability and high toleration to the moisture.