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铈基催化剂水中苯酚催化湿式氧化的研究

Catalytic Wet Air Oxidation (CWAO) of Phenol on Cerium  
Based Catalysts

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**Catalytic Wet Air Oxidation (CWAO) of Phenol on Cerium  
Based Catalysts**

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## 摘要

催化湿式氧化(CWAO)是一种有效的处理工业废水手段,尤其在针对高毒性含酚废水方面,可以解决生物法难以应对的问题。稀土金属氧化物  $\text{CeO}_2$  在 CWAO 处理苯酚的应用较为普遍,可以作为活性中心、助剂、载体。由于苯酚的降解是在水中进行,水对催化剂的影响至关重要。理论计算发现,  $\text{CeO}_2$  表面的缺陷有助于产生较为稳定的羟基。然而,这方面的研究仅处于理论方面,在 CWAO 处理苯酚领域更没有进行过相关的研究。因此,本论文以此为突破口,重点研究了铈基催化剂的结构与表面性质对 CWAO 处理苯酚的影响。

首先,基于目前对  $\text{CeO}_2$  催化剂在苯酚氧化领域的认识,通过水热法合成了具备不同表面氧缺陷的纳米棒状、立方体  $\text{CeO}_2$  催化剂,旨在研究表面氧缺陷对苯酚催化湿式氧化的影响。研究发现,具备更多表面氧缺陷的纳米棒状  $\text{CeO}_2$  可以更有效地降解苯酚。通过 TEM、XPS、TPR 等表征手段证明表面氧缺陷有助于促进  $\text{Ce}^{4+}$  和  $\text{Ce}^{3+}$  之间的转换,提高催化剂的氧化还原能力,使催化剂的表面氧化能力更强。

为进一步研究  $\text{CeO}_2$  催化剂表面氧缺陷对苯酚催化湿式氧化的影响,本文对纳米棒状  $\text{CeO}_2$  进行了后续处理,制备出含有不同氧缺陷和  $\text{Ce}^{3+}$  含量的催化剂。研究发现  $\text{H}_2\text{O}_2$  超声处理可以溶解  $\text{CeO}_2$  催化剂表面的  $\text{Ce}^{3+}$ ,增加表面  $\text{Ce}^{3+}$  浓度,降低  $\text{CeO}_2$  的禁带宽度,并生成更多的氧缺陷。大量的氧缺陷团簇又提升了表面氧的移动性,促进催化剂表面  $\text{Ce}^{4+}$  和  $\text{Ce}^{3+}$  之间的转换,降低催化剂表面还原温度,提升催化剂表面氧化能力。同时,  $\text{H}_2\text{O}_2$  超声处理后的纳米棒状  $\text{CeO}_2$  表面羟基含量也有所增加,进一步提高了催化剂的氧化性能。不同方法处理后的纳米棒状  $\text{CeO}_2$  对苯酚催化湿式氧化也有不同的活性。结合 XPS 和活性数据可以发现随着催化剂  $\text{Ce}^{3+}$  的增加,苯酚氧化的活性也在增加。经过  $\text{H}_2\text{O}_2$  超声处理后的纳米棒状  $\text{CeO}_2$  含有最高的  $\text{Ce}^{3+}$  比例,其催化活性也最高。

$\text{CeO}_2$  的掺杂是另一种制造氧缺陷的手段,同时还增加了双金属相互作用,从根本上提高催化剂的效率。研究了向纳米  $\text{CeO}_2$  中掺杂 Mn 元素,合成了纳米棒状和立方体  $\text{MnO}_x\text{-CeO}_2$  催化剂。结果显示,纳米棒状  $\text{MnO}_x\text{-CeO}_2$  催化剂拥有

更多的表面氧缺陷，提高了催化剂表面的氧化还原能力，并产生了更多的活性氧物种。同时，还发现纳米棒状比纳米立方体  $\text{MnO}_x\text{-CeO}_2$  形成的固溶体更均匀，有更多的 Mn 进入 Ce 的晶格中，说明纳米棒状  $\text{MnO}_x\text{-CeO}_2$  催化剂形成了更多的  $\text{-Mn-O-Ce-}$  键和 Mn/Ce 界面，从而导致了完全不同 Mn/Ce 电子传递。除此之外，纳米棒状  $\text{MnO}_x\text{-CeO}_2$  催化剂表面有较多的  $\text{Mn}^{4+}$ ，而纳米立方体  $\text{MnO}_x\text{-CeO}_2$  催化剂以  $\text{Mn}^{2+}$  为主。这些特性使纳米棒状  $\text{MnO}_x\text{-CeO}_2$  催化剂可以更有效地将苯酚及其中间产物完全氧化。

催化剂的失活是苯酚催化湿式氧化中所面临最大的挑战。研究发现上述  $\text{CeO}_2$  和  $\text{MnO}_x\text{-CeO}_2$  催化剂虽然具备较高的催化氧化活性，但在反复使用后活性减少明显。因此，本文通过水热浸渍法合成了一种新型的  $\text{Pt/CeO}_2\text{-TiO}_2$  催化剂。研究发现，不同的 Ce 含量会直接影响催化剂的活性和稳定性。当 Ce 含量为 3 wt.% 时， $\text{Pt/CeO}_2\text{-TiO}_2$  催化剂的活性最高，且在反应 5 次后依然保持 91% 的 TOC 转化率。对催化剂进行表征后发现，当 Ce 含量为 3 wt.% 时，Pt 的纳米颗粒粒径最小，提高了贵金属 Pt 的利用率，同时还增加了催化剂的氧化能力。另外，还发现  $\text{Pt/CeO}_2\text{-TiO}_2$  催化剂体相  $\text{Ce}^{4+}$  还原温度随着 Ce 含量的增加而增加，有明显的趋势。说明不同的 Ce 含量可导致不同的晶格氧移动性，而 Ce 含量为 3 wt.% 时，晶格氧的移动性能最为适宜，不但可以保证足够的氧传递，还可以避免 Pt 的过氧化。另外，元素分析还证明 Ce 含量为 3 wt.% 时催化剂表面积碳量最低，降低了活性中心被覆盖的几率，从而导致了高稳定性。

**关键词：**铈基催化剂；苯酚催化湿式氧化；纳米催化剂；氧缺陷；复合金属氧化物；催化剂稳定性； $\text{MnO}_x\text{-CeO}_2$

## Abstract

Catalytic wet air oxidation (CWAO) is an effective technique to treat industrial wastewater, especially for highly toxic phenolic streams, where bio-treatment is often less practical. Ceria is a common rare-earth metal oxide, which is widely used as active center, promoter, and support in CWAO of phenol. Since phenol oxidation is carried out in aqueous condition, the effect of water has to be taken into consideration. Theoretical studies have shown that water can be converted into stable hydroxyl groups on oxygen vacancies from the surface of ceria. This effect is expected to have large impact on CWAO of phenol. However, it is not reported in the literature. Herein, this thesis start from the effect of oxygen vacancies on phenol oxidation, and studied the physic-chemical properties of cerium based catalysts on CWAO of phenol.

First, based on the current knowledge about the application of cerium based catalysts on CWAO of phenol, we have developed nano-structured CeO<sub>2</sub> with different amount of oxygen vacancies, and used for phenol oxidation. It was found that CeO<sub>2</sub> nanorods contain greater amount of oxygen vacancies and resulted higher catalytic activity toward phenol oxidation. Characterizations including TEM, XPS, TPR have proved that the presence of oxygen vacancies can promote the transition between Ce<sup>4+</sup> and Ce<sup>3+</sup>, which can increase the redox properties of CeO<sub>2</sub> and make catalyst surface more oxidizing.

In order to further investigate the effect of oxygen vacancies on CWAO of phenol, we have used various methods to treat CeO<sub>2</sub> nanorods, and synthesized catalysts with different amount of oxygen vacancies and Ce<sup>3+</sup> concentration. It was found that CeO<sub>2</sub> nanorods treated in H<sub>2</sub>O<sub>2</sub> with sonification can dissolve surface Ce<sup>3+</sup>, increase Ce<sup>3+</sup> fraction, decrease the band gap of CeO<sub>2</sub> nanorods, and create more oxygen vacancies. The oxygen vacancy clusters can promote the transition between Ce<sup>4+</sup> and Ce<sup>3+</sup>, and improve the oxidizing ability of CeO<sub>2</sub> nanorods surface. Meanwhile, H<sub>2</sub>O<sub>2</sub> sonification treatment also increased the concentration of surface hydroxyl group, which can improve the catalytic activity. CeO<sub>2</sub> nanorods treated with

various methods displayed different catalytic activities on CWAO of phenol. The results suggested that catalytic activity is directly related to the concentration of  $\text{Ce}^{3+}$ .  $\text{CeO}_2$  nanorods treated in  $\text{H}_2\text{O}_2$  with sonification showed highest  $\text{Ce}^{3+}$  fraction and phenol oxidation activity. This is due to the increased oxygen mobility by oxygen vacancies.

Doping is another technique to increase the amount of oxygen vacancies on ceria. Meanwhile, the interactions between metal oxides can also improve catalytic activity. Mn was doped into nano-ceria to produce  $\text{MnO}_x\text{-CeO}_2$  nanorods and nanocubes. The results showed that  $\text{MnO}_x\text{-CeO}_2$  nanorods have more surface oxygen vacancies, which improved the redox properties of  $\text{MnO}_x\text{-CeO}_2$  and created more active oxygen species. It was also discovered that  $\text{MnO}_x\text{-CeO}_2$  nanorods can form more homogeneous solid-solution than  $\text{MnO}_x\text{-CeO}_2$  nanocubes, and more Mn have entered Ce lattice to form -Mn-O-Ce- bonds. Different Mn/Ce interactions have also caused different electron transfer ability between Mn and Ce, where  $\text{MnO}_x\text{-CeO}_2$  nanorods contain higher amount of  $\text{Mn}^{4+}$  and  $\text{MnO}_x\text{-CeO}_2$  nanocubes have greater  $\text{Mn}^{2+}$  concentration. These characteristics enabled  $\text{MnO}_x\text{-CeO}_2$  nanorods to have the highest catalytic activity amount all the catalysts studied.

Deactivation of catalyst is a big challenge for CWAO of phenol. The above catalysts were recycled and used for several times. It was found that  $\text{CeO}_2$  and  $\text{MnO}_x\text{-CeO}_2$  catalysts deactivated after the first reaction. By summarizing the literature, we have synthesized  $\text{Pt/CeO}_2\text{-TiO}_2$  catalysts through hydrothermal impregnation method. The results suggested that the amount of Ce loading can directly affect the activity and stability of  $\text{Pt/CeO}_2\text{-TiO}_2$  catalyst. When Ce loading is 3 wt.%, the catalyst has highest activity and stability, where the TOC conversion remains 91% after 5 consecutive reactions. Different characterizations revealed that 3 wt.% of Ce gives smallest Pt particles, which improves the utilization of Pt and enables  $\text{Pt/CeO}_2\text{-TiO}_2$  catalyst with the highest oxidation ability. Furthermore, the reduction temperature of the bulk  $\text{Ce}^{4+}$  is directly related to the amount of Ce loading.



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