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「課程博士用」

学 位 論 文 の 要 旨

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学位論文題目	Efficient transition metal oxides-based catalysts for the catalytic oxidation of volatile organic compounds (VOCs)（揮発性有機化合物（VOCs）の酸化分解用高性能遷移金属酸化物ベース触媒の開発）		

学位論文要旨

In this work, transition metal oxides-based catalysts were investigated and used for the catalytic oxidation of VOCs. In order to improve the catalytic activity of Co_3O_4/NF (Nickel foam) catalyst, firstly, we prepared a series of hetero-metal doped Co-based catalysts by using facile electrodeposition method, and the effect of different metal doping on the catalytic performance of toluene was investigated. It was found that hetero-metal doping significantly influenced the morphology and surface elemental compositions of Co-based catalyst, but over doping of hetero-metals such as Ni and Mn elements content made a negative influence on the catalyst structure. H_2-TPR and O_2-TPD analysis results suggested that the hetero-metal doping enhanced the low temperature reducibility and resulted in the formation of lattice defects, which are favorable to generate more easily reducible species and facilitate the oxygen mobility, thereby improved the performance for the catalytic oxidation of toluene. Especially, when compared with pure Co_3O_4/NF catalyst, mixed metal oxides based catalyst of Co-Cu/NF exhibited much lower toluene conversion (T_{90}) of around 248 ºC, which should be contributed by its low-temperature reducibility, increased surface and lattice oxygen species, and high content of active Co^{3+} species promoted by the interaction of the mixed metal oxides.

Based on the first work, we used the same method to prepare Ce modified Co-based catalysts for the catalytic oxidation of toluene. The catalysts of Co-Ce mixed oxides supported on three-dimensional NF by using a unipolar pulse electro-deposition (UPED) in the solutions of Co $(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ with molar ratios of Co to Ce (Co/Ce) of 15:1, 10:1, and 5:1, respectively. The experimental results showed that Co-Ce mixed oxide with a well nanosheet structure could be uniformly deposited on NF support. H_2-TPR analysis indicated that Ce doping improved the reducibility of Co-Ce/NF catalyst due to the synergistic effect between Co and Ce. In the toluene catalytic oxidation, the 10Co-Ce/NF catalyst prepared with a molar ratio of Co/Ce at 10 achieved the best catalytic performance among all the catalysts with a complete toluene conversion temperature of 268 ºC and CO_2 selectivity of 100%. This can be contributed to the superior physiochemical properties of uniform nanosheet structure, increase of surface and lattice active oxygen species at low temperatures, high content of Co^{3+} active species with high oxygen vacancies and Ce^{4+}/Ce^{3+} redox couples in the catalyst.

Cerium oxide (CeO_2) has been proved to be active to the catalytic oxidation. Consequently, catalysts of Ag-CeO_2@CNWs/CF were designed and applied for the catalytic oxidation of toluene. The catalysts with different Ag loading amount was prepared by applying a three-step electrochemical process, in which copper nanowires (CNWs) were generated on the surface of CF (Cu foam) by an electro-oxidization process at first and then, CeO_2 was uniformly coated on the

CNWs by a UPED method and finally highly dispersed Ag nanoparticles were embedded on the surface of CeO_2 using a constant voltage electrodeposition method. It is found that the suitable Ag loading amount effectively enhanced the low-temperature reducibility, the generation of oxygen vacancies, and distribution of surface acid sites, which are favorable to the catalytic oxidation of toluene. Especially, the obtained 80Ag-CeO_2@CNWs/CF catalyst with an electrodeposition time of 80 s for Ag loading exhibited the best catalytic activity with the T_{10}, T_{50} and T_{90} of toluene conversion at 222, 240 and 256 ºC, respectively. Long-term stability tests indicated that the 80Ag-CeO_2@CNWs/CF catalyst had good stability and water resistance ability.

Finally, in order to investigate the influence of the catalyst supports of NF and CF on the catalytic performance of the prepared catalysts, the Mn-Co mixed metal oxides as active species were prepared and applied for the catalytic oxidation of toluene. We fabricated a series of Mn-Co/CF catalysts with different molar ratio of Mn/Co in the initial solution for the electrodeposition. SEM images displayed that Mn-Co mixed metal oxides were uniformly coated on the Cu nanowires by the electrochemical method. The intimate contact between Mn and Co nanocrystals was found by HRTEM, which is important for realizing synergetic effects on improving catalytic activity. Meanwhile, the formation of the active surface oxygen species and the increase of the active species of Mn^{4+} and Co^{3+} were considered to make significant contribution to the catalytic oxidation of toluene. The catalyst with Mn-Co mixed metal oxides exhibited higher performance than the single metal oxides, and especially 0.10Mn-0.01Co/CF catalyst with the Mn/Co molar ratio of 10:1 achieved the highest catalytic activity with a low toluene conversion temperature (T_{90}) of 251 ºC, and displayed excellent catalytic stability even in the presence of water vapor. However, Mn-Co mixed oxides based catalysts which prepared by using un-pretreated CF (without electro-oxidation) and NF supports performed poor catalytic activity when compared the optimum catalysts of 0.10Mn-0.01Co/CF. Consequently, catalysts prepared by CF support which possesses nanowires was more favorable to the catalytic oxidation of toluene in this work.

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