Influence of Co addition on Ni-Co mixed oxide catalysts toward the deep oxidation of low-rank unsaturated hydrocarbons

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1. Introduction

During gasoline combustion, a great amount of pollutants including volatile organic compounds (VOCs) and other toxic emissions are released to the atmosphere [1]. Among VOCs type, olefins are known to affect emissions differently, which could thereby alter the strategies of atmospheric pollution control [2]. Therefore, methods and processes capable to eliminate VOCs are urgently needed. Catalytic oxidation can totally degrade VOCs into CO₂ and H₂O [3], and thus attracts a great attention. Among catalysts, most considerable attention has been paid to transition metal oxides (TMOs). An appropriate composition of Ni-Co bimetal oxides can form spinel nickel cobaltite (NiCo₂O₄) that should lead to the promising improvement of the catalytic performance of the resulted materials as a highly active and stable catalyst in the reaction of deep oxidation of olefins. Favorable effect of Co addition during the catalytic oxidation of VOCs including olefins was observed [4,5]. Within this context, pure Co₃O₄, NiO and Ni-Co mixed oxide including NiCoO₂ and NiCo₂O₄ were controllably synthesized, characterized and applied as catalyst toward oxidation of low-rank unsaturated hydrocarbons. Explanation has been suggested to understand the reaction process and the enhancement of the catalytic oxidation performance of Ni-Co bimetal oxides catalysts.

2. Results

The X-ray diffraction (XRD) indicates that NiO, Co₃O₄, NiCoO₂ and NiCo₂O₄ catalyst were obtained no further peaks which can be ascribed to impurities were observed, attesting to the purity and the good crystallinity. The morphology of samples revealed thin films displaying sphere-like nanocrystals with variable particles size in general, and the mixed oxide (NiCo₂O₄) the film is well aggregate smallest grains with an open porosity. Meanwhile, the chemical composition analysis confirmed the presence of Co, Ni and O species with respective ratio of their oxidation state Co²⁺/Co³⁺, Ni²⁺/Ni³⁺, and the surface-adsorbed oxygen (O_{Ads.}) to lattice oxygen (O_{Lat.}) species ratio increasing with Co content on the the Ni-Co oxides phase. When tested as catalysts towards the total oxidation of olefins, superior to pure oxide, Ni-Co binary oxides exhibit remarkable catalytic performance and stability. NiCo2O4 thin films catalyst with the highest OAds/OLat ratio of 1.35 and the large population of solid-state redox couple (Co³⁺/Co²⁺ and Ni³⁺/Ni²⁺) shows excellent performances over the temperature range of 100–260 °C for the C₂H₂ conversion and 100-350 °C for C₃H₆. In that contest, the performance of single phases (Co₃O₄ and NiO) and their mixed phase (NiCoO₂ and NiCo₂O₄) were therefore be analyzed here in respect to the participation of surface-active sites such as Co²⁺, O_{Ads.} And O_{Lat.} species, and thin films microstructure and morphology in the reaction process. Therefore, the excellent performance of NiCo₂O₄ could be associated with its higher surface oxygenated species concentration and good lattice oxygen mobility as consequence of the predominance of surfaces actives sites $(Co^{3+}, Co^{2+}, Ni^{3+} and Ni^{2+})$.



Fig. 2: XRD patterns of a) Co₃O₄, b) NiCo₂O₄, c) NiCoO₂, d) NiO.

Fig. 2: Ligth-off curves of C2H2 total oxidation on the overall catalyst

To further highlight the remarkable catalytic performance of the NiCo₂O₄ for the combustion of selected olefins, the performance of the best catalyst in this work was compared to that of the other catalysts reported in the literature. Obviously, NiCo₂O₄ catalyst exhibit much better performance compared to other TMOs and some noble metals catalyst base on the gas composition and the T_{50} and T_{90} values.

3. References

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