Co_3O_4 morphology and supported catalysts for total oxidation of methylbenzene

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Abstract: Co_3O_4 morphology catalysts, including cube and sphere, and Co_3O_4 cube supported on YSZ and TiO_2 catalysts were prepared by one step hydrothermal method. Their physicochemical and redox properties were characterized by ICP-OES, N_2 sorption, XRD, SEM, HR-TEM and H_2-TPR. Their catalytic performances were evaluated for the total oxidation of methylbenzene (MB). Co_3O_4 cube catalyst presented higher MB catalytic activity than Co_3O_4 sphere one, despite its very close crystallographic structure, physicochemical and redox properties, which could be attributed to the morphology and surface termination effects.

Keywords: Co_3O_4 morphology, oxidation, methylbenzene.

1. Introduction

One of the major challenges of today is the degradation of air quality by the release of volatile organic compounds into the air after the combustion of fossil fuels. Catalytic oxidation is regarded as the most promising technology to reduce the emissions of pollutants with low energy consumption and with selective conversion into harmless molecules. Moreover, the most important factor is to design and prepare the catalysts. Thus, the researchers are focused on the relationship between the catalytic reaction activity and the morphology and surface termination[1,2].

2. Experimental

Co_3O_4 morphology catalysts, including cube and sphere, and Co_3O_4 cube supported on YSZ and TiO_2 catalysts were prepared by one step hydrothermal process with different amount of $Co(NO_3)_2 \cdot 6H_2O$ and NaOH[3]. The synthesized Co_3O_4 morphology catalysts, together with Co_3O_4 cube supported on YSZ and TiO_2 catalysts were characterized and tested in the MB total oxidation, in order to evaluate the influence of the morphology on both physicochemical and redox properties and catalytic activity.

3. Results and discussion

SEM images have demonstrated that the morphology of Co_3O_4 was strongly depended on the amount of precursor during the preparation (Figure 1). The Co_3O_4 cube exposed {001} planes, according to the HRTEM analysis, with the particle size of 300 nm, while the Co_3O_4 sphere had the average particle size of 600 nm. Co_3O_4 morphology catalysts presented two reduction peaks[4], while the Co_3O_4 commercial catalyst showed an overlap peak. This could be inferred that the Co_3O_4 cube and sphere had a better reducibility than Co_3O_4 commercial. Moreover, preliminary characterization results showed the Co_3O_4 cube supported on TiO_2 and YSZ catalysts showed a higher specific surface area (61 and 13 m^2g^{-1}, respectively) than raw Co_3O_4 cube catalyst (7 m^2g^{-1}). The formation of the Co_3O_4 cube phase on the different supports was confirmed by XRD. In addition, H_2-TPR profiles (not shown) showed the reducibility varied as follows: Co_3O_4/YSZ > Co_3O_4 > Co_3O_4/TiO_2. The reduction peak shifted to higher temperature, nearly 400ºC, in presence of TiO_2 as catalytic support of Co_3O_4 particle, while YSZ supported catalyst showed a reduction temperature peak close to that of the raw Co_3O_4 cube.

The Co_3O_4 cube had shown better MB catalytic activity than that of the Co_3O_4 sphere and the commercial one (Figure 2). With the same profiles in XRD and H_2-TPR, Co_3O_4 cube and Co_3O_4 sphere presented almost the same crystallographic structure and redox properties. Therefore, the different catalytic activity should be attributed to the morphology and surface termination effects. Then, the cube structure exposed {001} planes, with Co^{2+} cations on the surface, acted as the active site of the total oxidation reaction, increasing the catalytic activity[5]. Moreover, MB catalytic activity of the Co_3O_4 supported catalyst showed the improved performance of the YSZ supported catalyst by decreasing the temperature of 20°C, while TiO_2 supported catalyst showed an opposite effect on the MB total oxidation, even worse to that of the raw Co_3O_4 cube. The presence of YSZ support induced surface interactions between its oxygen vacancies and Co_3O_4 particles and higher mobility of oxygen ions from YSZ toward the surface of the support, which probably introduced highly reactive active sites that allowed the catalytic reaction[6,7].

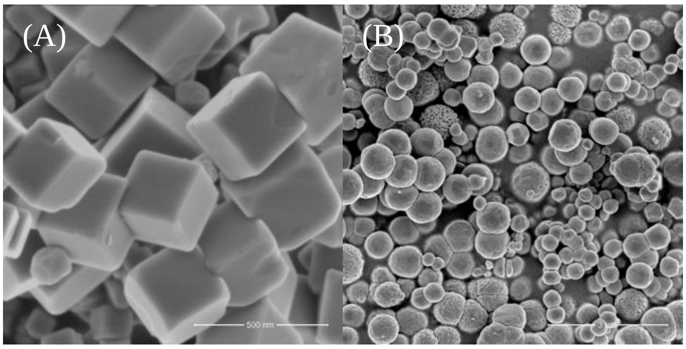

Figure 1. SEM images of Co3O4 (A) cube, (B) sphere

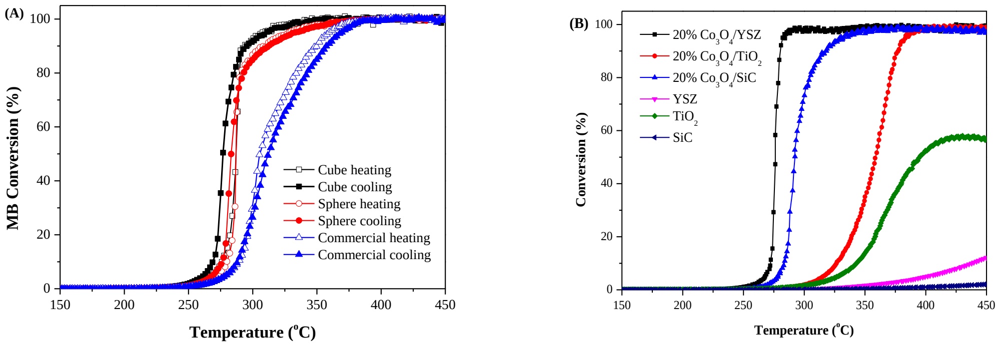

Figure 2. Light-off for MB total oxidation of Co_3O_4 (A) morphology and (B) supported catalysts, during the cooling ramp.

4. Conclusions

The influence of the morphology and the surface termination of Co_3O_4 crystallite on the physicochemical properties and catalytic performance on MB total oxidation was evaluated. MB catalytic activity followed the order of Co_3O_4 cube > Co_3O_4 sphere > Co_3O_4 commercial. The highest activity Co_3O_4 cube catalyst was related to the higher amount of Co^{2+} cations on the surface of this catalyst, which promoted the oxidation reaction. Moreover, one step hydrothermal synthesis of Co_3O_4 supported catalysts modified their physicochemical and redox properties. However, only in presence of YSZ as a catalytic support, the MB catalytic activity was increased, which could be probably attributed to the Co_3O_4-support interaction and the oxygen vacancies of the YSZ. Nevertheless, the isotopic exchange experiments will be performed in order to better understand this different behaviors.

References

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