An efficient heterostructured Ru/Co₃(PO₄)₂-MCFs catalyst for catalytic oxidation of vinyl chloride and CO

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Introduction

During the industrial production process of polyvinyl chloride (PVC), large amount of vinyl chloride (VC) with low concentration are emitted, which is greatly harmful to environment and public health. Catalytic oxidation is considered as one of the most promising technologies for purification of the chlorinated VOCs.

 $Co_3(PO_4)_2$ was previously considered as an inert support or catalyst for VOCs oxidation. In this work, an efficient heterostructured Ru/Co₃(PO₄)₂-MCFs catalyst was developed for catalytic oxidation of VC and CO, in which Ru/Co₃(PO₄)₂-MCFs catalyst exhibited much higher catalytic activity than Ru/MCFs and Ru/Co₃(PO₄)₂ catalysts.

Materials and Methods

Heterostructured Co₃(PO₄)₂-MCFs support was prepared by the in-situ growth method as follow [1, 2]: MCFs was added into the deionized water containing the cobalt precursor. After completely evaporating water in a vacuum condition, the product was calcined in air to obtain CoOx-MCFs. CoOx-MCFs was added into the deionized water containing potassium dihydrogen phosphate as the phosphorus source, which was further stirred at 25 °C for 24 h. Then the suspension was washed with the deionized water for several times by centrifugation, and the precipitate was separated to dry overnight at 80 °C. Ru-based catalyst was prepared by the impregnation method with ethanol aqueous solution of RuCl₃. The nominal metallic Ru loadings of all catalysts were 1 wt.% of the support weight. The experiments for evaluation of catalytic activity were investigated in a fixed-bed continuous-flow reactor with 0.1 vol.% VC/Air at GHSV = 48,000 mL (h g_{cat})⁻¹.

Results and Discussion

The light-off curves of catalytic oxidation of VC and CO are shown in **Figure 1** (T_{50} and T_{90} , corresponding to the reaction temperatures at 50% and 90% of VC and CO conversion). Ru/Co₃(PO₄)₂-MCFs catalyst exhibited the best catalytic performance for VC oxidation (T_{50} =244 and T_{90} =280°C) or CO oxidation (T_{50} =90 and T_{90} =98°C), which had an obvious improvement compared with Ru/MCFs catalyst. Ru/Co₃(PO₄)₂-MCFs catalyst showed better catalytic performance for CO oxidation than Ru/MCFs catalyst.

As shown in **Figure 1**, $Co_3(PO_4)_2$ showed very low catalytic activity for VC oxidation, even after impregnation with 1 wt.% Ru. Compared with $Co_3(PO_4)_2$ and MCFs, heterostructured $Co_3(PO_4)_2$ -MCFs support was featured predominantly by more acid amount and stronger acidity brought by rod-like $Co_3(PO_4)_2$ nanocrystals (about 50 nm in width) grown on the surface of MCFs with high surface area, which was revealed by NH₃-TPD. That was one possible reason for this observed difference in catalytic activity induced by the support.



Figure 1. Light-off curves of catalytic oxidation of VC and CO.



Figure 2. NH₃-TPD profiles of the supports and TEM images of Ru-based catalysts.

On the other hand, because of the unique properties of nanosized phosphates, $Co_3(PO_4)_2$ -MCFs support had a stronger interaction with Ru nanoparticles than other supports. The surface area of Ru/Co₃(PO₄)₂-MCFs sample was 345 m²/g, which was similar to that of $Co_3(PO_4)_2$ -MCFs sample. But there was a sharp decrease from 565 m²/g of MCFs sample to 365 m²/g of Ru/MCFs sample. TEM images also showed clearly that Ru was supported on the surface of MCFs, whereas almost no variation was observed on Ru/Co₃(PO₄)₂-MCFs. Moreover, TPR profiles of H₂ and CO provided further evidences for the stronger interaction between Ru nanoparticles with heterostructured $Co_3(PO_4)_2$ -MCFs support.

Significance

Heterostructured Ru/Co₃(PO₄)₂-MCFs catalyst showed better catalytic performance for catalytic oxidation of VC and CO, which was probably due to the acid sites and the stronger interaction between Ru nanoparticles with heterostructured Co₃(PO₄)₂-MCFs support.

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References

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