

Complete oxidation of formaldehyde over TiO₂ supported subnanometer Rh catalyst at ambient temperature

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Abstract: Catalytic oxidation of formaldehyde to CO₂ and H₂O under ambient condition is highly desired for purifying indoor air quality. In this work, it was found for the first time that TiO₂ supported subnanometer Rh catalyst exhibited a remarkable activity with complete removal of HCHO at room temperature. Therein, the subnano Rh species which facilitated the dissociation of O₂ and the hydroxyl species from water which promoted the decomposition of formates to CO₂ were responsible for the high performance. This study can provide a novel insight for the design of Rh-based catalysts for ambient HCHO oxidation.

Keywords: Formaldehyde; Rhodium; Oxidation.

1. Introduction

Formaldehyde (HCHO) is regarded as one of the dominant pollutants in airtight houses¹. Long-time exposure to HCHO may induce health problems such as headache, respiratory tract or cancer. It is necessary to reduce the indoor concentration of HCHO or eliminate it to satisfy the stringent environmental regulations and human health needs. Among the various eliminations, the catalytic oxidation to harmless CO₂ and H₂O is generally recognized as a promising green technique for HCHO abatement due to its high removal efficiency, energy-saving consideration and environmental-friendly reaction conditions.

Compared with the various formulations for HCHO removal, the supported noble metal catalysts have been extensively studied at relatively low or even room temperatures. Therein, the Pt-based ones have been considered as one of the most outstanding catalysts for HCHO oxidation². However, the other Pt group metals as alternatives have been rarely explored in the elimination of HCHO. Particularly, the Rh-based catalysts are never reported for HCHO oxidation at room temperature probably due to not only the relatively higher price but also the much inferior activity. There is still large space to improve the performance of Rh-based catalyst to realize complete elimination of HCHO under ambient condition.

2. Experimental

A series of Rh/TiO₂ (P25) catalysts with different Rh loadings from 0.5 to 1.5 wt% were synthesized by deposition-precipitation method as reported previously³.

The activity measurement for the catalytic oxidation of HCHO over Rh/TiO₂ catalysts was performed in a continuous-flow fixed bed reactor under atmospheric pressure. The structures of Rh/TiO₂ were characterized by XRD, BET and HAADF-STEM. Moreover, the reaction mechanism was explored by H₂-TPR, O₂ microcalorimetry and in situ DRIFT detections during HCHO oxidation.

3. Results and discussion

HCHO conversions over a series of different loading Rh/TiO₂ catalysts were detected as a function of reaction temperature ranging from 20 to 80 °C. As shown in Fig. 1, the 1.5 wt% Rh/TiO₂ catalyst can realize complete HCHO elimination at only 20 °C with a high concentration of 140 ppm HCHO. It is also found that the existence of H₂O dramatically improved the conversion of HCHO and the catalyst has excellent tolerance

to high concentration of moisture with good stability, further convincing its practical capacity. It is worth noting that the Rh-based catalyst is reported for the first time to catalyze the oxidation of HCHO totally to CO₂ and H₂O at room temperature.

The dispersion of Rh species was examined by HAADF-STEM. As presented in Fig. 2, the Rh species are uniformly dispersed on the two phases of anatase and rutile in subnano clusters. According to the microcalorimetric result (not presented), the subnano Rh clusters are favorable for the dissociative adsorption of O₂ into O atoms which is critical for the HCHO oxidation. In addition, the in situ DRIFTS experiments reflected the reaction mechanism during the HCHO oxidation. As shown in Fig. 3, the DOM and formates are the intermediates and when exposed to O₂, the peaks of DOM disappear which are converted into the formates. With the further introduction of O₂+H₂O, the OH peaks significantly increase while the formates peaks remarkably decrease indicating the facile decomposition of these species under the presence of O₂+H₂O.

It is interesting to find here that the Rh/TiO₂ catalyst exhibits complete oxidation of HCHO at room temperature. The Rh species in subnanometer scale play a vital role in the process of HCHO oxidation. Moreover, the presence of H₂O which reacts with the O atoms to OH greatly promotes the decomposition of formates to CO₂. These results indicate that the high performance of Rh/TiO₂ for the oxidation of HCHO derives from the reaction between intermediate of formates and OH species.

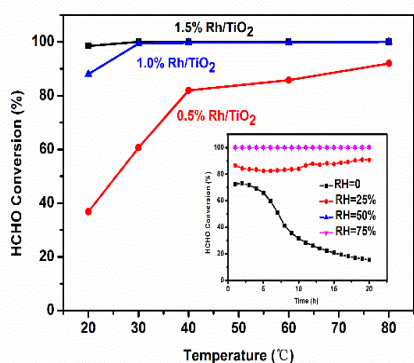


Fig 1. HCHO conversions on different Rh/TiO₂ catalysts and under different humidity. Reaction condition: 140 ppm HCHO, 20 vol% O₂, an balance He,

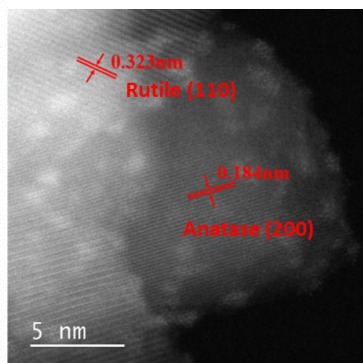


Fig 2. Typical HAADF-STEM images of the reduced 1.5 wt% Rh/TiO₂ catalysts

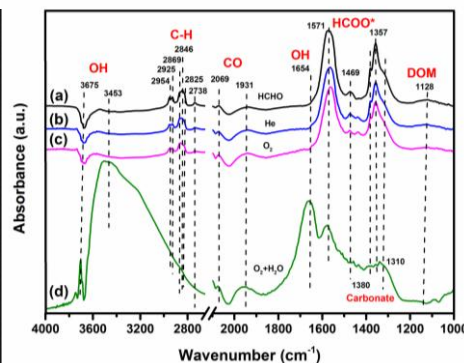


Fig 3. In situ DRIFTS of introducing HCHO (a), then He (b), O₂ (c), and finally O₂+H₂O (d) over 1.5 wt% Rh/TiO₂ catalyst.

4. Conclusions

In summary, a catalyst of subnanometer Rh species dispersed on TiO₂ with loading of 1.5 wt% was found for the first time to exhibit excellent performance with complete conversion and stability in the HCHO oxidation at room temperature. Such high performance can be attributed to the Rh subnano clusters, the support TiO₂ and the formation of surface hydroxyls during the reaction. This study of subnanometer Rh/TiO₂ catalyst with the ability of effective HCHO removal as well as the good durability and tolerance of moisture can provide important implication for practical applications and arouse interest in the design of novel Rh-based catalysts.

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References

1. T. Salthammer, S. Mentese, R. Marutzky, Formaldehyde in the Indoor Environment, *Chem. Rev.*, 110 (2010) 2536-2572.
2. C. Zhang, F. Liu, Y. Zhai, H. Ariga, N. Yi, Y. Liu, K. Asakura, M. Flytzani-Stephanopoulos, H. He, Alkali-metal-promoted Pt/TiO₂ opens a more efficient pathway to formaldehyde oxidation at ambient temperatures, *Angew. Chem. Int. Ed.*, 51 (2012) 9628-9632.
3. H. Guan, J. Lin, B. Qiao, X. Yang, L. Li, S. Miao, J. Liu, A. Wang, X. Wang, T. Zhang, Catalytically active Rh sub-Nanoclusters on TiO₂ for CO oxidation at cryogenic temperatures, *Angew. Chem., Int. Ed.*, 55 (2016) 2820-2824.