Insights into the role of Ba species on TiO₂ for photocatalytic NO_x storage process

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1. Introduction

Automobile emission regulations become restrictive globally; therefore, further improvements in automobile catalyst performance are desired. We have reported that Ba-modified TiO₂ photocatalyst exhibits excellent NO_x storage capacity, as lean NO_x trap at a low temperature [1]. In this study, the role of modified Ba on TiO₂ for photocatalytic NO_x storage process was investigated.

2. Experimental

Ba-modified TiO₂ catalysts (Ba/TiO₂) with different loading amounts (100-1000 µmol g^{-1}) were synthesized by а typical impregnation method using Ba(NO₃)₂ as a precursor. Photocatalytic NO_x storage reaction was performed in a fixed bed flow system under UV light irradiation in the reaction gas (NO 200ppm, O2 3%, He balance, GHSV 50,000 h^{-1}). Ba/TiO₂ catalysts were characterized with XRD, TPD, XAFS, and DRIFT.

3. Results and discussion

Figure 1 shows the temperature programmed desorption profiles (TPD) of NO_x from Ba/TiO₂ with different Ba(NO₃)₂ loading amounts. The sample with a loading amount of 100 μ mol g⁻¹ had one desorption peak around 660 K, while other samples had two peaks around 660 K and 830 K, hereafter referred to as LT and HT peaks, respectively. Since NO_x desorption from the bulk Ba(NO₃)₂ was detected around 840 K, the HT peak was attributed to crystalline Ba(NO₃)₂. Ba K-edge XANES for the catalyst with a small loading

amount of 100 µmol g⁻¹ was different from that of bulk Ba(NO₃)₂, BaO or BaTiO₃, and the catalyst did not show XRD patterns due to Ba species. Therefore, the LT peak must be due to the highly-dispersed Ba species on TiO₂. The linear combination of XANES spectra with the highly-dispersed Ba species and Ba(NO₃)₂ well-simulated the spectra of all Ba/TiO₂ samples. The estimated amounts of the dispersed Ba species corresponded well to the photocatalytic NO_x storage activities (Figure 2). In-situ DRIFT revealed that NO_x was trapped on not Ba sites but Ti sites on Ba/TiO₂. Considering these results, we conclude that the dispersed Ba species enhances the NO_x adsorption ability of the neighboring Ti sites.



Fig. 1 TPD profiles of Ba/TiO₂ catalysts with various Ba loadings of (a) 100, (b) 250, (c) 500, (c) 750, and (e) 1000 μ mol g⁻¹. (f) Physical mixture of Ba(NO₃)₂ and TiO₂.



Fig. 2 Relationship between photocatalytic NO_x storage capacities and amounts of highly-dispersed Ba species in Ba/TiO₂.

REFERENCES

[1] A. Yamamoto, Y. Mizuno, K. Teramura, S. Hosokawa, and T. Tanaka, Appl. Catal. B, 180 (2016) 283.