Titania nanosheets with highly exposed (001) reactive facets for photocatalytic NOx abatement in flue gas

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Abstract: The particular role of reactive facets TiO_2 for photocatalytic NOx removal was systematically explored by using titania nanosheet photocatalysts with exposed (001) facets. The synthetic pathway of transformation from TBOT (Ti precursor) to TiO_2 nanosheet was clearly revealed that $TiOF_2$ is the intermediate during the hydrothermal process. The NOx removal of titania nanosheets was found to be higher than the conversion of commercial P25 and TiO_2 synthesized by the sol-gel method. Lastly, we found one of the titania nanosheets, FT1.5 (TBOT and HF with the F/Ti atomic ratio = 1.5), displayed the highest efficiency of NOx removal at 393 K [1].
Keywords: TiO_2 nanosheet, (001) facet, photocatalyst.

1. Introduction

Anatase TiO_2 with a high percentage of reactive (001) facets, so-called titania nanosheet due to its shape, was reported in 2008. The (001) surface with a surface energy of 0.98 J m^{-2}, which has been demonstrated to have a higher reactivity than (101) surface of 0.49 J m^{-2} or (100) surface of 0.58 J m^{-2}. Titania nanosheet and its derived materials have been applied in diverse categories of photocatalysis with outstanding performance, including organics degradation, H_2 production, CO_2 reduction. Although the (001) surface has a very high surface energy, maximizing the percentage of exposed (001) area might not be a good direction. There exists an optimal ratio of the exposed (001) and (101) facets under certain conditions. Based on the calculation results of density functional theory (DFT), a suitable ratio of the exposed (001) and (101) facets could avoid the electrons and holes accumulate on the (101) facets or overflow to the (001) facets. The optimal ratio of exposed (001) and (001) facets can improve the migration of electrons and holes between (101) and (001) facets so that photocatalytic activity is enhanced. Therefore, this study intends to find an optimal synthetic recipe for titania nanosheet to efficiently remove nitrogen oxide (NO(g)), which is one of the main components in flue gas emitted from stationary sources during the combustion processes.

2. Experimental

The titania nanosheets were prepared by the hydrothermal method. At first, 50.0 g of Titanium (IV) n-butoxide (TBOT, Alfa Aesar, 99+%) was mixed with different amounts of hydrofluoric acid (HF, Sigma-Aldrich, 48%), 6.124, 9.186 and 12.248 g. These amounts of HF were intendedly calculated based on the nominal F/Ti atomic molar ratio which equaled to 1, 1.5, and 2. Therefore, they were named as “FT1”, “FT1.5”, and “FT2”, respectively.

We conducted X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) with dispersive X-ray spectroscopy (EDS), BET surface area analysis, UV-vis spectrometer, dynamic light scattering (DLS), photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS) to fully characterize the photocatalysts.

3. Results and discussion

With regards to environmental points of view, NO conversion and NO_2 selectivity should be considered together [2], therefore, NOx removal is shown in **Figure 1**. At 313 K, the values of NOx removal were low for all photocatalysts due to different reasons. For P25 and SG, it was owing to the relatively low NO conversion as compared to titania nanosheets. For titania nanosheets, it was because of their high NO_2 selectivity. Nonetheless, the NOx removal could be improved by increasing the reaction temperature. Note that it was a trade-off relationship between NO conversion and NO_2 selectivity [3]. Increasing the reaction temperature could reduce the NO_2 selectivity but also decrease the NO conversion. For FT1.5 and FT1, the NOx removal reached to their maximum at 393 K so it could be concluded that moderately high temperature was benefited for NOx removal in photo-selective catalytic reduction (photo-SCR). For the practical applications, photo-SCR can be used in the post-treatment of exhaust gas or flue gas, which is emitted at high temperature. The waste heat from exhaust gas flue gas can heat up the photocatalyst to not only get the better performance but also prevent water condensation in the pipeline. Overall, it is wholly reasonable to apply at this temperature, 393 K.

The outstanding activity of titania nanosheets, especially for FT1 and FT1.5 could be attributed to the following reasons: high exposed (001) facets, and high BET surface area. In view of the SG and all titania nanosheets, higher exposed (001) facets and higher BET surface of titania nanosheets corresponded to the higher NO conversion. Moreover, among FT1, FT1.5, and FT2, the activity arrangement order was totally consistent with the BET surface area order: FT1.5 > FT1 > FT2. Furthermore, the recombination rates of electron-hole pairs got from PL spectra (**Figure 2**) showed the same trend with the photo-activities. To be more specific, the lower the recombination rate was, the higher the photoactivity would be.

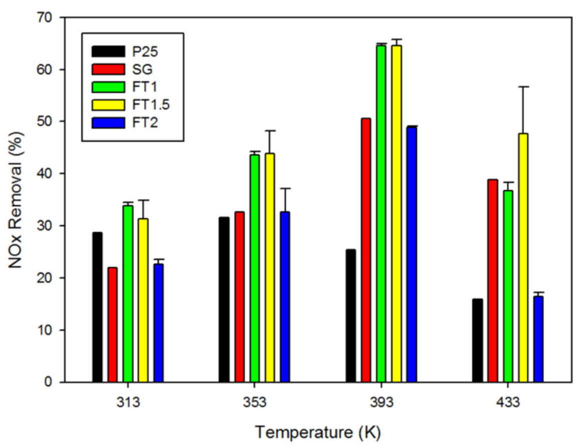

Figure 1. NOx removal of P25, SG, FT1, FT1.5, and FT2 photocatalysts at different temperatures for photo-SCR reaction (Feed gas compositions: 400 ppmv NO, 2000 ppmv C_4H_{10}, 4 v% H_2O, 4 v% O_2, and N_2 balance.)

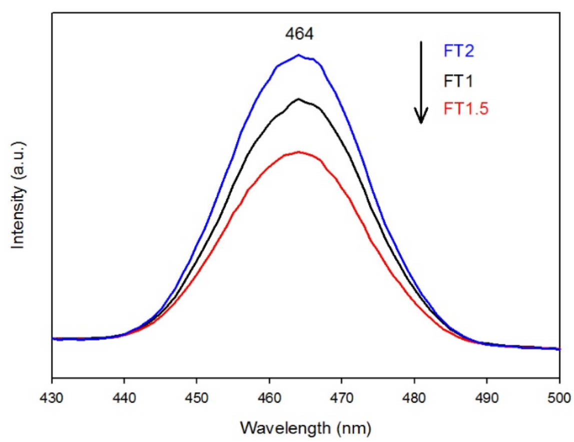

Figure 2. PL spectra of titania nanosheets.

4. Conclusions

In this study, titania nanosheet photocatalysts were successfully synthesized by hydrothermal method and fully characterized. One of the best synthetic processes for TiO_2 nanosheet is to use TBOT and HF with the F/Ti atomic ratio = 1.5 at 453 K for 24 h in hydrothermal treatment. The titania nanosheet synthesized under this condition can get rid of the formation intermediate $TiOF_2$. TiO_2 nanosheet exhibits outstanding performance in photocatalysis due to its high BET surface area and highly exposed (001) facet in comparison with the TiO_2 synthesized by sol-gel method and P25.

References

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