

Reactivity Enhancement of 2-Propanol Photocatalysis on $\text{SO}_4^{2-}/\text{TiO}_2$ Catalyst: Insights from Solid-State NMR Spectroscopy

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Heterogeneous photocatalytic oxidations have been attracting considerable attention for their removing of low concentration organic pollutants in both gas and liquid phases. TiO_2 , for its outstanding photocatalytic activity, chemical stability, low cost and non-toxicity, is widely used as a photocatalyst. In order to improve the photocatalytic activity of TiO_2 , a number of modification techniques have been developed. Recently, sulphated TiO_2 ($\text{SO}_4^{2-}/\text{TiO}_2$) solid acid has been introduced as a photocatalyst for its higher catalytic activity compared with pure TiO_2 in the photodegradation of some organic compounds. However, how the sulphation affects the surface acidity as well as the reactivity of the catalyst is poorly understood.

In the present study, solid-state NMR techniques have been employed to investigate the surface acidic properties of TiO_2 and sulphated TiO_2 , as well as their photocatalytic activities towards 2-propanol. On anatase TiO_2 , apart from Lewis acid sites, some less acidic bridging hydroxyl groups are present. After the sulfation of TiO_2 , three different types of strong Brønsted acid sites are generated, and their acid strengths are slightly stronger than that of zeolite HZSM-5, but still weaker than that of 100% H_2SO_4 . The results can help us to understand the formation of surface-bound species: on the pure TiO_2 , both hydrogen-bonded 2-propanol and Ti-bound 2-propoxy species are present with the former being predominant, while on the $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst the formation of Ti-bound 2-propoxy species is preferred. Our NMR experiments also give a comprehensive understanding the photocatalytic degradation of 2-propanol: on the pure TiO_2 , the physisorbed 2-propanol can be converted to acetone that is difficult to be further converted into CO_2 , and the conversion of 2-propoxy species to 2-propanol hampers its direct mineralization; while on the $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst, the dominant Ti-bound 2-propoxy species can be directly converted to the final product CO_2 , which enhances the activity of 2-propanol photocatalysis. In addition, the surface S-bound 2-propoxy species are also formed on the $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst and these species are nearly unreactive, probably due to the relatively longer distance between the S-bound 2-propoxy species and the TiO_2 surface which may block the transfer of photogenerated hole.

Keywords: photocatalysis; sulphated TiO_2 ; solid-state NMR; surface acidity; reaction mechanism

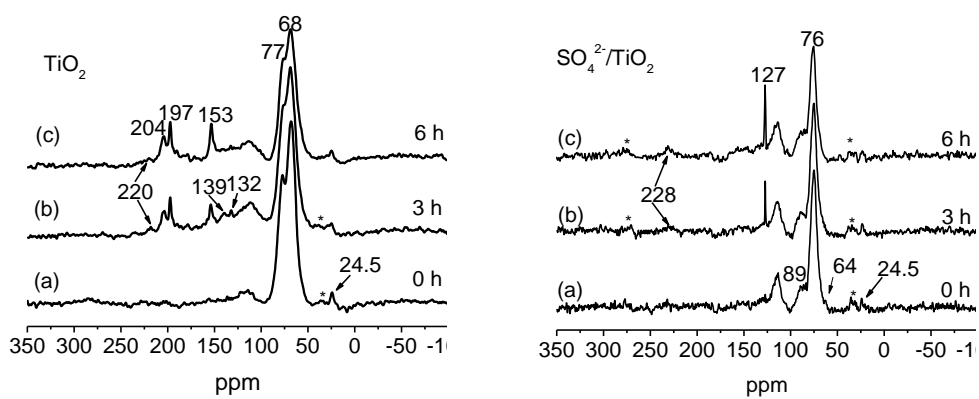


Figure 1. ^{13}C MAS spectra of 2-propanol on TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ during photocatalytic oxidation. Irradiation times are noted as shown. Asterisks denote spinning sidebands. The signal at *ca.* 112 ppm is due to the background of the NMR rotor.