High Pore Volume TiO$_2$ – new possibilities for catalytic applications

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Introduction

For decades Al$_2$O$_3$ or SiO$_2$ have mostly been used as catalytic support materials due to their versatile properties and tunable parameters (e.g. pore size and specific surface area (SSA)). A wide range of SSA, pore diameter and pore volume has been realized and introduced in numerous catalytic applications. For standard TiO$_2$, this has not been the case in the past, mostly due to the low pore volumes (0.2 - 0.3 cc/g) and –sizes (~4 nm), which were considered as major disadvantages, despite the large surface area (300 m$^2$/g) and the well-known benefits for catalytic applications. In order to overcome these issues, TiO$_2$ was often subjected to a thermal treatment at elevated temperatures before use in catalytic applications, which resulted in increased pore diameters (~10 nm) at the cost of a significantly decreased SSA (100 m$^2$/g). The combination of high pore volumes, large mesopores and high SSA, as known from e.g. Al$_2$O$_3$, was not possible, at least not on an industrial scale [1].

In the present contribution we will report on a novel High Pore Volume (HPV) TiO$_2$ material developed and scaled up to multi ton scale by Sachtleben Chemie GmbH, which combines all of these important parameters. We were able to generate products which simultaneously offer high pore volumes of up to 0.7 cc/g, surface areas ranging from 300 – 100 m$^2$/g and large pore diameters of up to 30 nm. Moreover, it is possible to preserve these characteristics even under extreme conditions (up to 800°C) by implementation of SiO$_2$ as a stabilizing agent. Impregnation experiments on the HPV materials with ~18wt.% metal loading showed a high degree of sintering and utilization even under extreme conditions (~1h at 800°C). The degree of sintering correlates with the amount of SiO$_2$ as a stabilizing agent, i.e. HPV TiO$_2$ stabilized with 12wt.% SiO$_2$ (M411) shows a higher SSA in comparison to products stabilized with lower SiO$_2$ amounts. In contrast the respective pore volumes only decreased marginally compared to raw material. Impregnation experiments with HPV TiO$_2$ material incorporating 14.6wt.% MoO$_3$ and 3.1wt.% CoO revealed a high degree of remaining mesoporosity. This important feature is expected to reduce diffusion limitations due to reduced pore plugging during reaction.

Results and Discussion

The stabilized HPV (M411) materials show a strong resistance against sintering and utilization even under extreme conditions (~1h at 800°C). The degree of sintering correlates with the amount of SiO$_2$ as a stabilizing agent, i.e. HPV TiO$_2$ stabilized with 12wt.% SiO$_2$ (M411) shows a higher SSA in comparison to products stabilized with lower SiO$_2$ amounts. In contrast the respective pore volumes only decreased marginally compared to raw material. Impregnation experiments with HPV TiO$_2$ material incorporating 14.6wt.% MoO$_3$ and 3.1wt.% CoO revealed a high degree of remaining mesoporosity. This important feature is expected to reduce diffusion limitations due to reduced pore plugging during reaction.

Realistic catalyst testing under hydrotreating conditions showed a higher activity of the HPV TiO$_2$ based catalyst, for both HDS and HDN, compared to the state of the art Al$_2$O$_3$ based catalyst. Due to a 1:1 dilution with SiC both catalyst materials do not reach full conversion of the sulphur and nitrogen containing educts. It was however observed, that for the HDS reaction remaining sulphur educt levels of around 700 ppm are reached at a 25°C lower temperature for the HPV TiO$_2$ based catalyst. Moreover an almost 2 times lower amount of accumulated carbon and sulphur species are found on the surface of the spent HPV TiO$_2$ based catalyst compared to the Al$_2$O$_3$ based catalyst material in addition to a larger pore volume, indicating its long term stability potential. The consequences of these findings for catalytic applications will be discussed.

Significance

HPV TiO$_2$ material is an attractive alternative for industrial catalytic applications, e.g. for hydrotreating, where it showed better performance compared to established catalytic systems.

Materials and Methods

The HPV TiO$_2$ (M411) was extruded and impregnated with 3.1wt.% CoO$_2$ and 14.6wt.% MoO$_3$ via incipient wetness impregnation, dried (120°C, 10h) and calcined (400°C, 1h). For the hydrotreating activity tests (HDS and HDN) 50 ml of the resulting catalyst were diluted with SiC (1:1), for an easier control of the reaction temperature during reaction, and placed into a 100 ml flow pressure reactor. The experiments were conducted under realistic conditions with a refinery vacuum distillation feed at different temperatures ranging from 370 to 420°C. The obtained results were compared to a state of the art Al$_2$O$_3$ based catalyst (4.6wt.% CoO$_2$, 26.3wt.% MoO$_3$) tested under identical conditions.

Long term stability tests regarding SSA, pore volumes and sizes of the HPV TiO$_2$ powder were conducted in a kiln. The HPV materials were tempered at 500°C for 1h and subsequently held for 50h at 400°C. All materials were characterized by N$_2$ adsorption (SSA and pore volume), ICP-OES and XRF.

References