Mesoporous titania prepared by monolayer grafting of Ti on SBA-15: a model support for studying the surface sulfidation of TiO₂ in HDS conditions?

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Introduction
In order to improve our understanding of MoSₓ/TiO₂ catalysts there is a strong need for molecular-scale characterization of the evolution of the titania surface upon sulfidation. In this regard, titania coated silica materials are promising model supports because the surface nature of the titania overlayer leads to the presence of mainly surface Ti and allows therefore to observe modifications of the surface (reduction and/or sulfidation) that would otherwise be hidden by the bulk. These materials are also promising supports and have been successfully used for the preparation of a NiMoS catalyst by Gutiérriez et al.⁴, who observed a two fold increase in HDS activity with regards to catalysts supported on pure silica SBA-15 materials.

The aim of the present communication is to follow the sulfidation and/or reduction of Ti-grafted SBA-15 materials using X-ray Absorption spectroscopy at the Ti K-edge.

Results and discussion

a) characterization of TiO₂/SBA-15 materials:
Grafting of 1 to 4 titania layers on the surface of a SBA-15 was performed in 1-propanol using Ti(OPrᵢ)₄ as titania source. Each grafting was followed by a calcination step at 500°C. The successive graftings led to a gradual decrease of the surface area (from 800 initially to 420 m².g⁻¹ after 4 graftings) and pore diameter (from 65 to 42 Å). These differences were assigned to the coating of the mesopores with titania. Imaging of the material composition by energy-filtered transmission electron microscopy clearly shows that TiO₂ is homogeneously dispersed at the surface of the SBA-15 mesopores. UV-visible and XAS spectroscopies indicate the formation of small titania polymers at the surface of the support.

b) XAS study (Ti K-edge) of the sulfidation process:
Ti-grafted SBA-15 materials were characterized after sulfidation in gas-phase (320 to 600°C, atmospheric pressure in 5% H₂S in H₂, see Figure 1). At temperatures commonly used for the sulfidation of the active phase, no sulfidation and/or reduction of the TiO₂ overlayer was observed and only a small fraction of Ti is sulfided after increasing the sulfidation temperature up to 600°C, although a bulk sulfidation is expected at this temperature.² These results suggest that grafting of TiO₂ on SiO₂ prevent sulfidation probably due to the different chemical nature of the titania overlayer with respect to a bulk TiO₂ phase.

Conclusions
The present study shows that grafting of Ti alkoxide on SBA-15 is a successful route for the synthesis of ordered mesoporous materials with an homogeneous layer of Ti oxide on the mesopores of SBA-15. However, it is shown that the Ti oxide overlayer is structurally different from bulk TiO₂. XAS spectroscopy at the Ti K-edge shows that sulfidation of TiO₂/SBA-15 do not lead to any reduction and/or sulfidation of the titania overlayer in contradiction to literature results. This discrepancy may be due to differences in the chemical nature of bulk TiO₂ and TiO₂/SBA-15. The latter is probably stabilized by grafting on SiO₂. TiO₂/SBA-15 materials were used as supports for MoSₓ. The morphology of the MoS₂ slabs (TEM) and the HDS activity (with regards to MoS₂ supported on bulk TiO₂) are currently under investigation.

References

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