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Mesoporous titania prepared by monolayer grafting of Ti on SBA-15: a model support for studying the surface sulfidation of TiO_2 in HDS conditions ?

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Introduction

In order to improve our understanding of MoS_x/TiO_2 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 TiO_2/SBA-15 materials:

Grafting of 1 to 4 titania layers on the surface of a SBA-15 was performed in 1-propanol using $Ti(OPr^i)_4$ 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 $m^2.g^{-1}$ 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 TiO_2 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% H_2S in H_2, see Figure 1). At temperatures commonly used for the sulfidation of the active phase, no sulfidation and/or reduction of the TiO_2 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 TiO_2 on SiO_2 prevent sulfidation probably due to the different chemical nature of the titania overlayer with respect to a bulk TiO_2 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 TiO_2. XAS spectroscopy at the Ti K-edge shows that sulfidation of TiO_2/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 TiO_2 and TiO_2/SBA-15. The latter is probably stabilized by grafting on SiO_2. TiO_2/SBA-15 materials were used as supports for MoS_2. The morphology of the MoS_2 slabs (TEM) and the HDS activity (with regards to MoS_2 supported on bulk TiO_2) are currently under investigation.

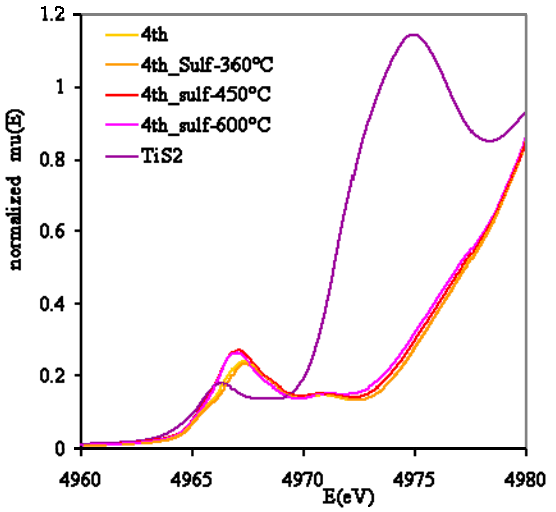

Fig. 1 XANES (Ti Kedge) spectra of TiO_2-SBA-15 (4^{th} grafting) before and after sulfidation at various temperatures

References

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