Controlled gas-phase preparation and characterization of highly dispersed silica-supported vanadia catalysts

J. Keränen1,2, C. Guimon3, E. Iiskola2, A. Auroux1, L. Niinistö2

1Institut de Recherches sur la Catalyse, CNRS, 2 av. Albert Einstein, F-69626 Villeurbanne, France. 2Helsinki University of Technology, P.O. Box 6100, FIN-02015 Espoo, Finland. 3LPCM, 2 av. du Président Angot, F-64000 Pau, France.

Introduction
The preparation mode influences greatly the dispersion of surface vanadia species on relatively inert silica supports [1]. Deposition through aqueous-phase impregnation often leads to poorly spread vanadium oxide species. On the other hand, gas phase techniques based on chemisorption-controlled growth have been shown to result in homogeneous and catalytically active vanadia species on silica surface [2,3]. The atomic layer deposition (ALD) technique is a gas-phase preparation method based on surface-saturating precursor adsorption on support hydroxyl groups, allowing a high dispersion of the deposited species on porous carriers [4]. In this work, the ALD technique was employed to prepare highly dispersed V2O5/SiO2 catalysts.

Experimental
The depositions were performed in a fixed-bed flow-type ALD reactor (F-120, ASM Microchemistry Ltd.) [4]. The saturating reaction of vanadyl triisopropoxide with a high surface area silica was carried out by letting the flow of volatilized precursor pass downward through the heated bed of support. The chemisorption of the precursor onto the surface sites of silica was followed by inert gas and calcination treatments. Optimal values of various parameters affecting the adsorption of the precursor on silica, e.g. the support pretreatment and reaction temperatures, were first established through elemental analyses and inert atmosphere DRIFTS measurements. Increasing amounts of vanadia were then deposited onto the support by successive precursor-oxygen cycles. The texture, structure and dispersion of the solids were examined in detail by N2 adsorption, XRD, XPS and Raman spectroscopy. XPS of NH3 adsorption was used to determine both the nature and amount of the adsorbed species on surface acid sites. Quantitative information about the number and distribution of acid sites was acquired by adsorption microcalorimetry. A series of standard aqueous-phase impregnated samples were prepared and characterized for comparison with the ALD catalysts.

Results and Discussion
The surface-controlled chemisorption of vanadyl triisopropoxide precursor onto silica pretreated at 873 K was obtained at reaction temperatures between 363 and 393 K. The atomic layer deposition growth of vanadia on silica pretreated at 723, 873 and
1023 K led to precise and reproducible vanadium densities of ~1.6, ~1.2 and 1.0 V at/nm$^2$$_{\text{sup}}$, respectively, throughout the support bed. However, due to the catalytically active nature of surface vanadia species, it was possible to perform the deposition in a controlled manner only up to a near monolayer level (~2.3 V at/nm$^2$$_{\text{sup}}$, 2 ALD cycles) on silica at 873 K.

The surface area and porosity of the silica support were only slightly affected and no crystalline V$_2$O$_5$ peaks were observed by XRD in the catalysts when the controlled deposition was performed in a gas phase. However, when the corresponding amounts of vanadium were added by impregnation in a liquid phase, the vanadia species agglomerated, decreasing the support surface area and forming vanadium pentoxide crystals.

Raman spectroscopy confirmed the differences in the surface species and crystallinity of the catalysts prepared by atomic layer deposition or impregnation. The ALD catalysts were composed of isolated tetracoordinated vanadate species whose peak intensity increased linearly upon increasing the vanadium content. In the impregnated catalysts, clear V$_2$O$_5$ crystal features were detected along with those of the monomeric species. The XPS measurements confirmed the high surface dispersion of the vanadia species in the ALD catalysts.

Adsorption XPS and microcalorimetry experiments showed that the acidity of the ALD catalysts, as expressed in terms of number and strength of surface acid sites, was in every case higher than the acidity of the corresponding impregnated catalysts.

To conclude, the results of the various characterization techniques confirmed that the properties of the silica-supported vanadia catalysts were strongly affected by the preparation method; the controlled atomic layer deposition growth resulted in highly dispersed VO$_x$ species on silica surface.

References