High Frequency EPR Investigation of Vanadium Supported on SBA-15 and $\gamma$-Alumina

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Introduction

Supported vanadium oxides have been widely used as catalysts for a number of reactions. The molecular structure of the surface vanadium oxide species and the catalytic properties are influenced by the method of preparation, the nature of support, the presence of promoters and finally the environmental conditions [1]. Vanadia species dispersed on alumina offer a broad range of VO$_x$ structures [2] and show a high activity and selectivity for the production of alkenes from the corresponding alkanes [3].

Standard “low frequency” EPR spectra indicate the presence of different sites being active in alkane dehydrogenation [2, 4-6] but their role and nature are still under discussion [7]. The presence of V$^{4+}$ centers was already confirmed by observing the characteristic hyperfine splitting of well-isolated V$^{4+}$ species in distorted octahedral coordination [8-10]. Sometimes the hyperfine signals are obscured by a broad isotropic line, which might arise from magnetically interacting V$^{4+}$ species. Spectra simulation revealed that the latter comprise the majority of the octahedral V$^{4+}$ species. The identification of unique active sites would be of utmost importance for developing a better understanding of the catalytic action.

Preliminary Results and Discussion

Preliminary experiments performed in April 2007 at the NHMFL have shown that catalytically active samples can be studied with the existing high frequency EPR spectrometers. For this reason a comparative study of unstructured alumina and well structured SBA-15 supports is scheduled for winter 2008. Even these first high frequency EPR experiments performed on “virgin” catalyst material allowed to distinguish between different Vanadium sites and to obtain reliable data about the hyperfine tensor and the g-matrix. The difference in g-factors of Manganese (II) and Vanadium (IV) allows to separate the spectrum of the contaminating Mn (II) at high fields.

Conclusions

From an analysis of highly resolved Vanadium (IV) EPR spectra the influence of the support material and the heterogeneity of the active centers could already be detected. No evidence for Vanadium (III), however, could be detected, not surprising because only “virgin” material was investigated so far. Taking advantage of the rather high sensitivity of the resonator-free set up, it will be possible to investigate catalytically active samples either as open samples or in small sealed containers. This unique advantage allows to study the influence of reducing or otherwise active atmospheres, by which the reaction conditions can be simulated.

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References