Magnetic Resonance Imaging to Study Impregnation Processes on γ-Al_2O_3 Support Bodies

Leticia Espinosa-Alonso[1], Anna A. Lysova[2], Krijn P. de Jong[1], Igor V. Koptyug[2] and Bert M. Weckhuysen[1*]

[1]*Inorganic Chemistry and Catalysis Group, Utrecht University, Sorbonnelaan 16, Utrecht 3584 CA (The Netherlands)*

[2]*International Tomography Center SB RAS 3A Institutskaya Street, Novosibirsk 630090 (Russia)*

*b.m.weckhuysen@ uu.nl

Introduction

In order to improve the efficiency of an industrial process, it is crucial to have a clear knowledge of what factors determine the macro-distribution of the active component and its metal-phase. Different spectroscopic techniques have been developed to monitor the transport of the active component and its molecular structure, during the elementary steps of catalyst preparation, in a space and time resolved manner. [1, 2] Nowadays, arising techniques in this field are non-invasive and they enable to study the preparation process not interfering with the system. Representative examples are magnetic resonance imaging (MRI) and tomographic energy dispersive diffraction imaging (TEDDI). [3, 4]

Here, we will present MRI studies on the impregnation of Ni/γ-Al_2O_3 hydrogenation catalyst bodies with Ni^{2+} (aq) in different coordinations; i.e. $[Ni(H_2O)_6]^{2+}$ and $[Ni(edtaH_x)]^{(2-x)-}$ (x = 0, 1 and *edta* = ethylenediaminetetraacetic acid). We will show how MRI can be used in a quantitative manner to monitor $[Ni(H_2O)_6]^{2+}$ dynamics within a catalyst body. And how the combination of MRI with UV-Vis micro-spectroscopy allows for a better understanding on the dynamics and adsorption/desorption phenomena of $[Ni(edtaH_x)]^{(2-x)-}$ and $[Ni(H_2O)_6]^{2+}$ species when they are co-impregnated.

Materials and Methods

Pore volume impregnation of single cylindrical γ-Al_2O_3 extrudates (12 mm long, 3.85 mm diameter, 145 $m^2 \cdot g^{-1}$ and 0.36 mL g^{-1}) was performed drop-wise with Ni^{2+} solutions. A Bruker Avance DRX 300 MHz wide-bore spectrometer equipped with imaging accessories was used to record 2D ^1H MRI images on the impregnated extrudates. MRI images were collected imposing T_1 contrast or T_2 contrast. The contrast indicated the presence/ absence of Ni^{2+} due to the influence that paramagnetic ions have on the relaxation rates of proton nuclei.

Results and Discussion

T_2-contrast images of a γ-Al_2O_3 catalyst body after impregnation with a solution of 0.5 M $Ni(H_2O)_6^{2+}$ indicated that a uniform distribution of this metal-ion was only achieved after one hour. Moreover, the dynamics was followed in a quantitative manner after deriving a calibration between NMR signal intensity and Ni^{2+} concentration. If the catalyst body was impregnated with a solution of 0.1 M $[Ni(edtaH_x)]^{(2-x)-}$, the transport rate of the metal-ion complexes depended on the solution pH. A low pH enhanced the retention of the complex close to the edges of the catalyst body, and 16 h were required to obtain a uniform distribution. This slow transport was due to the strong electrostactic interactions between the positively charged alumina surface at acidic pH and $[Ni(edtaH)]^-$. $[Ni(edtaH_x)]^{(2-x)-}$ species was only detected when T_1-contrast was applied because of the shielding effect that *edta* ligands have on the Ni^{2+} paramagnetic properties.

If both species, $Ni(H_2O)_6^{2+}$ and $[Ni(edtaH_x)]^{(2-x)-}$, were co-impregnated $(Ni(NO_3)_2$ 0.6 M and Na_4edta 0.1 M, at pH 6) a breeze Ni egg-shell distribution was achieved after 2 h. MRI provided with T_2-contrast images which indicated that $Ni(H_2O)_6^{2+}$ was uniformly distributed in the catalyst body. The images also suggested a faster relaxation rate of protons in the edges of the pellet, an example is shown in Figure 1. The red ring indicates a low NMR signal intensity, namely a fast relaxation rate of the protons. This was a direct consequence of the presence of both species in the external rim of the catalyst body. UV-Vis micro-spectroscopic data confirmed that $[Ni(edtaH_x)]^{(2-x)-}$ was located close to the edges. Figure 1 summarizes the adsorption phenomena that took place on alumina surface 2 h after impregnation.

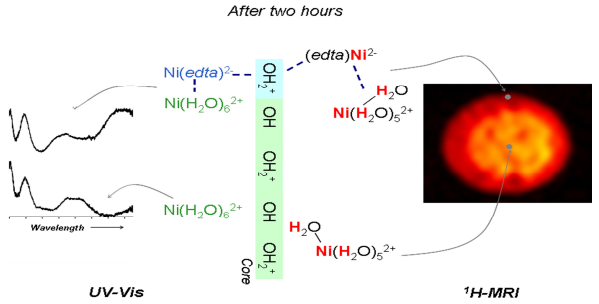

Figure 1. Ni^{2+}-*edta* speciation 2 h after impregnation of a solution containing $Ni(NO_3)_2$ 0.6 M + Na_4edta 0.1 M at pH 6. UV-Vis spectra (left) and ^1H MRI image (right) are shown.

Significance

The fact that $Ni(H_2O)_6^{2+}$ transport can be monitored in a quantitative manner, thanks to MRI, provides insight into the way a catalyst should be design to improve its efficiency. Moreover, this technique shows that the use of *edta* facilitate the formation of Ni egg-shell distributions, which are preferred profiles in chemical processes with diffusional restrictions and are not so easily achieved.

References

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