Operando FTIR-MS Study of ammonia-ammonium interplay in a genuine monolithic V_2O_5/TiO_2/Sepiolite catalyst during Selective Catalytic Reduction of NO with NH_3

Søren B. Rasmussen, Miguel A. Bañares, Pedro Ávila and Marco Daturi

Instituto de Catálisis y Petroleoquímica (ICP), Consejo Superior de Investigaciones Científicas (CSIC), Marie Curie 2, E-28049, Madrid, SPAIN

Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen

Introduction and Objectives

Recently, we have demonstrated the viability of *operando* spectroscopic analyses of monolithic catalysts using transmission FT-IR coupled with mass spectrometry on real conformed monolithic catalysts.[1] During the first decade of development of the *operando* concept much attention has been on development of sound spectrokinetic cells to ensure proper kinetic measurement during operando spectroscopy. [2,3,4] Expanding the *operando* approach from being solely a valuable tool for the catalyst researcher to also providing spatial information is highly valuable for the catalyst engineer.

Almost all industrial implementations of catalysis for environmental applications have been done with the use of monoliths, since they combine excellent gas-solid contact conditions with extremely low-pressure drops. Our work in this area has been concentrated on assessing the water-dependent interplay between NH_3 and NH_4^+ in working monolithic V_2O_5/TiO_2 based NH_3-SCR catalysts for the removal of NO_X:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

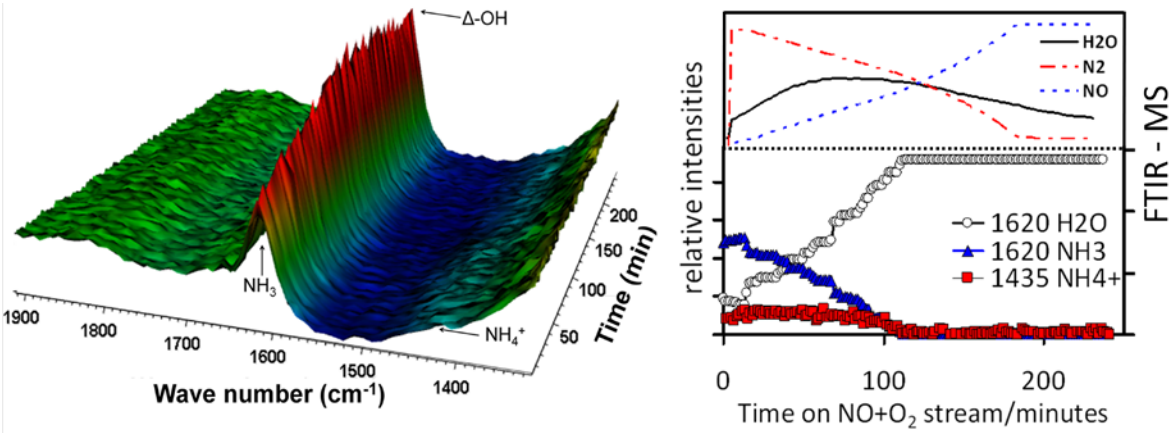

Figure 1 *Operando* FTIR-MS study of 1000 pm NO + 3.5% O_2 reaction with pre-adsorbed ammonia over a 5 cm monolithic V_2O_5/TiO_2/sepiolite catalyst at 250C. The mass spectrometric traces of reactants and products are given at the right.

Both adsorbed ammonia on oxo-vanadia Lewis acid sites and ammonium ions associated with Brønsted acid sites can act as active sites. The relation between Lewis and Brønsted acid V-O sites is not inherent, but dependent on the humidity of the gas phase. This work is performed without added water in the reaction feed; it demonstrates that reaction-generated water, eq. (1), hydrolyzes the surface V=O sites along the channels of a monolith, transforming Lewis acid sites into Brønsted acid sites. Furthermore, during a reaction sequence in the integral monolithic reactor with NO and O_2 titrating the catalyst surface for pre-adsorbed ammonia, it can be seen how adsorbed ammonia is either used for the SCR reaction, or converted into the ammonium ions, which then participates in the SCR reaction. These observations complement more fundamental work performed on kinetically restricted pelletized or powdered catalysts, since it is now possible to achieve direct observation on secondary effects of water produced upstream.

Results and Discussion

Figure 1 illustrates some dynamic variations at 1620 and 1435 cm^{-1} during reaction. The ammonium ions observed at the latter wavenumber disappear after approx. 200 minutes, which is essentially the time when N_2 traces disappear, as confirmed by online mass spectrometry. However, literature reports that adsorbed ammonia exhibit an IR mode near 1610 cm^{-1}. Alas, that band significantly overlaps with that of molecular water, which increases during reaction time in the experiment. Such rehydroxylation of surface vanadia is due to the SCR reaction-formed water.

The presence of water is unavoidable to genuinely reproduce working reaction conditions of a real industrially used catalyst with binder material, and at the same time operations in the presence of significant amount of water produced during the fuel combustion process. Therefore, these observations motivated us to perform a *multi component analysis* (MCA) of the 1620 cm^{-1} peak using commercial indirect hard modeling software (PEAXACT),[5] in order to see if a un-biased hard mathematical model could be able resolve a decreasing band from adsorbed ammonia and an increasing OH band.

Results showed that it was possible to successfully identify the distribution of ammonia and ammonium ions distributed over the catalyst support, which open up new possibilities for FTIR investigations of metal oxide supported V_2O_5 catalysts in wet conditions.

References

[1] S.B. Rasmussen, M.A. Bañares, P. Bazin, J. Due-Hansen, P. Ávila and M. Daturi, Phys. Chem. Chem. Phys., 2012, DOI: 10.1039/C1CP22629K
[2] M.O. Guerrero-Pérez, J.L.G. Fierro, M.A. Vicente, M.A. Bañares, J. Catal. 206 (2002) 339-348
[3] M.A. Bañares, S.J. Khatib, Catal. Today, 96 (2004) 251-257
[4] C.M. Kalamaras, G.G. Olympiou, A.M. Efstathiou, Catal. Today 138 (2008) 228
[5] E. Kriesten, D. Mayer, F. Alsmeyer, C.B. Minnich, L. Greiner, W. Marquardt, Chemometr. Intell. Lab. 93 (2008) 108