Experimental microkinetic approach of NH$_3$-SCR process: determination of individual heat of adsorption of NH$_3$ adsorbed species on TiO$_2$.

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Introduction
This work is dedicated to the understanding of the mechanism of the Selective Catalytic Reduction (SCR by NH$_3$) of NO$_x$ contained in the exhaust gases of coal-fired power plants [1], on V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts (NH$_3$-SCR) using an experimental microkinetic approach. One of the key steps in the mechanism is the adsorption of NH$_3$ [2] on the catalyst. The aim of the present study is the development of experimental procedures allowing the measurement of individual heats of adsorption of NH$_3$ species adsorbed on the catalyst surface in the conditions of the NH$_3$-SCR process.

This has been realized by adapting a method, denoted AEIR (Adsorption Equilibrium Infrared Spectroscopy) described previously for the characterization of adsorption of CO on different metal-supported catalysts [3] and using TiO$_2$ P25 from Degussa as solid representative of the support of NH$_3$-SCR catalysts.

Materials and Methods
The AEIR method consists in following the evolution of the IR bands of adsorbed species in isobaric condition during heating/cooling cycles. This provides the area evolutions of the IR bands characteristic of each adsorbed species as a function of the adsorption temperature $T_a$. These data give the evolutions of the experimental coverage $\theta(T_a)$ of each adsorbed species X in isobaric conditions. The comparison of the $\theta(T_a)$ curve to that obtained from a theoretical model (Langmuir, Temkin) provides the values of the heats of adsorption of each adsorbed species as a function of surface coverage. Which are key thermodynamic parameters in the modeling of heterogeneous catalytic processes.

The development of the procedure was made using (a) a home made IR cell in transmission mode and (b) a TiO$_2$ pellet treated in situ under O$_2$ at 440$^\circ$C during 20 min. After cooling to 300 K, the adsorption of ammonia is performed using a gas flow rate of 0.1%NH$_3$/He. After the adsorption equilibrium, the adsorption temperature was increased progressively while registering IR spectra of adsorbed species periodically with a FTIR spectrometer (Nicolet 6700).

Results. Figure 1 shows the evolution of experimental coverage of the two adsorbed species on the Lewis-acid sites of TiO$_2$ P25; noted NH$_{3ads-L1}$ and NH$_{3ads-L2}$ using their characteristic IR bands (a) $\delta_L$ at 1149 cm$^{-1}$ (symbols *) and 1228 cm$^{-1}$ (symbols ▲) respectively and (b) $\delta_p$ at 1596 cm$^{-1}$ with is a common IR band (symbols ●). The heats of adsorption at high and low coverage were deduced for each species by fitting the theoretical curves of Temkin model (continuous lines) to the experimental points: 56 and 105 kJ/mol for NH$_{3ads-L1}$; 105 and 160 kJ/mol for NH$_{3ads-L2}$. The $\delta_p$ IR band allows measuring the proportion of the two species on TiO$_2$ surface at 303K: $x_p=0.73$ and $x_L=0.27$.

![Figure 1. Evolution of the coverage of the NH$_3$ adsorbed species on TiO$_2$ P25 (P$_{arb}$= 1mbar).](image)

Significance
This study allowed identifying two NH$_3$ species adsorbed on Lewis sites of TiO$_2$ P25. The individual heats of adsorption of these species and their relative proportions on TiO$_2$ surface at SCR temperature condition were determined. Forthcoming articles show that the present method can be applied to model and industrial NH$_3$-SCR catalysts.

References