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_2O_5-WO_3/TiO_2 catalysts (NH_3-SCR) using an experimental microkinetic approach. One of the key step 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 $\theta_X(T_a)$ of each adsorbed species X in isobaric conditions. The comparison of the $\theta_X(T_a)$ 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°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 $NH_{3ads\text{-}L1}$ and $NH_{3ads\text{-}L2}$ using their characteristic IR bands (a) δ_s at 1149 cm^{-1} (symbols □) and 1228 cm^{-1} (symbols ▲) respectively and (b) δ_{as} 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 $NH_{3ads\text{-}L1}$; 105 and 160 kJ/mol for $NH_{3ads\text{-}L2}$. The δ_{as} IR band allows measuring the proportion of the two species on TiO_2 surface at 303K: x_1= 0.73 and x_2=0.27.

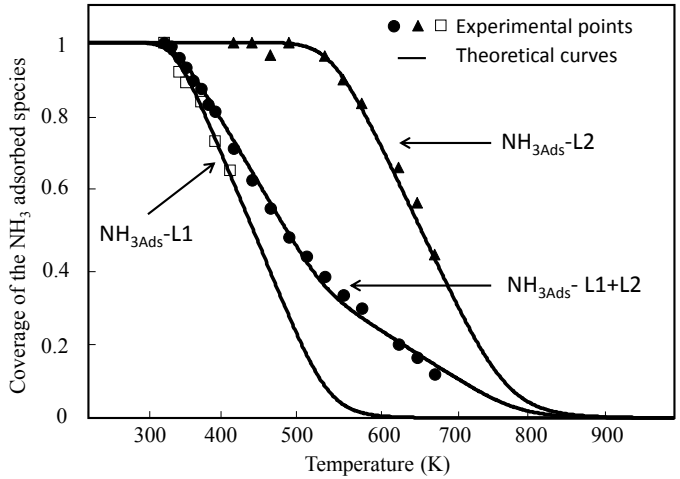

Figure 1. Evolution of the coverage of the NH_3 adsorbed species on TiO_2 P25 (P_{ads}= 1mbar).

Significance

This study allowed identifying two NH_3 species adsorbed on Lewis sites of TiO_2 P25. The individual heats of adsorption oh 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

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