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Individual amounts of Lewis and Brønsted acid sites on metal oxides from NH₃ adsorption equilibrium: Case of TiO₂ based solids --Manuscript Draft--

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Abstract:	<p>ABSTRACT: The present study is dedicated to the development of an original method for the measurement of the individual amounts QASi of the acid sites ASi (acidity of Lewis and Brønsted) present on three TiO₂ based solids of increasing composition complexity: TiO₂-P25, 6% WO₃/TiO₂-P25 and a sulfated 0.7% V₂O₅/9% WO₃/TiO₂ NH₃-SCR catalyst. The method is based on quantitative characterizations of the NH₃ adsorption equilibrium (adsorption temperature Ta and pressure Pa) by the association of (a) the AEIR method providing the individual coverage qASi(Ta, Pa) of the adsorbed NH₃ species on the ASi sites and (b) the total amount (in μmol/g) of the adsorbed NH₃ species: QTNH₃(Ta, Pa) by using a mass spectrometer. For a solid having n types of ASi sites, the QASi values are obtained from the numerical solution of linear equation systems (with at least n equation) obtained considering that QTNH₃(Ta, Pa) is equal to the sum of the contribution of each adsorbed NH₃ species: QASi qASi(Ta, Pa). This imposes the measurement of at least n QTNH₃(Ta, Pa) in a Ta range preventing the contribution of parallel surface processes (i.e NH₃ oxidation). On TiO₂-P25, n= 3 (two Lewis and one weak Brønsted acid sites) and the QASi amounts are obtained from three QTNH₃(Ta, Pa) values. The others solids having two Lewis (L1 and L2) and two Brønsted (B1 and B2) acid sites impose a series of m measurements of QTNH₃(Ta, Pa) with m>> n: the QASi are obtained by optimization between theoretical and experimental QTNH₃(Ta, Pa) curves such as 109, 202, 70 and 130 μmol/g for QL2, QL1, QB2 and QB1 respectively of 0.7% V₂O₅/9% WO₃/TiO₂. It is shown that these four amounts of sites permit to conclude that the L2 Lewis acid site is the one forming the pivotal NH₃ads-L2 species of the reaction by using nitrogen mass balances between the amounts of adsorbed NH₃ species and the N₂ production in the presence of NO.</p>

Highlights

- The individual amounts of acid sites on metal oxides are measured using NH_3 adsorption equilibrium conditions.
- The original method is based on the association of quantitative FTIR spectroscopy and volumetric measurements.
- The method is applied to TiO_2 , WO_3/TiO_2 and a $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ NH_3 -SCR catalyst.
- The measurements permit the identification of the active acid site of $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ for the NH_3 -SCR reaction.

Graphical Abstract

Individual amounts of Lewis and Brønsted acid sites on metal oxides from NH₃ adsorption equilibrium: Case of TiO₂ based solids

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ABSTRACT: The present study is dedicated to the development of an original method for the measurement of the individual amounts Q_{AS_i} of the acid sites AS_i (acidity of Lewis and Brønsted) present on three TiO_2 based solids of increasing composition complexity: TiO_2 -P25, 6% WO_3/TiO_2 -P25 and a sulfated 0.7% $V_2O_5/9\% WO_3/TiO_2$ NH_3 -SCR catalyst. The method is based on quantitative characterizations of the NH_3 adsorption equilibrium (adsorption temperature T_a and pressure P_a) by the association of (a) the AEIR method providing the individual coverage $\theta_{AS_i}(T_a, P_a)$ of the adsorbed NH_3 species on the AS_i sites and (b) the total amount (in $\mu mol/g$) of the adsorbed NH_3 species: $Q_{TNH_3}(T_a, P_a)$ by using a mass spectrometer. For a solid having n types of AS_i sites, the Q_{AS_i} values are obtained from the numerical solution of linear equation systems (with at least n equation) obtained considering that $Q_{TNH_3}(T_a, P_a)$ is equal to the sum of the contribution of each adsorbed NH_3 species: $Q_{AS_i} \theta_{AS_i}(T_a, P_a)$. This imposes the measurement of at least n $Q_{TNH_3}(T_a, P_a)$ in a T_a range preventing the contribution of parallel surface processes (i.e NH_3 oxidation). On TiO_2 -P25, $n=3$ (two Lewis and one weak Brønsted acid sites) and the Q_{AS_i} amounts are obtained from three $Q_{TNH_3}(T_a, P_a)$ values. The others solids having two Lewis (L1 and L2) and two Brønsted (B1 and B2) acid sites impose a series of m measurements of $Q_{TNH_3}(T_a, P_a)$ with $m \gg n$: the Q_{AS_i} are obtained by optimization between theoretical and experimental $Q_{TNH_3}(T_a, P_a)$ curves such as 109, 202, 70 and 130 $\mu mol/g$ for Q_{L2} , Q_{L1} , Q_{B2} and Q_{B1} respectively of 0.7% $V_2O_5/9\% WO_3/TiO_2$. It is shown that these four amounts of sites permit to conclude that the L2 Lewis acid site is the one forming the pivotal $NH_{3ads-L2}$ species of the reaction by using nitrogen mass balances between the amounts of adsorbed NH_3 species and the N_2 production in the presence of NO.

Keywords: $V_2O_5/WO_3/TiO_2$, ammonia adsorption, amount of acid sites, NH_3 -SCR, active site.

1. Introduction

The flue gas denitrification in coal-fired power plants [1, 2] by the reduction of NO_x with NH_3 in the presence of O_2 (named NH_3 -SCR) on $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalysts [1-4] is one of the industrial processes using a catalytic reaction performed on the acid sites on metal oxides [5]. It is known that a number of Lewis (named LAS) and Brønsted (named BAS) acid sites can be present on the surface of dispersed metal oxides due to different (a) unsaturated cations $\text{M}_i^{+\delta}$ [6] and (b) hydroxyl groups OH_i able to provide a proton [7] respectively. The present study is dedicated to the development of an analytical method for the quantification of the individual amounts of the different LAS and BAS sites on metal oxides. Then these data are used to identify the active sites of a $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ NH_3 -SCR catalyst.

The identification of the acid sites of metal oxides is realized via the adsorption of probe base molecules such as CO, nitriles, NH_3 and amines implying that the experimental data are dependent on the properties of the sites and the probe molecule [6, 7]. Consequently, working on the relationships between acid sites and a catalytic reaction, it is recommended using the reactant as probe molecule [6] such as NH_3 in the present study considering the NH_3 -SCR reaction. FTIR spectroscopy is of particular interest for the study of the adsorbed species formed by the probe molecules as detailed in a number of review articles [6, 8, 9] and references therein). For the adsorption of NH_3 , the presence of LAS and/or BAS is revealed by the symmetric (δ_s) and asymmetric (δ_{as}) deformation IR bands of the $\text{NH}_{3\text{ads-L}}$ and NH_4^+ species in the $1700\text{-}1100\text{ cm}^{-1}$ range [8-13]. The position of the δ_s IR band of $\text{NH}_{3\text{ads-L}}$ species is strongly sensitive to the nature of the LAS and the detection of more than one IR band in the range $1250\text{-}1100\text{ cm}^{-1}$ was ascribed to different LAS such as two on TiO_2 solids [10-13].

FTIR spectroscopy can be used for the quantification of the amounts of LAS and BAS adsorbing NH_3 via the Beer-Lambert law after the measurement of the intensities (in absorbance mode A_i) of IR bands characteristic of the $\text{NH}_{3\text{ads-L}}$ and NH_4^+ species and using

extinction coefficients from literature. However, this parameter is dependent on the solid composition, the experimental conditions and the environment of the adsorbed species [6, 14] leading to significant differences in literature data such as for the extinction coefficient (in $\text{cm } \mu\text{mol}^{-1}$) of the IR band of the NH_4^+ species at $\approx 1450 \text{ cm}^{-1}$: 13 ± 0.3 [15], 9.4 ± 0.7 [16] and 3.03 [17]. This explains the interest for temperature programmed desorption methods (TPD) [18, 19] which may differentiate the adsorbed NH_3 species formed at 300 K according to their activation energy of desorption. The differences in their either true (TPD without readsorption) or net (TPD with readsorption) rates of desorption measured with a mass spectrometer (MS) during the linear increase in the temperature in an inert gas lead to different peaks of NH_3 production. These peaks are characterized by the temperature T_M of their maximum: the higher is E_d , the higher is T_M and the stronger is the strength of the site. The amount of NH_3 produced in each peak should be related to the amounts of the different acid sites. However an accurate quantification is rarely allowed because the TPD peaks generally overlap as for the NH_3 -TPD on V_2O_5 - WO_3 - TiO_2 catalysts [20-28]. This is due to (a) the presence of $\text{NH}_{3\text{ads-L}}$ and NH_4^+ species having activation energies of desorption depending on the coverages θ : $E_d(\theta)$ and (b) the contribution of NH_3 readsorption during the TPD which is rarely prevented on conventional catalysts as shown by Demmin and Gorte [29]. For instance, it has been shown that the heat of adsorption of the $\text{NH}_{3\text{ads-L}}$ species formed on the strongest LAS of a TiO_2 solid decrease linearly with the increase in the coverage from 160 kJ/mol to 104 kJ/mol at low and high coverages respectively [30]. For this species, Fig S1 shows the theoretical changes in its coverage and the rate of NH_3 production during TPD experiments without and with NH_3 readsorption. For the two situations a very broad peak (extended on $\Delta T > 300 \text{ K}$) is observed particularly considering readsorption. Thus if several types of acid sites are present on a solid, this explains that strongly overlapped NH_3 peaks are observed preventing their accurate decomposition and so the quantification of the sites. For these situations, NH_3 -TPD data are

mainly used for the quantification of weak, medium and strong acid sites (whatever their natures) by considering the amount of NH_3 desorbed in temperature range such as $T_d < \approx 473$ K, $473 \approx T_d < \approx 573$ and $T_d > \approx 573$ K respectively [25-27]. In some studies, the NH_3 -TPD peak is decomposed into a number of symmetrical peaks (i.e. three in ref [31]). However, without a theoretical support this remains an approximate quantification of the sites. Finally, another difficulty can be associated to NH_3 -TPD on some metal oxides; the contribution of parallel reactions such as the oxidation of NH_3 at high temperatures [20, 21].

Niwa and Katada [14] and references therein have developed an analytical procedure (named IRMS-TPD) to overcome the difficulties associated to TPD methods by the association of FTIR and MS measurements according to operando procedures in experimental conditions leading to free readsorption. IRMS-TPD consists in the simultaneous measurement during the linear increase in the temperature ($dT = \beta dt$) of the net desorption rates of (a) NH_3 using a mass spectrometer and (b) $\text{NH}_{3\text{ads-L}}$ and NH_4^+ species using the decrease in the intensity A_i of their IR bands according to $-dA_i/dT$. Using the coincidence of the T_M values obtained from the MS and FTIR data, IRMS-TPD provides the enthalpy and entropy of adsorption of each adsorbed species. Moreover, the amounts of the LAS and BAS can be quantified [32] by assuming that the sum of concentrations of ammonia from all the adsorbed species should be equal to that C_g measured by MS over the temperature range according to: $C_g = \sum X_i \left(-\frac{dA_i}{dt} \right)$ where $X_i = \alpha \varepsilon_i^{-1}$ and α is a constant depending on the experimental conditions (i.e heating and gas flow rates) and ε_i is the molar extinction coefficient ($\text{cm}^{-1} \text{m}^2 \text{mol}^{-1}$) for the IR band characterizing the adsorbed species i [32]. Because each $-dA_i/dT$ have their unique temperature dependency, the set of coefficients X_i giving the best fitting between C_g and $-(dA_i/dT)$ can be obtained by a numerical method (i.e least squares method [32]). Then this provides the adsorption coefficient ε_i for each IR bands and finally the amount of adsorbed NH_3 and NH_4^+ species. However, one

disadvantage of TPD procedures, considering the measurement of the amounts of LAS and BAS, is the isothermal desorption performed before the increase in T often at $T_d = 373$ K [16, 20, 25-28] and for 1 h. The purpose of this procedure is the removal of NH_3 physisorbed like species. However, calculations show that this leads to the desorption of a significant fraction of NH_3 species formed on strong acid sites. For instance, Fig S2 shows that $\approx 40\%$ of the $\text{NH}_{3\text{ads-L}}$ species formed on the strongest LAS of a TiO_2 solid are desorbed after 1 h at $T_d = 373$ K. This situation explains the interests for the measurement of the individual amounts of acid sites based on procedures using NH_3 adsorption equilibrium as developed in the present study.

The present method is an extension of those developed in previous works named adsorption equilibrium infrared spectroscopy (AEIR) [33, 34] and temperature programmed adsorption equilibrium (TPAE) [35] using two separate FTIR and MS setups in contrast with IRMS-TPD [14, 32]. It is based on the measurement of the total amounts of NH_3 adsorption: $Q_{\text{TNH}_3}(T_a, P_a)$ at the adsorption equilibrium for adsorption temperature T_a and pressure P_a by using the MS setup. This amount is related to the different acid sites AS_i according to:

$$Q_{\text{TNH}_3}(T_a, P_a) = \sum_{i=1}^n Q_{\text{AS}_i} \theta_{\text{NH}_{3\text{ads-AS}_i}}(T_a, P_a) \quad (1)$$

where: n is the number of different acid sites AS_i (LAS and/or BAS), Q_{AS_i} is the amount of the AS_i sites and $\theta_{\text{NH}_{3\text{ads-AS}_i}}(T_a, P_a)$ is the coverage of the adsorbed $\text{NH}_{3\text{ads-AS}_i}$ species (either $\text{NH}_{3\text{ads-L}}$ or NH_4^+) on AS_i at T_a and P_a . Note that eq (1) concerns the adsorption equilibrium coverage of the adsorbed species whereas IRMS-TPD focus on the net desorption rate [14, 16, 32]. Equation (1) shows that the Q_{AS_i} values can be obtained from a n linear equations system by (a) measuring $Q_{\text{TNH}_3}(T_a, P_a)$ and (b) determining the coverages of the $\text{NH}_{3\text{ads-AS}_i}$ species for n (T_a, P_a) couples. In matrix term the linear equation system is as follows:

$$Q_{\text{TNH}_3} = \Theta \times Q_{\text{ASI}} \quad (2)$$

where $QTNH_3$ is the column matrix of the $QTNH_3(T_a, P_a)$ values, Θ is $n \times n$ matrix having as coefficients the coverages of the n adsorbed NH_3 species for n experimental conditions and $QASI$ is the column matrix of the unknown amounts of each of the n AS_i sites. The linear equations system can be solved by numerical methods [36]. In these calculations, the coefficients of the Θ matrix must be known. This has been performed in previous works using the AEIR method for three solids of increasing composition complexity [30, 37, 38]: a commercial TiO_2 , its modification by deposition of WO_3 and a $V_2O_5/WO_3/TiO_2$ NH_3 -SCR catalyst. From the evolution of the intensity of IR bands ascribed to NH_{3ads-L} and NH_4^+ species during the increase in the adsorption temperature T_a under isobaric condition, the AEIR method [33, 34] provides the evolution of the coverage of each adsorbed NH_3 species and then either individual heats of adsorption considering (a) localized adsorbed species for the expression of their adsorption coefficients and (b) either the Temkin or the Langmuir adsorption model. These data allow determining the adsorption equilibrium coverage of each NH_3 species for all sets of T_a and P_a values providing the coefficients of the Θ matrix.

The aim of the present study is to show the advantages and limits of the original method based on eq (1) for the determination of the amounts of the different acid sites of the three selected solids. Then, for the NH_3 -SCR catalyst, it is shown that these data allow identifying the acid site which is involved in the reaction by using transient experiments.

2. Material and Methods

2.1 Solids, Preparation and Pretreatment Procedures

Three TiO_2 based solids of different compositions have been used (a) TiO_2 -P25 from Degussa ($\approx 55 \text{ m}^2/\text{g}$, $\approx 85\%$ anatase and $\approx 15\%$ rutile with traces of SiO_2 : 0.2 wt%) and (b) two solids prepared in previous studies: a 6 wt% WO_3/TiO_2 -P25 [37] and a sulfated 0.7 wt% $V_2O_5/9 \text{ wt\% } WO_3/TiO_2$ catalyst ($80 \text{ m}^2/\text{g}$, 1.34% S) [38]. Briefly, the incipient wetness method has been used with aqueous solutions of (a) ammonium metatungstate for the

deposition of WO_3 on TiO_2 -P25 and (b) ammonium metavanadate dissolved in the presence of oxalic acid using as support the sulfated 9% WO_3/TiO_2 solid (DT52) from Millennium Inorganic Chemicals ($85 \text{ m}^2/\text{g}$, pure anatase, 1.35% S) [38]. After impregnation the solids were dried 24 h in air at room temperature and then 24 h at 110°C before heating ($\approx 1 \text{ K/min}$) to 713 K for 6 h. Raman and IR spectroscopy have shown that depositions formed were well-dispersed VO_y and WO_z groups (mono-oxo) with limited interactions between these groups and with the sulfate groups of DT52 [37, 38]. However, the composition was provided as V_2O_5 and WO_3 similarly to literature data. Before NH_3 adsorption the solids were treated on the analytical systems as follows: O_2 (713 K, 10 min) $\rightarrow$ He (713 K, 5 min) $\rightarrow$ He (adsorption temperature T_a). The same catalyst sample was used to perform a series of experiments and it was pretreated as above before each experiment.

2.2 Amounts of adsorbed NH_3 species at T_a and P_a using a Mass Spectrometer (MS)

The MS setup is the same that the one used in previous work [30, 37, 38]. Briefly, different valves allowed performing switches between controlled gas flow rates of known compositions (at atmospheric pressure) at the inlet of a quartz CSTR microreactor containing the solid supported on quartz wool. The solids were slightly compressed (density: $\approx 1.4 \text{ g/cm}^3$), crushed and sized ($\approx 230 \text{ }\mu\text{m}$) before using $\approx 0.15\text{-}0.3 \text{ g}$ of particles. The temperature of the catalyst, controlled via a furnace of low inertia, was measured by a coaxial K type thermocouple ($\varnothing = 0.25 \text{ mm}$) inserted in the catalyst sample. A quadrupole mass spectrometer (Inficon, Transpector CPM) provided, via a selection of m/e peaks, the molar fractions of the gases at the reactor outlet after calibrations using gas mixtures of known compositions. The tubes, valves and inlet system of the MS were heated at 383 K. The MS system provided the total amount of NH_3 adsorbed at the adsorption equilibrium for adsorption temperature T_a and pressure P_a according to two procedures. The first was as follows: the pretreated solids were cooled in helium to the adsorption temperature T_a ($T_a \geq 300 \text{ K}$) and then a switch $\text{He} \rightarrow x\%$

$\text{NH}_3/\text{x}\%$ Ar/He was performed (Ar was a tracer) leading to the progressive attainment (with time on stream t) of the adsorption equilibrium at T_a and $P_a = x \cdot 10^3$ Pa. The total amount of NH_3 adsorption (i.e in $\mu\text{mol/g}$ of catalyst) was obtained from the integration of the apparent rate of NH_3 adsorption according to:

$$QT_{\text{NH}_3}(T_a, P_a) = \int_0^{t_e} \frac{[(x_{\text{Ar}}(t))_{\text{out}} - (x_{\text{NH}_3}(t))_{\text{out}}] F}{m_c V_M} 10^6 dt \quad (3)$$

where, $(x_{\text{Ar}}(t))_{\text{out}}$ and $(x_{\text{NH}_3}(t))_{\text{out}}$ are the molar fractions of Ar and NH_3 at the outlet of the reactor at time t (in s) of the adsorption, F is the gas flow rate (in cm^3/s), m_c is the mass of catalyst (in g), V_M is the gaseous molar volume in the experimental conditions of the measurement (in cm^3/mole) and t_e is the duration to obtain the adsorption equilibrium corresponding to $(x_{\text{Ar}}(t_e))_{\text{out}} = (x_{\text{NH}_3}(t_e))_{\text{out}}$. The measurements were repeated after the pretreatment procedure of the solid sample using different T_a or/and P_a . The amount of weakly adsorbed species at T_a was obtained by the switch $\text{x}\%$ $\text{NH}_3/\text{x}\%$ Ar/He $\rightarrow$ He. The second method for the measurement $QT_{\text{NH}_3}(T_a, P_a)$ was provided by the TPAE procedure [35] which permitted obtaining a number of values from one experiment according to the following procedure. After measuring $QT_{\text{NH}_3}(300 \text{ K}, x \cdot 10^3 \text{ Pa})$ by the first method, T_a was increased linearly (i.e $\alpha \approx 10 \text{ K/min}$) in the presence of $\text{x}\%$ $\text{NH}_3/\text{x}\%$ Ar/He. This led to the progressive decrease in the adsorption equilibrium coverages of the different adsorbed NH_3 species which was associated with the increase in the amount of NH_3 in the gas phase (net NH_3 desorption rate). According to the design of the TPAE experiment (by the selection of a set of α , m_c and x values) the increase in P_{NH_3} in the CSTR reactor was limited to $\approx 30\%$ of that at the inlet of the reactor ($x \cdot 10^3 \text{ Pa}$) which allowed assuming isobaric conditions favoring the exploitation of the experimental data [35]. The amount of NH_3 removed from the surface (in $\mu\text{mol/g}$) by the increase from $T_a = 300 \text{ K}$ at $t=0$ to $T_a = 300 + \alpha t_{T_a}$ was:

$$Q_{DNH_3}(300\text{ K} \rightarrow T_a) = \int_0^{t_{Ta}} \frac{[(x_{NH_3}(t))_{out} - x_{Ar}(t)_{out}]}{m_c V_M} F \cdot 10^6 dt \quad (4)$$

and the total amount of NH_3 adsorbed at T_a and $P_a \approx x \cdot 10^3$ Pa (in $\mu\text{mol/g}$) was:

$$Q_{TNH_3}(T_a, x \cdot 10^3 \text{ Pa}) = Q_{TNH_3}(300 \text{ K}, x \cdot 10^3 \text{ Pa}) - Q_{DNH_3}(300 \text{ K} \rightarrow T_a) \quad (5)$$

Similar calculations were made for different t_{Ta} providing, from one experiment a set of $Q_{TNH_3}(T_a, x \cdot 10^3 \text{ Pa})$ values for $T_a \geq 300 \text{ K}$ with an accuracy of $\approx \pm 5 \mu\text{mol/g}$.

2.3 IR cell Microreactor

FTIR characterizations of the adsorbed NH_3 species have been performed using a Nicolet-6700 FTIR spectrometer equipped with a small pathlength ($\approx 2 \text{ mm}$) home made stainless steel IR cell in transmission mode using CaF_2 windows and described in more details previously [39]. Briefly, it allowed in-situ treatments of a compressed disk of solid ($\Phi = 2.1 \text{ cm}$, $m \approx 40\text{-}80 \text{ mg}$), in the $293\text{-}800 \text{ K}$ temperature range with a controlled gas flow rate in the range of $150\text{-}2000 \text{ cm}^3/\text{min}$ at atmospheric pressure selected using different switching valves and purified by different traps in particular cold traps for H_2O impurities (77 K using helium). The FTIR system has been used for the identification of the adsorbed NH_3 species and their evolution at the adsorption equilibrium for $T_a \geq 300 \text{ K}$ using $x\%$ NH_3/He gas mixtures.

3. Results and Discussion

The procedure for the measurement of the individual amounts of acid sites on metal oxides using NH_3 adsorption equilibrium is presented by its application to the solid having the simplest composition: $TiO_2\text{-P25}$ and then to WO_3/TiO_2 and $V_2O_5/WO_3/TiO_2$.

3.1 Individual amounts of the acid sites on TiO_2 P25 using NH_3

Equation (1) imposes the identification of the different acid sites on the surface of the pretreated solid for the adsorption of NH_3 . This has been done by using FTIR spectroscopy [30] and the main results and conclusions are briefly summarized to facilitate the presentation. In the range $1700\text{-}1100 \text{ cm}^{-1}$, the adsorption of 0.1% NH_3/He at 300 K on $TiO_2\text{-P25}$ leads to

spectrum a in Fig. 1 with IR bands similar to those observed by different authors on the same solid and ascribed as follows [10-13]: (a) the strong IR band at 1142 cm^{-1} and the shoulder at 1215 cm^{-1} comes from the δ_s vibrations of two adsorbed NH_3 species on different LAS named $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ respectively, (b) the IR band at 1596 cm^{-1} is due to the overlap of the δ_{as} vibrations of these two species, (c) the broad and weak IR band at 1475 cm^{-1} and the shoulder at 1680 cm^{-1} are ascribed to the deformation vibrations of $\text{NH}_4^+\text{-B}$ species formed on a BAS. Considering DFT literature data, the two types of LAS have been located on different surfaces of TiO_2 particles [30].

Figure 1: FTIR spectra of adsorbed species formed by NH_3 on $\text{TiO}_2\text{-P25}$ at different adsorption temperature T_a using 0.1% NH_3/He : (a)-(e) $T_a = 300, 373, 473, 573$ and 673 K . **Inset:** Evolution of the coverage of the three adsorbed NH_3 species with T_a for $P_{\text{NH}_3} = 0.1\text{ kPa}$ according to eqs (ES1)-(ES2) and the heats of adsorption in Table 1.

It has been shown [30] that the intensities of the IR bands of the $\text{NH}_{3\text{ads-L}}$ species are not modified at $T_a = 300\text{ K}$ by increasing P_{NH_3} from 0.1 kPa to 1 kPa , indicating the saturation of the two LAS due to the high heats of adsorption of the two $\text{NH}_{3\text{ads-L}}$ species (strong LAS) whereas the intensity of the IR bands of the $\text{NH}_4^+\text{-B}$ species increases (weak BAS). The evolutions of the IR bands with the increase in the T_a for $P_a = 0.1\text{ kPa}$ (Fig. 1 spectra b-e) show

that (a) the IR bands of the NH_4^+ species disappear at $T_a \approx 393$ K, (b) the δ_s IR band of $\text{NH}_{3\text{ads-L1}}$ species decreases significantly in the T_a range of 300-573 K (associated to a shift to higher wavenumbers: i.e. from 1142 cm^{-1} to 1190 cm^{-1} at 300 K and 573 K respectively) and (c) the δ_s IR band of $\text{NH}_{3\text{ads-L2}}$ species is unmodified until $T_a \approx 590$ K and then it decreases progressively. This indicates that the strength of the LAS are in the order $\text{L2} > \text{L1}$. The data in Fig. 1 indicate that eq. (1) for $\text{TiO}_2\text{-P25}$ is:

$$Q\text{TNH}_3(T_a, P_a) = Q_{\text{L1}} \theta_{\text{NH}_{3\text{ads-L1}}}(T_a, P_a) + Q_{\text{L2}} \theta_{\text{NH}_{3\text{ads-L2}}}(T_a, P_a) + Q_{\text{B}} \theta_{\text{NH}_4^+\text{-B}}(T_a, P_a) \quad (6)$$

The amounts of B, L1 and L2 acid sites in eq. (6): Q_{B} , Q_{L1} and Q_{L2} respectively can be obtained by measuring $Q\text{TNH}_3(T_a, P_a)$ at three adsorption equilibrium conditions. In eq. (6), the adsorption equilibrium coverages of the $\text{NH}_{3\text{ads-L1}}$, $\text{NH}_{3\text{ads-L2}}$ and NH_4^+ species at T_a and P_a are known [30, 40] from the application of the AEIR method.

Solid	$\text{NH}_{3\text{ads-L1}}$			$\text{NH}_{3\text{ads-L2}}$		
	E(1) kJ/mol	E(0) kJ/mol	x_1	E(1) kJ/mol	E(0) kJ/mol	x_2
$\text{TiO}_2\text{-P25}^{\text{a}}$	58	102	0.73	102	160	0.27
6% $\text{WO}_3/\text{TiO}_2\text{-P25}^{\text{b}}$	55	105	0.65	110	147	0.35
0.7% $\text{V}_2\text{O}_5/9\% \text{WO}_3/\text{TiO}_2\text{-S}^{\text{b}}$	59	97	0.65	100	142	0.35
	$\text{NH}_4^+\text{-B1}$			$\text{NH}_4^+\text{-B2}$		
	E(1) kJ/mol	E(0) kJ/mol	x_1	E(1) kJ/mol	E(1) kJ/mol	x_2
$\text{TiO}_2\text{-P25}^{\text{c},*}$	43	80	1			0
6% $\text{WO}_3/\text{TiO}_2\text{-P25}^{\text{b}}$	59	105	0.60	75	140	0.40
0.7% $\text{V}_2\text{O}_5/9\% \text{WO}_3/\text{TiO}_2\text{-S}^{\text{b}}$	57	90	0.65	75	135	0.35

^a: Ref [30]; ^b: Ref [37] ; ^c: Ref [40], *: $\text{TiO}_2\text{-P25}$ has only one weak BAS.

Table 1: Heats of adsorption at low (E(0)) and high (E(1)) coverages (accuracy $\approx \pm 5$ kJ/mol) and proportions of the adsorbed NH_3 species on three TiO_2 based solid according to the AEIR method.

It has been shown [30, 40] that their coverages follow the Temkin adsorption model (eq. ES1 in SI) with heats of adsorption decreasing linearly with the increase in the coverage and Table 1 gives the values at low and high coverages for the three species assuming localized

adsorbed species for their adsorption coefficients (eq ES2 in SI). The accuracy on the heats of adsorption provided by the AEIR method is of $\approx \pm 5$ kJ/mol [33, 34]. From the data in Table 1 and eqs ES1-ES2, the individual coverages of the three adsorbed NH_3 species on the pretreated TiO_2 -P25 can be determined whatever T_a and P_a . For instance, the inset of Fig. 1 shows the evolution of the coverages with T_a in isobaric conditions for $P_a = 0.1$ kPa: it can be observed that at $T_a = 300$ K, the coverage of the $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ species is 1 for $P_a = 0.1$ kPa and that their individual amounts are those of Q_{L1} and Q_{L2} respectively. This means that considering spectrum a in Fig. 1 recorded at 300 K and assuming similar IR extinction coefficients for the δ_s IR bands at 1142 and 1215 cm^{-1} , then the ratio of their intensities (after their decomposition [30]) provides that of Q_{L1}/Q_{L2} and then to the contributions (in proportion) of the L1 and L2 sites to the total amount of LAS: $x_1 \approx 0.7$ and $x_2 \approx 0.3$ [30]. Using the evolution of the intensity of their common IR band at 1596 cm^{-1} with the increase in T_a in isobaric condition, AEIR method provided accurate values of x_1 and x_2 [30] as indicated in Table 1. The interest of x_1 and x_2 for the present study is that the relationship $Q_{L1} = (x_1/x_2) Q_{L2}$ may reduce the number of unknown parameters in eq. (6) to two (i.e Q_B and Q_{L2}).

Figure 2: Adsorption of NH_3 on the pretreated TiO_2 -P25 at different temperatures using the M.S system: Parts A₁ and A₂ in Helium and Parts B₁ and B₂ in 0.5% NH_3 /0.5% Ar/He at 300 K: Part C increase in T_a from 300 to 715 K (TPAE procedure).

The measurements of $Q_{\text{TNH}_3}(T_a, P_a)$ under different experimental conditions have been performed with the MS system according to Fig. 2 which shows the evolutions of the Ar and NH_3 molar fractions during the switch He (Part A₁) $\rightarrow$ 0.5% NH_3 /0.5% Ar/He (Part B₁) at 300 K on the pretreated TiO_2 -P25 solid. The total amount of NH_3 adsorbed at the adsorption equilibrium (eq. (3)) is $Q_{\text{TNH}_3}(300 \text{ K}, 0.5 \text{ kPa}) = 332 \text{ } \mu\text{mol of NH}_3/\text{g}$ due to the $\text{NH}_{3\text{ads-L1}}$, $\text{NH}_{3\text{ads-L2}}$ and $\text{NH}_4^+\text{-B}$ adsorbed species (Fig. 1). Equations ES1-ES2 and Table 1 indicate that $\theta_{\text{NH}_4^+ \text{-1}}(300 \text{ K}, 0.5 \text{ kPa}) = 0.83$ and $\theta_{\text{NH}_3\text{-L1}}(300 \text{ K}, 0.5 \text{ kPa}) = \theta_{\text{NH}_3\text{-L2}}(300 \text{ K}, 0.5 \text{ kPa}) = 1$ leading to the first equation of a three linear equations system:

$$0.83 Q_B + Q_{L1} + Q_{L2} = 332 \text{ } \mu\text{mol/g} \quad (7)$$

The switch 0.5% NH_3 /0.5% Ar/He (Part B₁) $\rightarrow$ He (Part A₂) leads to the desorption of 96 $\mu\text{mol of NH}_3/\text{g}$ ascribed to the weakly adsorbed $\text{NH}_4^+\text{-B}$ species and a fraction of the $\text{NH}_{3\text{ads-L1}}$ species. This amount is readsorbed during the following switch He (Part A₂) $\rightarrow$ 0.5% NH_3 /0.5% Ar/He (Part B₂). The increase in T_a (Part C of Fig. 2) in the presence of 0.5% NH_3 /0.5% Ar/He (TPAE procedure) leads to a net NH_3 desorption due to the progressive decrease in the adsorption equilibrium coverages of the three adsorbed species (inset of Figure 1) according to a broad peak with a maximum at $T_m = 405 \text{ K}$ and a shoulder at 315 K. At the end of the heating stage for $T_a \approx 710 \text{ K}$, the molar fractions of NH_3 and Ar are equal indicating the attainment of the adsorption equilibrium for $T_a = 710 \text{ K}$ and $P_a = 0.5 \text{ kPa}$. Figure 2 shows that there is a small H_2O production at high temperatures (without N_2 production) ascribed to the dehydration of the solid in the presence of adsorbed NH_3 species [30] and references therein. The accuracy on the measurements of the amount of NH_3 removed from the surface (eq. (4)) in the high T_a range is limited because for low apparent NH_3 desorption rates the difference between the molar fractions of Ar and NH_3 is very small. This means that $Q_{\text{TNH}_3}(T_a, P_a)$ from eqs (4)-(5) must be measured for $T_a \leq 650 \text{ K}$. Note that the highest adsorption pressure in the CSTR reactor: 0.65 Pa at $T_a = 405 \text{ K}$ permits assuming quasi isobaric

condition during the TPAE [35]. Part C in Fig. 2 and eqs (4)-(5) provide the experimental evolution of the total amount of NH_3 adsorbed at the adsorption equilibrium on $\text{TiO}_2\text{-P25}$ with the increase in T_a in quasi isobaric conditions as shown by curve a in Fig. 3 (symbols $\bullet$) obtained for time intervals of ≈ 60 s. These data are used to discuss the advantages and limits of two calculation methods (named M1 and M2) for the determination of Q_B , Q_{L1} and Q_{L2} .

Figure 3: Total amount of NH_3 adsorbed and coverage of the adsorbed NH_3 species on $\text{TiO}_2\text{-P25}$ at different adsorption temperatures T_a : (a) experimental amount for NH_3 from part C in Fig.2; (b), (c) and (d) coverages of the $\text{NH}_4^+\text{-B}$, $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ species respectively for $P_a = 0.5$ kPa; (e) theoretical total of NH_3 adsorbed considering $Q_B = 22.5$ $\mu\text{mol/g}$, $Q_{L1} = 225$ $\mu\text{mol/g}$ and $Q_{L2} = 83.4$ $\mu\text{mol/g}$; (f) theoretical total of NH_3 adsorbed considering $Q_B = 22.5$ $\mu\text{mol/g}$, $Q_{L1} = 225$ $\mu\text{mol/g}$ and $Q_{L2} = 83.4$ $\mu\text{mol/g}$.

3.1.1 Individual amount of acid sites on $\text{TiO}_2\text{-P25}$ from method M1

The acidic properties of $\text{TiO}_2\text{-P25}$ offer a favorable situation for the measurement of Q_B , Q_{L1} and Q_{L2} as shown by the evolutions of the coverages of the $\text{NH}_4^+\text{-B}$, $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ species (curves b, c and d in Fig. 3 respectively) with T_a for $P_a = 0.5$ kPa using eqs (ES1)-(ES2) and the heats of adsorption from Table 1. These curves show that $Q_{\text{TNH}_3}(T_a, P_a)$

is due to (a) only L2 at $T_a \geq 620$ K, (b) L1 and L2 in the 520-620 K range and (c) the three acid sites in the 300-520 K range. This situation leads to a triangular (3×3) Θ matrix (eq. (2)) providing easily the different amounts of acid sites. For instance at $T_a = 620$ K: $Q_{NH_3}(620 \text{ K}, 0.5 \text{ kPa}) = 66 \text{ } \mu\text{mol/g}$ (curve a Fig. 3) while $\theta_{NH_3-L_2}(620 \text{ K}, 0.5 \text{ kPa}) = 0.78$ (curve d in Fig. 3) leading to $Q_{L_2} \approx 84 \text{ } \mu\text{mol/g}$. Similarly, in Fig. 3 for $T_a = 550$ K: $Q_{NH_3}(550 \text{ K}, \approx 0.5 \text{ kPa}) = 107 \text{ } \mu\text{mol/g}$ (curve a, Fig. 3) while $\theta_{NH_3-L_1}(550 \text{ K}, 0.5 \text{ kPa}) = 0.11$ and $\theta_{NH_3-L_2}(550 \text{ K}, 0.5 \text{ kPa}) = 0.97$ leading to: $(0.11 Q_{L_1} + 0.97 Q_{L_2}) = 107 \text{ } \mu\text{mol/g}$ and then $Q_{L_1} = 227 \text{ } \mu\text{mol/g}$. Note that $Q_{L_2}/(Q_{L_1} + Q_{L_2}) = 0.27$ which is consistent with the data in Table 1 obtained from the AEIR method. Finally, eq. (7) for the adsorption at 300 K provides $Q_B = 25 \text{ } \mu\text{mol/g}$.

For solids having different acidic properties, the above calculations are not allowed: the Θ matrix is rarely triangular due to the contributions of several adsorbed NH_3 species to $Q_{TNH_3}(T_a, P_a)$ in the available T_a and P_a ranges. The impacts of this situation can be evaluated using the data on TiO_2 -P25 for $T_a < 460$ K such as $T_a = 300$ K, 392 K and 445 K (see Fig. 3 curves b, c, d) corresponding to $Q_{TNH_3}(T_a, P_a)$ of 332 $\mu\text{mol/g}$, 261 $\mu\text{mol/g}$ and 204 $\mu\text{mol/g}$ respectively (Fig. 3 curve a) leading to the linear equation system:

$$0.83 Q_B + Q_{L_1} + Q_{L_2} = 332 \quad (8)$$

$$0.33 Q_B + 0.77 Q_{L_1} + Q_{L_2} = 261 \quad (9)$$

$$0.096 Q_B + 0.54 Q_{L_1} + Q_{L_2} = 204 \quad (10)$$

The numerical solutions of this system (using Mathcad) are significantly different from those determined using the triangular Θ matrix: $Q_B \approx 52 \text{ } \mu\text{mol/g}$, $Q_{L_1} \approx 194 \text{ } \mu\text{mol/g}$ and $Q_{L_2} \approx 94 \text{ } \mu\text{mol/g}$. This is due to the impacts of the experimental uncertainties on $Q_{TNH_3}(T_a, P_a)$. For instance, assuming in eq. (10) that at 445 K the amount of adsorbed NH_3 species is 207 $\mu\text{mol/g}$ then the solutions of the linear equation are $Q_B \approx 64 \text{ } \mu\text{mol/g}$, $Q_{L_1} \approx 170 \text{ } \mu\text{mol/g}$ and $Q_{L_2} \approx 109 \text{ } \mu\text{mol/g}$. For solids having more complex acidic properties than TiO_2 -P25, the experimental uncertainties on $Q_{TNH_3}(T_a, P_a)$ may lead to numerical solutions with negative values. This

situation can be overcome by using a calculation method taking into account a large number of experimental data as shown for the TiO₂-P25 solid.

3.1.2 Individual amount of acid sites on TiO₂-P25 from method M2

This method is based on the determination of Q_B , Q_{L1} and Q_{L2} by optimization of their values to obtain an agreement between the experimental $Q_{NH3}(T_a, P_a) = f(T_a)$ curve (i.e curve a in Fig. 3) at $P_a \approx 0.5$ kPa and the theoretical curve provided by eq. (6). To facilitate the optimization procedure, the relationship: $Q_{L1}/Q_{L2} = x_1/x_2 = 0.73/0.27$ (Table 1) is used to reduce the number of variables and eq. (6) gives:

$$Q_{TNH3}(T_a, P_a) = Q_B \theta_{NH4^+-B}(T_a, P_a) + Q_{L2} [0.73 \theta_{NH3-L1}(T_a, P_a)/0.27] + \theta_{NH3-L2}(T_a, P_a) \quad (11)$$

In eq. (11) the different coverages are provided by the Temkin adsorption model assuming localized adsorbed species (eqs ES1-ES2) with the heats of adsorption in Table 1. An optimization function (i.e. Minerr of Mathcad) indicates that the best agreement between eq. (11) and curve a in Fig. 3 is obtained using $Q_B = 22$ $\mu\text{mol/g}$ and $Q_{L2} = 83$ $\mu\text{mol/g}$ ($Q_{L1} = 225$ $\mu\text{mol/g}$). These values (reported in Table 2) are consistent with those obtained with the triangular Θ matrix in method M1 and lead to the theoretical (eq. (11)) curve e in Fig. 3 overlapping the experimental data (standard deviation: S.D= 0.9).

Solids	Brønsted acid sites $\mu\text{mol/g}$		Lewis acid sites $\mu\text{mol/g}$		$Q_{NH3}(300, 0.5 \text{ kPa})$	S.D [#]
	B1	B2	L1	L2		
TiO ₂ -P25	22		225	83	330	0.9
	15*		233	86*	334	1.3
	42*		216	80*	338	1.3
6% WO ₃ /TiO ₂ -P25	12	8	230	124	374	0.8
	5	3*	238	128*	374	0.8
	30	20*	210	113*	373	1.2
0.7% V ₂ O ₅ /9% WO ₃ /TiO ₂	130	70	202	109	503	1.5
	108	58*	223	120*	509	6.8
	145	78*	186	100*	509	4.5

Standard deviation

* Highest and lowest values leading to theoretical curves $Q_{\text{NH}_3}(T_a, 0.5 \text{ kPa})$ consistent with the experimental data (curve a in Fig. 3).

Table 2: Individual amount of acid sites on TiO_2 -based solids from eq. (11) using the total amount of NH_3 adsorbed at the adsorption equilibrium for $T_a \geq 300 \text{ K}$ and $P_a \approx 0.5 \text{ kPa}$ and an optimization function.

It must be noted that accepting a small increase in S.D such as from 0.9 to 1.3, theoretical curves consistent with the experimental data can be obtained with other Q_B and Q_{L2} values: Q_{L2} cannot be strongly different that $83 \text{ } \mu\text{mol/g}$, however small variations of Q_{L2} lead to a significant modification of Q_B (the higher is Q_{L2} the lower is Q_B). For instance, Q_{L2} and Q_B couples in the range ($Q_{L2} = 80 \text{ } \mu\text{mol/g}$ and $Q_B = 42 \text{ } \mu\text{mol/g}$) and ($Q_{L2} = 86 \text{ } \mu\text{mol/g}$ and $Q_B = 15 \text{ } \mu\text{mol/g}$) (see S.D in Table 2) give theoretical curves consistent with the experimental data considering the experimental uncertainties whereas $Q_{L2} = 70 \text{ } \mu\text{mol/g}$ and $Q_B = 90 \text{ } \mu\text{mol/g}$ lead to curve f in Fig. 3 differing significantly of curve a. Finally, method M2, which can be used whatever the acidic properties of a solid, provides the amounts of the strong L2 acid sites on TiO_2 -P25 with a reasonable accuracy ($83 \pm \approx 3 \text{ } \mu\text{mol/g}$) whereas the uncertainty on the weak BAS is significantly higher. This situation is encountered for the other TiO_2 -based solids: the accuracy on the strong acid sites is significantly higher than those on the weak acid sites.

3.2 Individual amounts of the acid sites on 6% WO_3/TiO_2 -P25 using NH_3

The FTIR study of the adsorption of NH_3 on the 6% WO_3/TiO_2 -P25 solid has been described in detail in a previous work [37] and the results of interests for the present study are shortly summarized to facilitate the identification of the different acid sites. Figure S3 compares in the range of $1700\text{-}1100 \text{ cm}^{-1}$, the IR spectra after adsorption of 0.1% NH_3/He at 300 K on 6% WO_3/TiO_2 -P25 and TiO_2 -P25 using disks of similar weights. After deposition of the WO_x groups there are (a) a strong IR band at 1198 cm^{-1} and a shoulder at 1280 cm^{-1} ascribed similarly to TiO_2 -P25 to the δ_s vibration of two adsorbed NH_3 species on L1 and L2 LAS named $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ respectively, (b) an IR band at 1602 cm^{-1} due to the δ_{as}

vibration of the two $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ species and (c) a broad IR band at 1445 cm^{-1} and a shoulder at 1680 cm^{-1} are ascribed to the deformation vibrations of NH_4^+ species. Moreover, it has been shown that the overtone IR band at 2013 cm^{-1} of the W=O vibration of WO_x species is strongly modified by the adsorption of NH_3 showing that WO_x are involved as adsorption sites [37]. Figure S3 shows that the WO_x groups lead to (a) strong shifts to higher wavenumbers of the δ_s IR bands of the $\text{NH}_{3\text{ads-L}}$ species which is consistent with different literature data [41-43] and with the view that this vibration is very sensitive to the nature and environment of the sites (the common δ_{as} IR band is slightly modified as compared to $\text{TiO}_2\text{-25}$) and (b) the IR band of the NH_4^+ species at 1445 cm^{-1} is significantly increased indicating that WO_x species favor the BAS [41-43].

The evolutions of the IR bands of the two $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ species with the increase in T_a in the range of 300-700 K are qualitatively similar to those on the $\text{TiO}_2\text{-P25}$ support and their individual heats of adsorption and proportions according to the AEIR method [37] are reported in Table 1. Similarly, the AEIR method has been applied to the IR band of the NH_4^+ at 1445 cm^{-1} at 300 K which decreases progressively with the increase in T_a . However, it is detected at 700 K using 0.1% NH_3/He [37] indicating that the WO_x groups are associated with strong BAS consistent with literature data [44-46]. It has been shown [37] that two NH_4^+ species, named $\text{NH}_4^+\text{-B1}$ and $\text{NH}_4^+\text{-B2}$, formed on B1 and B2 BAS (1 and 2 in the increasing order of strength) contribute to the evolution of the intensity of the IR band with the increase in T_a for $P_a = 0.1\text{ kPa}$. Their individual heats of adsorption and proportions are provided in Table 1 [37]. Finally, the FTIR study of the adsorption of NH_3 on 6% WO_3/TiO_2 leads to the conclusions that two LAS and two BAS are involved in the NH_3 adsorption at 300 K and eq. (1) becomes:

$$Q\text{TNH}_3(T_a, P_a) = Q_{L1}\theta_{\text{NH}_{3\text{ads-L1}}}(T_a, P_a) + Q_{L2}\theta_{\text{NH}_{3\text{ads-L2}}}(T_a, P_a) + Q_{B1}\theta_{\text{NH}_4^+\text{-B1}}(T_a, P_a) + Q_{B2}\theta_{\text{NH}_4^+\text{-B2}}(T_a, P_a) \quad (12)$$

Figure 4 shows the evolution of the molar fractions of the gases during the switch He (Part A)→ 0.5% NH₃/0.5% Ar/He (Part B) on the pretreated 6% WO₃/TiO₂-P25 solid indicating that QTNH₃(300 K, 0.5 kPa)≈ 373 μmol of NH₃/g. The increase in T_a (Fig. 3 Part C) leads to a net NH₃ desorption rate due to the decrease in the coverages of the four adsorbed NH₃ species according to a broad peak with a maximum at 362 K. At T_a> 590 K there are productions of H₂O and N₂ which increase with T_a associated with a net NH₃ consumption at T_a> 680 K. This indicates that at high temperatures and similarly to V₂O₅/TiO₂ solids [20, 21] there is an oxidation of NH₃ via oxygen species (O_s) provided by the solid according to:

Considering the absence of N₂ production on TiO₂-P25 (Fig. 2), the O_s species must originate from the WO_x species.

Figure 4: Adsorption of NH₃ on the pretreated 6% WO₃/TiO₂-P25 solid at different temperatures using the M.S system: Part A in Helium and Part B in 0.5% NH₃/0.5% Ar/He at 300 K: Part C increase in T_a from 300 to 700 K (TPAE procedure).

The consumption of NH₃ implies that QTNH₃(T_a, P_a) must be measured at T_a < 590 K to prevent the contribution of the NH₃ oxidation. Curve a in Fig. 5 shows the experimental evolution of QTNH₃(T_a, ≈0.5 kPa) in the 300-590 K range from Part C in Fig. 4 (eqs (4) and (5)). Curves (b), (c), (d) and (e) in Fig. 5 give the evolutions of the coverages of the NH_{3ads-L1}, NH₄⁺-B1, NH₄⁺-B2 and NH_{3ads-L2} species respectively from eq ES1-ES2 and the data in Table

1. These curves show that the four adsorbed species are present on the surface for $T_a \leq 590$ K and that method M2 based on an optimization function must be used for the measurement of their individual amounts. Similarly to $\text{TiO}_2\text{-P25}$, the number of variables is decreased before calculation by using the ratios $Q_{L2}/Q_{L1} = 0.65/0.35$ and $Q_{B2}/Q_{B1} = 0.6/0.4$ (Table 1) provided by the AEIR method leading from eq (12) to:

$$Q_{\text{TNH}_3}(T_a, P_a) = [\theta_{\text{NH}_3\text{-L1}}(T_a, P_a) \frac{0.65}{0.35} + \theta_{\text{NH}_3\text{-L2}}(T_a, P_a)] Q_{L2} + [\theta_{\text{NH}_4^+\text{-1}}(T_a, P_a) \frac{0.6}{0.4} + \theta_{\text{NH}_4^+\text{-2}}(T_a, P_a)] Q_{B2} \quad (14)$$

Figure 5: Total amount of NH_3 adsorbed and coverage of the adsorbed NH_3 species on 6% WO_3/TiO_2 at different adsorption temperatures T_a : (a) experimental amount for NH_3 from part C in Fig.4; (b), (c), (d) and (e) coverages of the $\text{NH}_{3\text{ads-L1}}$, $\text{NH}_4^+\text{-B1}$, $\text{NH}_4^+\text{-B2}$ and $\text{NH}_{3\text{ads-L2}}$ species respectively for $P_a = 0.5$ kPa; (f) theoretical total amount of NH_3 adsorbed considering $Q_{B2} = 8.1 \mu\text{mol/g}$, $Q_{L2} = 123.9 \mu\text{mol/g}$; (g) theoretical total of NH_3 adsorbed considering $Q_{B2} = 20 \mu\text{mol/g}$, $Q_{L1} = 113 \mu\text{mol/g}$ ($Q_{B1} = 30 \mu\text{mol/g}$, $Q_{L1} = 210 \mu\text{mol/g}$).

The optimization function using eq. (14) provides $Q_{L2} = 123 \mu\text{mol/g}$ and $Q_{B2} = 8 \mu\text{mol/g}$ leading to curve f in Fig. 5 which overlaps the experimental curve a in (standard deviation: S.D= 0.8). However, similarly to $\text{TiO}_2\text{-P25}$, accepting an increase in S.D, others Q_{L2} and Q_{B2} values can be consistent with the experimental data. For instance curve g is obtained using $Q_{L2} = 113 \mu\text{mol/g}$ and $Q_{B2} = 20 \mu\text{mol/g}$ (standard deviation of 1.23) (lower Q_{L2} values lead to theoretical curves significantly different of curve a in the high T_a range). Note that Q_{L2} cannot

by significantly higher than $123 \mu\text{mol/g}$ because this leads to negative Q_{B2} values. Table 2 summarizes the Q_{B1} , Q_{B2} , Q_{L1} and Q_{L2} values obtained from the optimization function and the highest and lowest values leading from eq. (14) to a theoretical curve consistent with curve a accepting a small increase in S.D.

3.3 Individual amounts of the acid sites on $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ using NH_3

Raman and IR spectroscopy have shown that V and W of this NH_3 -SCR catalyst are present as well dispersed mono-oxo VO_x and WO_y groups [37]. Similarly to 6% WO_3/TiO_2 , four adsorbed NH_3 species are formed on the NH_3 -SCR catalyst for $T_a = 300 \text{ K}$ and $P_a = 0.5 \text{ kPa}$, on two LAS (L1 and L2) and two BAS (B1 and B2) and their individual heats of adsorption and proportions have been determined using the AEIR method (Table 1) [38].

Figure 6: Adsorption of NH_3 on the pretreated sulfated 0.7% $\text{V}_2\text{O}_5/9\% \text{WO}_3/\text{TiO}_2$ catalyst at different temperatures using the M.S system: Parts A_1 , A_2 in Helium and Parts B_1 , B_2 in 0.5% $\text{NH}_3/0.5\% \text{Ar/He}$ at 300 K; Part C increase in T_a from 300 to 700 K (TPAE procedure).

For this solid, the individual amounts of acid sites present a particular interest taking into account that NH_3 is one of the reactant of the NH_3 -SCR reaction and that there is a debate on the nature of the acid site (either BAS or LAS) involved in its activation by adsorption [47-51]. Figure 6 shows the evolution of the molar fractions of NH_3 and Ar at the microreactor

outlet during the switch He (Part A₁)→ 0.5% NH₃/0.5% Ar/He (Part B₁) at 300 K on the pretreated 0.7% V₂O₅/9% WO₃/TiO₂ catalyst leading from eq. (3) to QTNH₃(300 K, 0.5 kPa)= 502 μmol/g. This amount exceeds significantly the total amount of mono-oxo species: ≈ 77 μmol of VO_x/g and ≈ 388 μmol of WO_y/g indicating that some acid sites are located on the TiO₂ support in agreement with Busca et al. [52] and with the densities 2.9 W/nm² and 0.6 V/nm² in the catalyst which are lower than the accepted values for a monolayer ≈ 4.5 W/nm² and 8 V/nm² [48]. The switch 0.5% NH₃/0.5% Ar/He→ He (Figure 6, part A₂), shows the desorption of 130 μmol of NH₃/g (readsorbed in Part B₂ during the switch He→ 0.5% NH₃/0.5% Ar/He) due to NH₃ species having low heats of adsorption at full coverage (mainly NH_{3ads-L1} and NH₄⁺-B1, see Table 1). Part C in Fig. 6 gives the evolutions of the molar fractions of the gases during the linear increase in T_a in the presence of 0.5% NH₃/0.5% Ar/He. A broad NH₃ peak is observed with a maximum at T_m= 326 K due to the progressive decrease in the coverage of the four adsorbed species. There is production of N₂ (with H₂O, not shown) for T_a> 520 K, indicating that a fraction of NH₃ is oxidized by Os species of the catalyst and for T_a> 580 K, this oxidation leads to a net consumption of NH₃. This indicates that the measurements of QTNH₃(T_a, P_a) must be performed at T_a<≈ 520 K.

Figure 7: Total amount of NH₃ adsorbed and coverage of the adsorbed NH₃ species on 0.7% V₂O₅/9% WO₃/TiO₂ at different adsorption temperatures T_a: (a) experimental amount for NH₃ from part C in Fig. 6 (▲, ■ measurements similarly to part B₁ of Fig. 6 at 464 K and 480 K); (b), (c), (d) and (e) coverages of the NH₄⁺-B1, NH_{3ads}-L1, NH₄⁺-B2 and NH_{3ads}-L2 species respectively for P_a= 0.5 kPa; (f) theoretical total amount of NH₃ adsorbed considering the heats of adsorption in Table 1 with Q_{B2}= 95 μmol/g, Q_{L2}= 73 μmol/g (S.D= 3.8); (g) theoretical total amount of NH₃ adsorbed after a slight decrease in the heats of adsorption of the two weakly adsorbed NH₃ species: E(0)= 95 kJ/mol and E(1)= 54 kJ/mol for NH_{3ads}-L1 species and E(0)= 85 kJ/mol and E(1)= 52 kJ/mol for NH₄⁺-B1 with Q_{B2}= 70 μmol/g, Q_{L2}= 109 μmol/g (S.D= 1.5). (see the text for more details).

Curve a in Fig. 7 shows the experimental evolution of Q_{TNH₃}(T_a, ≈0.5 kPa) (eqs (4), (5)) from Part C in Fig. 6 in the T_a range 300-520 K. Curves (b), (c), (d) and (e) in Fig. 7 give the evolutions of the coverages of the NH₄⁺-B1, NH_{3ads}-L1, NH₄⁺-B2 and NH_{3ads}-L2 species respectively from eq ES1-ES2 and the data in Table 1. These curves show that the four adsorbed species contribute to the adsorption of NH₃ in the T_a range of curve a and that method M2 must be used for the measurement of the amount of each acid site. Similarly to TiO₂-P25 and 6% WO₃/TiO₂-P25, the number of variables is decreased by using the ratios Q_{L2}/Q_{L1}= 0.65/0.35 and Q_{B2}/Q_{B1}= 0.65/0.35 (Table 1) leading from eq (1) to:

$$Q_{TNH_3}(T_a, P_a) = [\theta_{NH_3-L1}(T_a, P_a) \frac{0.65}{0.35} + \theta_{NH_3-L2}(T_a, P_a)] Q_{L2} + [\theta_{NH_4^+-B1}(T_a, P_a) \frac{0.65}{0.35} + \theta_{NH_4^+-B2}(T_a, P_a)] Q_{B2} \quad (15)$$

Using eqs ES1-ES2 and Table 1, the optimization function provides Q_{L2}≈ 73 μmol/g and Q_{B2}= 95 μmol/g leading to curve f in Fig. 7 (S.D = 3.8). This curve is consistent with the experimental data in the high adsorption temperatures range whereas a significant difference is observed for T_a< 341 K (at T_a= 300 K the theoretical amount of adsorbed NH₃ species is ≈ 480 μmol/g as compared to 502 μmol/g in curve a in Fig. 7). This seems due to the impacts of the uncertainties on the heats of adsorption of the weakly adsorbed NH_{3ads}-L1 and NH₄⁺-B1 species. For instance, a decrease by an amount equal or lower than the uncertainty of the AEIR method (±5 kJ/mol) of the heats of adsorption of the NH_{3ads}-L1 and NH₄⁺-B1 species leads from the

optimization function to $Q_{B2} = 70 \text{ } \mu\text{mol/g}$ ($Q_{B1} = 130 \text{ } \mu\text{mol/g}$) and $Q_{L2} = 109 \text{ } \mu\text{mol/g}$ ($Q_{L1} = 202 \text{ } \mu\text{mol/g}$) and then to curve g in Fig. 7 which overlaps the experimental data in the full T_a range (S.D= 1.5). Others values of Q_{B2} and Q_{L2} gives theoretical curves consistent with the experimental data accepting a slight increase in S.D: there are in the range 100-120 $\mu\text{mol/g}$ for Q_{L2} corresponding to 78-58 for Q_{B2} (see Table 2).

After the experiments in Fig. 6, the catalyst sample has been pretreated at 713 K and the total amount of NH_3 has been measured at 464 K using 0.5% NH_3 /0.5% Ar/He similarly to part B1 in Fig. 6 (symbol ▲ in Fig. 7). Then after a new pretreatment at 713 K, a similar measurement has been performed at 480 K (symbol ■ in Fig. 7). The overlap of symbols ▲ and ■ in Fig. 7 with curve a shows the repeatability of the experiments and the limited impact of the successive pretreatments on the adsorption capacity of the solid. To our knowledge, there are no literature data on the individual amount of LAS and BAS on a $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ NH_3 -SCR catalyst to be compared with the present study. However, eq. (15) and the data in Tables 1 and 2 allow us determining the total amount of NH_3 adsorbed at the adsorption equilibrium whatever T_a and P_a . This permits comparison with literature data on NH_3 -SCR catalysts having a composition similar to the present catalyst. For instance, Lietti et al. [53, 54] have determined 270 moles of NH_3/m^3 of catalyst at 493 K on a 1.4% V_2O_5 /9% WO_3/TiO_2 catalyst (BET surface area similar to the present study: $80 \text{ m}^2/\text{g}$) using 700 ppm NH_3 /1% O_2 /He. Equation (15) provides $Q_{\text{TNH}_3}(493 \text{ K}, 700 \text{ Pa}) = 217 \text{ } \mu\text{mol/g}$ using the heats of adsorption of the adsorbed species leading to curve g in Fig. 7 corresponding to ≈ 304 moles of NH_3 / m^3 (the density of the present catalyst is $\approx 1.4 \text{ g/cm}^3$) in reasonable agreement with Lietti et al. [53,54] considering the differences in the solid composition and preparation methods. Similarly, Xie et al. [55] on a commercial 1.15% V_2O_5 /2.84% WO_3/TiO_2 catalyst (BET surface area $46.5 \text{ m}^2/\text{g}$) have determined ≈ 233 moles of NH_3 / m^3 for $P_{\text{NH}_3} = 400 \text{ Pa}$ and

$T_a = 493$ K while eq 15 provides $Q_{\text{TNH}_3}(493 \text{ K}, 400 \text{ Pa}) = 202 \text{ } \mu\text{mol/g}$ and then 283 mol/m^3 . The difference is consistent with the BET surface area.

The measurement of the individual amount of acid sites is of particular interest for solids involved in catalytic reactions. For instance, after the identification of the active acid sites, the rate of the reaction can be expressed in TOF (s^{-1}) and compared to the theoretical reaction rate obtained from kinetic model supported by an experimental microkinetic approach. Moreover, these data can be used for the understanding of the surface processes involved a catalytic reaction. For instance, it is shown below that the individual amounts of the acid sites on the 0.7% V_2O_5 /9% WO_3 / TiO_2 catalyst (Table 2) permit performing nitrogen mass balances in relationship with the production of N_2 via the reaction of NO with the adsorbed NH_3 species leading to the identifications of (a) the acid site and (b) the pivotal adsorbed NH_3 species involved in the NH_3 -SCR reaction.

3.4 Nature of the acid sites involved in the NH_3 -SCR reaction on V_2O_5 - WO_3 - TiO_2

It is known [21, 56] that adsorbed NH_3 species on V_2O_5 - WO_3 - TiO_2 may react at $T_a > 400$ K with NO in the absence of O_2 via lattice oxygen species provided by the solid according to the global reaction:

The elementary steps of this reaction are parts of those of the NH_3 -SCR reaction according to [4]:

This means that the identification $\text{NH}_{3\text{ads}}$ in eq. (16) may provide that of the pivotal species of the NH_3 -SCR reaction. This can be performed by studying reaction (16) according to an experimental microkinetic approach based on transient experiments with the M.S system and working on the relationship between the individual amount of each adsorbed NH_3 species before reaction and the amount of N_2 production. For instance, Fig. 8 provides the amount of

adsorbed NH_3 species at 464 K on the pretreated solid according to the switch He (part A_1) $\rightarrow$ 0.5% NH_3 /0.5% Ar/He (part B_1): 261 μmol of NH_3 /g. This value is consistent taking into account the experimental uncertainties with the theoretical amounts of each adsorbed NH_3 species at $T_a = 464$ K and $P_a = 0.5$ kPa considering the data to obtain curve g in Fig. 7: 109, 60, 64 and 17 μmol /g for the $\text{NH}_{3\text{ads-L2}}$, $\text{NH}_4^+\text{-B2}$, $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_4^+\text{-B1}$ species respectively (theoretical total amount $Q\text{TNH}_3(464 \text{ K}, 0.5 \text{ kPa}) = 250 \mu\text{mol}/\text{g}$). These data are reported in line 2 of Table 3. The switch 0.5% NH_3 /0.5% Ar/He (part B_1) $\rightarrow$ He (part A_2) in Fig. 8 indicates the desorption of 98 $\mu\text{mol}/\text{g}$ of NH_3 after ≈ 6 min in helium leading to 163 $\mu\text{mol}/\text{g}$ of adsorbed NH_3 species (reported in Table 3 line 3 column 2). Neglecting the NH_3 readsorption during desorption then calculations similar to Fig. ES2 indicate that only the $\text{NH}_{3\text{ads-L2}}$ can be present on the surface after 6 min in helium at 464 K, with a theoretical coverage ≈ 0.07 corresponding to $\approx 8 \mu\text{mol}$ of NH_3 /g.

Figure 8: Isothermal reaction at 464 K between adsorbed NH_3 species and NO from transient experiments using successive switches between gas flow rates: A_x in helium, B_x in 0.5% NH_3 /0.5% Ar/He and C_x in 0.5% NO/0.5% Ar/He.

This amount is strongly smaller than the experimental data, confirming that NH_3 readsorption cannot be neglected in the interpretation of desorption experiments in agreement

with literature data [14, 16, 29]. In part A₂ of Fig. 8, the coverages of the different NH₃ species evolve as a succession of adsorption equilibriums with the decrease in P_{NH3}. For instance, in Fig. 8 at the end of part A₂, P_{NH3} ≈ 12 Pa and T_a = 464 K, then eq 15 and the data used for curve g in Fig. 7 provide Q_{TNH3}(464 K, 12 Pa) = 160 μmol/g which is consistent with the experimental data (the individual amounts of the four adsorbed species are indicated in Table 3 line 3). In Fig 8, the switch He (part A₂) → 0.5% NO/0.5% Ar/He (part C₁) leads to a sharp N₂ production peak during ≈ 70 s followed by a pseudo steady state indicating that reaction eq. (16) is operant. The total N₂ production in part C₁ is Q_{N2} = 45 μmol/g in parallel to a NO consumption of Q_{NO} = 43 μmol/g. The ratio Q_{NO}/Q_{N2} ≈ 1 is consistent with the stoichiometry of reaction eq. (16).

Experiment At 464 K	Q _{TNH3} (exp)	Q _{TNH3} (theo) eq 15	Q _{NH3ads-L2}	Q _{NH3ads-L1}	Q _{NH4+-2}	Q _{NH4+-1}
	μmol NH ₃ /g of catalyst					
Adsorption NH ₃ P _{NH3} = 500 Pa part B ₁	261	250	109	64	60	17
Desorption: 6 min P _{NH3} = 12 Pa end part A ₂	163	160	105	10	44	1
NO reaction: 4 min P _{NH3} = 7 Pa end part C ₁	105	151	103	6	42	0

* the difference with Q_{NH3T}(exp) comes from the consumption of the NH_{3ads-L2} species in the presence of NO.

Table 3: Experimental and theoretical (from eq 15) total amounts of adsorbed NH₃ species on 0.7% V₂O₅/9% WO₃/TiO₂ catalyst at 464 K during the experiments in Fig. 8 and contribution of the different adsorbed NH₃ species to Q_{TNH3}(theo).

Note that (a) NH₃ desorption continues in parallel to the N₂ production: ≈ 13 μmol of NH₃/g and P_{NH3} ≈ 7 Pa at the end of part C₁, (b) the transient increase in the sample temperature associated with the N₂ peak is consistent with the ΔH of the NH₃-SCR reaction: -407 kJ/mol [57] and explains the slight increase in the net NH₃ desorption rate at the introduction of NO and (c) H₂O is produced (not shown) together with N₂, however its production cannot be related to the stoichiometry of eq 16 due to its adsorption on the catalyst. The pseudo steady

state of the N_2 production in part C₁ of Fig. 8 comes from the progressive decrease in the rate of the reaction (eq 16) with the consumptions of (a) the adsorbed intermediate NH_{3ads} species and (b) the lattice oxygen species O_l . Moreover, as $Q_{NO} \approx Q_{N_2}$ there is no significant adsorption of NO in the presence of the adsorbed NH_3 species consistently with the Eley-Rideal mechanism used in numerous kinetic studies of the NH_3 -SCR on V_2O_5 - WO_3 - TiO_2 catalysts [5, 47, 49, 58-62]. The desorption of NH_3 continues after the switch 0.5% NO/0.5% Ar/He (part C₁) $\rightarrow$ He (part A₃): $\approx 7 \mu\text{mol/g}$, leading to $P_{NH_3} \approx 4 \text{ Pa}$ at the end of part A₃, indicating that adsorbed NH_3 species are present on the catalyst at the pseudo steady state of part C₁. This is consistent with the high heats of adsorption of the $NH_{3ads-L2}$ and NH_4^+ -B2 species which allow maintaining significant coverages for low adsorption pressures such as 0.64 and 0.34 respectively at $T_a = 464 \text{ K}$ and $P_a = 0.1 \text{ Pa}$ (P_{NH_3} must be $\leq 10^{-5} \text{ Pa}$ to obtain an adsorption equilibrium coverage of ≈ 0 at 464 K for $NH_{3ads-L2}$ species).

Nitrogen mass balances considering (a) the individual amounts of the four adsorbed NH_3 species at the end of part A₂ in Fig. 8 (line 3 Table 3) and (b) the N_2 production in part C₁ permit the identification of the NH_{3ads} species in reaction (16). The stoichiometry of eq. (16) indicates that the N_2 production: $45 \mu\text{mol}$ of N_2/g consumes the same amount of NH_{3ads} species: this species can be neither $NH_{3ads-L1}$ nor NH_4^+ -B1 which are present in amounts $< 45 \mu\text{mol/g}$ at the introduction of NO (Table 3 line 3). Moreover, the pseudo steady state of the N_2 production in part C₁ indicates that a significant amount of the NH_{3ads} involved in reaction (16) must be present at the end of part C₁. This fact (a) does not correspond to the NH_4^+ -B2 species because the N_2 production in part C₁ ($45 \mu\text{mol } N_2/\text{g}$) represents the total amount of this species before introduction of NO (Table 3, line 3, column 6) and (b) is consistent with the $NH_{3ads-L2}$ species: the N_2 production in part C₁ represents $\approx 43\%$ of its amount before introduction of NO. The conclusion that $NH_{3ads-L2}$ species is the species involved in eq. (16) is reinforced taking into account the desorption of NH_3 in parallel to the N_2 production: $\approx 13 \mu\text{mol/g}$. In Fig. 8, the N_2

and NH_3 productions in part C_1 indicate that $\approx 58 \mu\text{mol}$ of NH_3/g have been removed from the surface leading to $163-58 = 105 \mu\text{mol/g}$ of adsorbed NH_3 species whereas $P_{\text{NH}_3} \approx 7 \text{ Pa}$ before the switch $C_1 \rightarrow A_3$. The theoretical amounts of the four adsorbed NH_3 species at $T_a = 464 \text{ K}$ and $P_a = 7 \text{ Pa}$ are indicated in Table 3 (line 4) leading to $Q_{\text{TNH}_3}(464 \text{ K}, 7 \text{ Pa}) = 151 \mu\text{mol/g}$ which is higher than the experimental data: $105 \mu\text{mol/g}$, due to the consumption of the $\text{NH}_{3\text{ads-L2}}$ species for the N_2 production in the presence of NO . However, in Table 3, the theoretical decrease in the amounts of adsorbed NH_3 species due to the decrease in P_a from 12 Pa (line 3) to 7 Pa (line 4): $9 \mu\text{mol/g}$, is consistent taking into account the accuracy of the measurements with the experimental NH_3 desorption in part C_1 : $13 \mu\text{mol/g}$. Finally, in part C_1 of Fig. 8, the NH_3 production comes from the four adsorbed NH_3 species (main contribution of the $\text{NH}_{3\text{ads-L1}}$) whereas the N_2 production is due to the reaction of NO with the $\text{NH}_{3\text{ads-L2}}$ species (eq. (16)). This conclusion constitutes a contribution to the debate on the nature of the acid site/adsorbed NH_3 species which is active in the NH_3 -SCR on $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalyst and confirms recent works [48, 49] (and references therein) showing the key role of LAS in the reaction. However, Lai and Wachs [49] conclude that the surface vanadia species, in the V^{+5} oxidation state are the catalytic active sites for the SCR reaction on $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalyst while the surface tungsta species (W^{+6}) are not active for the SCR reaction (or less active than V^{+5} [48]) but promote the surface vanadia species. The present measurements shows that the situation is more complex considering that the amount of L2 sites involved in the reaction (16) on the NH_3 -SCR catalyst: $109 \mu\text{mol/g}$ is higher than the amount of V in the solid: $77 \mu\text{mol/g}$ indicating a contribution of a fraction of the W^{+6} sites.

The above N mass balances revealing the role of the $\text{NH}_{3\text{ads-L2}}$ species as pivotal species of the NH_3 -SCR via eq. 16 are validated and completed by the adsorption of NH_3 after the reaction with NO has shown in part B2 of Fig. 8. The switch $0.5\% \text{ NO}/0.5\% \text{ Ar/He}$ (part C_1) $\rightarrow$ He (part A_3) indicate the desorption of $7 \mu\text{mol}$ of NH_3/g leading to an experimental total

amount of adsorbed NH_3 species of $105-7= 98 \text{ } \mu\text{mol/g}$. The switch He (part A_3) $\rightarrow$ $0.5\% \text{ NH}_3/0.5\% \text{ Ar/He}$ (part B_2) leads to the adsorption of $163 \text{ } \mu\text{mol}$ of NH_3/g . This amount is lower than in part B_1 confirming the presence of adsorbed NH_3 species in part A_3 . The total amount of adsorbed NH_3 species at the adsorption equilibrium in part B_2 : $\approx 163 + 98= 261 \text{ } \mu\text{mol/g}$ is similar to that on the pretreated solid ($273 \text{ } \mu\text{mol/g}$, Table 3, line 2). The difference is maybe due to the adsorption of H_2O produced in part C_1 which may change the proportion of LAS and BAS [63]. After the switch $0.5\% \text{ NH}_3/0.5\% \text{ Ar/He} \rightarrow \text{He}$ (Fig. 8, part A_4) leading to the desorption of $121 \text{ } \mu\text{mol}$ of NH_3/g , the introduction of $0.5\% \text{ NO}/0.5\% \text{ Ar/He}$ (Part C_2) leads to a N_2 production: $31 \text{ } \mu\text{mol/g}$, without the sharp peak observed in part C_1 , associated with a NO consumption of $32 \text{ } \mu\text{mol/g}$ while $18 \text{ } \mu\text{mol}$ of NH_3/g desorb. The higher N_2 production rate at the introduction of NO in part C_2 than at the end of C_1 comes from the increase in the amount of pivotal $\text{NH}_{3\text{ads-L2}}$ species by the NH_3 adsorption. However, the N_2 peak at the introduction of NO in part C_2 is significantly smaller than in part C_1 because of the lower amount of lattice O_i species in the solid. The experiments have been repeated in part B_3 - C_3 leading to similar quantitative data with a progressive decrease in the N_2 production rate due to the decrease in the amount of lattice O_i species in the solid.

4. Conclusion

The present study has been dedicated to the development of an original method using NH_3 adsorption for the measurement of the individual amounts Q_{AS_i} of the different AS_i acid sites present on three TiO_2 based solids of increasing complexity: TiO_2 -P25, $6\% \text{ WO}_3/\text{TiO}_2$ -P25 and sulfated $0.7\% \text{ V}_2\text{O}_5/9\% \text{ WO}_3/\text{TiO}_2$ NH_3 -SCR catalyst. The method is based on the quantitative application of FTIR spectroscopy of adsorbed NH_3 species according to the AEIR method [34] associated with volumetric measurements using a mass spectrometer. TiO_2 -P25 which is widely used either alone (i.e photocatalytic reactions) or as support for active phases has been

used for the development of the method. FTIR spectroscopy indicates that TiO₂-P25 has two types of LAS: L1 and L2, and one weak BAS consistent with literature data whereas the others solids have two types of LAS and two types of BAS named L1, L2, B1 and B2 (1 and 2 in the increasing order of strength). The heats of adsorption of the different adsorbed NH₃ species on the three solids were known (Table 1) from the AEIR method [30, 37, 38]. This provides their adsorption equilibrium coverages on each of the AS_i acid sites: $\theta_{\text{NH}_3\text{ads-AS}_i}(T_a, P_a)$ whatever T_a and P_a . The volumetric measurements give the total amount of adsorbed NH₃ species for different adsorption equilibrium conditions at T_a and P_a : $Q_{\text{TNH}_3}(T_a, P_a)$ in $\mu\text{mol/g}$ which is equal to the sum of the contribution of each adsorbed species: $Q_{\text{AS}_i} \theta_{\text{NH}_3\text{ads-AS}_i}(T_a, P_a)$. The individual amounts Q_{AS_i} of n AS_i acid sites of a solid are obtained by numerical solutions of at least a n linear equations system obtained for the measurements of n $Q_{\text{TNH}_3}(T_a, P_a)$ values: this is the situation for TiO₂-P25. The others solids impose the measurements of a larger series of $Q_{\text{TNH}_3}(T_a, P_a)$ which is facilitated by using the TPAE method [35] which provides the experimental evolution $Q_{\text{TNH}_3}(T_a, P_a) = f(T_a)$ in quasi isobaric conditions P_a . Then an optimization function gives the Q_{AS_i} values leading to the best agreement between the experimental and a theoretical $Q_{\text{TNH}_3}(T_a, P_a)$ curves: i.e the individual amounts (in $\mu\text{mol/g}$) of the acid sites on the pretreated sulfated 0.7% V₂O₅/9% WO₃/TiO₂ solid are 109, 202, 70 and 130 in $\mu\text{mol/g}$ for Q_{L2} , Q_{L1} , Q_{B2} and Q_{B1} respectively. The Q_{AS_i} values are of particular interest for solids used as catalysts such as V₂O₅/WO₃/TiO₂ for the removal of NO by the NH₃-SCR reaction. For this solid we have shown how the amounts Q_{L2} , Q_{L1} , Q_{B2} and Q_{B1} permit the exploitation via N mass balances of transient experiments in relationship with the NH₃-SCR reaction leading to the conclusion that the L₂ acid site is the one forming the pivotal NH₃_{ads-L2} species of the reaction.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version

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D. Bianchi
Emeritus Professor
to
Professor J.J. Spivey
Editor in Chief of Catalysis Today

Villeurbanne, June, 9, 2020

Dear Prof. J.J. Spivey

Please find enclosed the revised version of the article submitted to Catalysis Today as contribution to the special issue for the 60th anniversary of IRC/IRCÉLYON: "Individual amounts of Lewis and Brønsted acid sites on metal oxides from NH₃ adsorption equilibrium: case of TiO₂ based solids"

We have considered some comments of the two reviewers to improve the manuscript. Particularly, according to the comments of R2 we have significantly shorten the abstract (-5 lines) and the introduction section (- 28 lines). The order of the references has been modified (removing one reference). However, considering one of the comments of R1 we have inserted 15 lines and a new reference (32) in the revised introduction.

R2 suggests discussing the location of the acidic sites according to the composition of the solids. As explained in the responses this was partially done in previous works using Raman and FTIR spectroscopy and literature data (i.e. WO_x and VO_y groups contribute to the NH₃ adsorption over WO₃/TiO₂ and V₂O₅/WO₃/TiO₂). We have inserted different sentences on this point in particular taking into account literature data on the active sites of V₂O₅-WO₃-TiO₂ catalysts and the present measurements. A detailed description of the location of the acid sites according to the solid composition can be the topic of the future works.

The comments of R1 are mainly relevant of a scientific debate and not of the evaluation of the present work. They concern the validity, the interests and the originalities of the AEIR and TPAE methods used in the study to quantify the individual amounts of LAS and BAS. This has been done in previous works (first article on the AEIR method in 1998 ref (39)). Particularly R1 proposes a comparison with the IRMS-TPD method in operando mode which was cited in the manuscript. This explains that we provide detailed responses taking into account the references cited by R1. We show how it is tricky using IRMS-TPD as compared to AEIR and TPAE. However, this debate cannot be inserted in the present manuscript except (a) the 15 lines in the new introduction section on a specific application of the IRMS-TPD for the quantification of LAS and BAS and (b) the modification of Figure S1 in line with comments on the impact of the readsorption during TPD.

All the modifications are in red in a copy.

We thank the two reviewers for their contributions to the improvement of the manuscript.

Best regards,

D. Bianchi

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: