Supporting Information to

Acidity of SiO₂ supported metal oxides in the presence of H₂O using the AEIR Method. 2. Adsorption and Coadsorption of NH₃ and H₂O on TiO₂/SiO₂ catalysts

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Adsorption Models of the Present Study

According to the Langmuir adsorption model, the coverage is given by:

$$\theta = \frac{A(T_a, P_a)}{A_M} = \frac{K(T_a, E_L)P_a}{1 + K(T_a, E_L)P_a} \quad \text{Eq. S1}$$

where $K(T_a, E_L)$ is the adsorption coefficient at T_a and E_L the heat of absorption of adsorbed species.

Considering the Temkin model, the heat of adsorption varies linearly with the coverage for intrinsic and/or induced heterogeneities of the adsorption sites and the coverage provided for non-dissociative adsorption is given by:^{S1}

$$\theta_{th}(T_a, P_a) = \frac{RT_a}{\Delta E} \times \ln\left(\frac{1 + K(T_a, E_0)}{1 + K(T_a, E_1)} \frac{P_a}{P_a}\right) \quad \text{Eq. S2}$$

where R is the ideal gas constant, E_0 ($K(T_a, E_0)$) and E_1 ($K(T_a, E_1)$) are the heats of adsorption (adsorption coefficients) at low and high coverages, respectively and $\Delta E = E_0 - E_1$. As justified in previous works (see Ref. S1 and references therein), the adsorption coefficient in equations S2 and S3 is provided by the statistical thermodynamic considering localized adsorbed species:

$$K(T_a, E) = \frac{h^3}{(2\pi m k)^{3/2}} \frac{1}{T_a^{5/2}} \exp\left(\frac{E_d - E_a}{R T_a}\right) \quad \text{Eq. S3}$$

where h is the Planck's constant, k is Boltzmann's constant, m is the mass of the molecule, E_d and E_a are the activation energies of desorption and adsorption, respectively. $E = E_d - E_a$ is the heat of adsorption.

Impact of T_a in the 3800-3100 cm^{-1} range on the IR bands of $\text{TiO}_2/\text{SiO}_2\text{-A}$ for 1% NH_3/He

Figure S1. Evolution of the IR bands between 3800 and 3100 cm^{-1} on 19.5% $\text{TiO}_2/\text{SiO}_2\text{-A}$ after the pretreatment procedure and (a)-(g) at the adsorption equilibrium in 1% NH_3/He at 300, 323, 353, 423, 553, 623 and 703 K and (h) in He at 703 K.

Determining of the intensity of the $\nu_4(\text{NH}_4^+)$ IR band at saturation of the sites on $\text{TiO}_2/\text{SiO}_2\text{-A}$

Figure S2. Evolution of the $\nu_4(\text{NH}_4^+)$ band of 19.5% $\text{TiO}_2/\text{SiO}_2\text{-A}$ with P_{NH_3} (0.5, 1 and 2 kPa) at 300 K and determining of its A_M value using the Langmuir model.

Adsorption of 0.2%NH₃/He on TiO₂/SiO₂-G

Figure S3: Evolution of the $\delta_{as}(\text{NH}_3)$ and $\nu_4(\text{NH}_4^+)$ bands with T_a on 20.4% TiO₂/SiO₂-G using 0.2% NH₃/He after a first heating stage to 723 K. (a)-(j) at the adsorption equilibrium at 300, 323, 353, 403, 433, 463, 493, 543, 573, 623 K. **Inset:** Comparison of these bands at the adsorption equilibrium at two adsorption temperatures before and after heating to 723 K in 0.2 %NH₃/He: (a) and (b) at 323 K and 383 K during the first heating stage; (c) and (d) at 323 K and 383 K during the cooling stage.

Heats of adsorption of the $\text{NH}_{3\text{ads}}$ species on $\text{TiO}_2/\text{SiO}_2\text{-G}$

Figure S4: Heats of adsorption of the $\text{NH}_{3\text{ads-L}}$ and NH_4^+ species on 20.4% $\text{TiO}_2/\text{SiO}_2\text{-G}$ using the AEIR method. Red square and blue circle symbols average experimental coverages of the $\text{NH}_{3\text{ads-L}}$ and NH_4^+ species for 0.2 % NH_3/He from the data in Fig. S3; (a) theoretical coverages considering the presence of two $\text{NH}_{3\text{ads-L1}}$ and $\text{NH}_{3\text{ads-L2}}$ species that obey to the Temkin adsorption model (see the parameters in Table 1); (b) and (c) individual coverages of the $\text{NH}_{3\text{ads-L2}}$ and $\text{NH}_{3\text{ads-L1}}$ species; (d) theoretical coverages considering the presence of two $\text{NH}_4^+ \text{-1}$ and $\text{NH}_4^+ \text{-2}$ species that obey to the Langmuir and Temkin model, respectively; (e) and (f) individual coverages of the $\text{NH}_4^+ \text{-2}$ and $\text{NH}_4^+ \text{-1}$ species.

Heats of adsorption of the $\text{H}_2\text{O}_{\text{ads}}$ species on $\text{TiO}_2/\text{SiO}_2\text{-G}$

Figure S5: Application of the AEIR method for the measurement of the heats of adsorption of H_2O species on 20.4% $\text{TiO}_2/\text{SiO}_2\text{-G}$. **Part A:** Evolution of the $\delta(\text{H}_2\text{O})$ band during an increase in T_a for 0.5% $\text{H}_2\text{O}/\text{He}$: (a)-(i) $T_a = 301, 313, 334, 353, 373, 413, 433, 493, 543$ K. **Inset :** comparison to the $\delta(\text{H}_2\text{O})$ bands at 373 K and 433 K using 2% $\text{H}_2\text{O}/\text{He}$ (a and b respectively) and 0.5% $\text{H}_2\text{O}/\text{He}$ (c and d respectively). **Part B:** blue square and red circles symbols: average experimental coverage of the adsorbed H_2O species for $P_{\text{H}_2\text{O}} = 2$ kPa and 0.5 kPa respectively; (a) and (b) theoretical coverages considering two $\text{H}_2\text{O}_{\text{ads-1}}$ and $\text{H}_2\text{O}_{\text{ads-2}}$ species that obey to the Langmuir and Temkin adsorption model, respectively (see the parameters in Table 1); (c) and (d) coverage of the $\text{H}_2\text{O}_{\text{ads-2}}$ and $\text{H}_2\text{O}_{\text{ads-1}}$ for $P_{\text{H}_2\text{O}} = 2$ kPa.

Impacts of T_a on the IR bands during the coadsorption of 0.2% NH_3 /1% H_2O /He on $\text{TiO}_2/\text{SiO}_2\text{-G}$

Figure S6. Evolution of the $\delta_{\text{as}}(\text{NH}_3)$ and $\nu_4(\text{NH}_4)^+$ bands of the adsorbed NH_3 species with T_a on $\text{TiO}_2/\text{SiO}_2\text{-G}$ at the adsorption equilibrium in 0.2% NH_3 /1% H_2O /He (a)-(f) at 473, 493, 513, 533, 553 and 603 K.

Reference

(S1) Bianchi, D. A Contribution to the Experimental Microkinetic Approach of Gas/Solid Heterogeneous Catalysis: Measurement of the Individual Heats of Adsorption of Coadsorbed Species by Using the AEIR Method. *Catalysts* **2018**, 8, 265/1–265/20.