Supplementary Information

Acidity and Characterization of 12-Tungstophosphoric Acid Supported on Silica-Alumina

Flávia C. G. de Mattos, Eduardo N. C. B. de Carvalho, Elon F. de Freitas, Mateus F. Paiva, Grace F. Ghesti, Julio L. de Macedo,* Sílvia C. L. Dias and José A. Dias*

Laboratório de Catálise, Instituto de Química, Universidade de Brasília, Campus Darcy Ribeiro, Asa Norte, CP 4478, 70904-970 Brasília-DF, Brazil

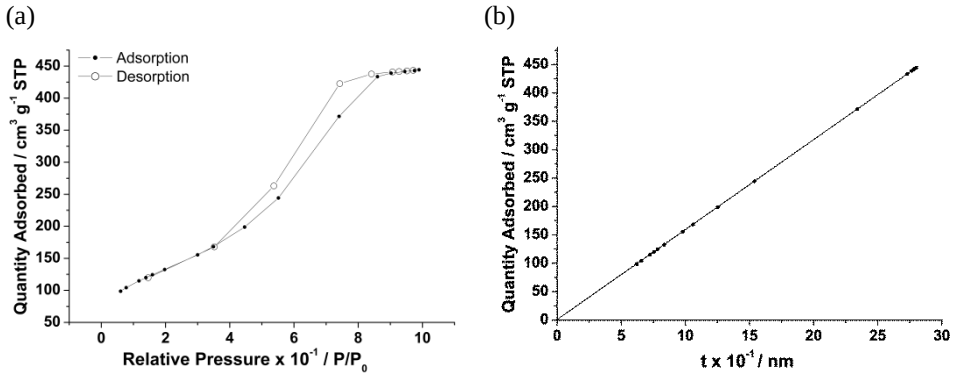

Figure S1. Adsorption and desorption nitrogen isotherms (a) and *t*-curve (b) for SiO_2-Al_2O_3.

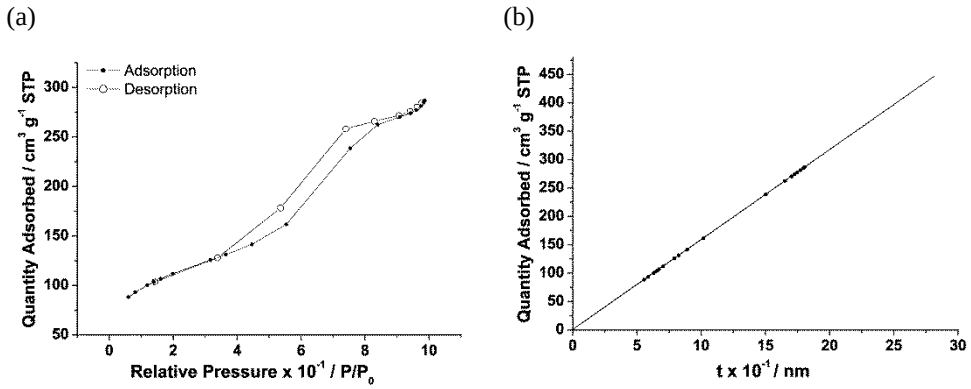

Figure S2. Adsorption and desorption nitrogen isotherms (a) and *t*-curve (b) for supported 15 wt.% H_3PW/SiO_2-Al_2O_3.

*e-mail: jdias@unb.br; julio@unb.br

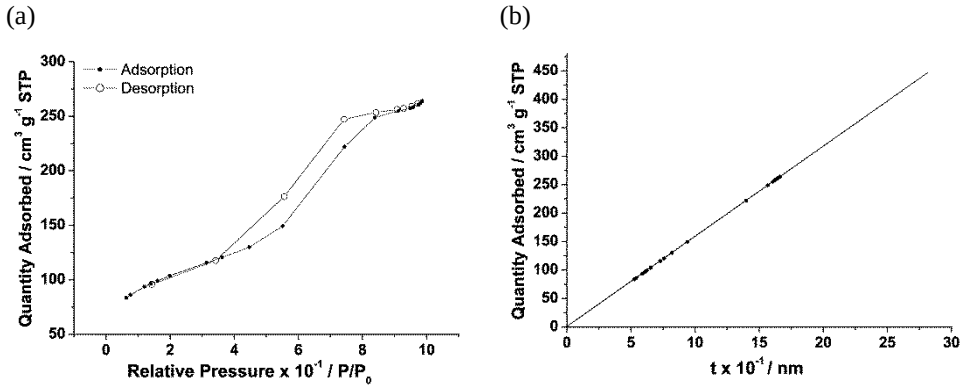

Figure S3. Adsorption and desorption nitrogen isotherms (a) and *t*-curve (b) for supported 20 wt.% H_3PW/SiO_2-Al_2O_3.

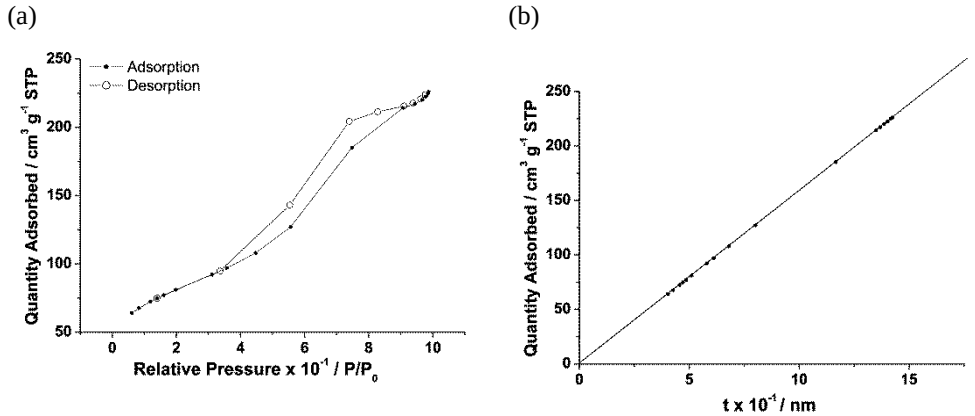

Figure S4. Adsorption and desorption nitrogen isotherms (a) and *t*-curve (b) for supported 30 wt.% H_3PW/SiO_2-Al_2O_3.

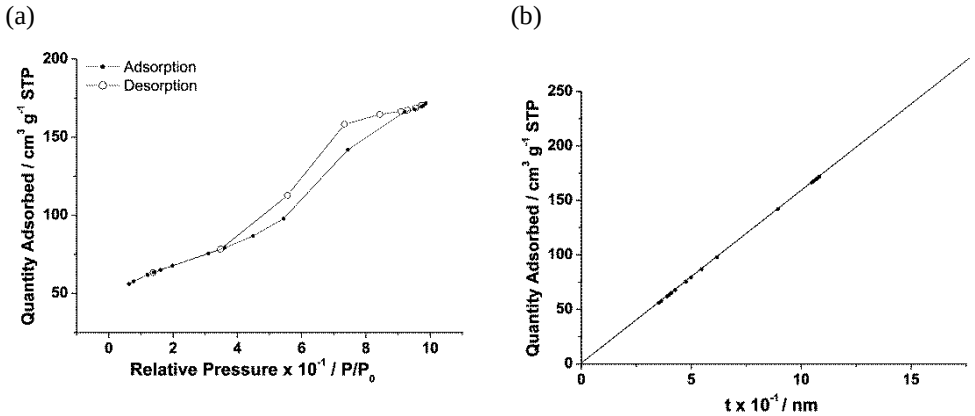

Figure S5. Adsorption and desorption nitrogen isotherms (a) and *t*-curve (b) for supported 40 wt.% H_3PW/SiO_2-Al_2O_3.

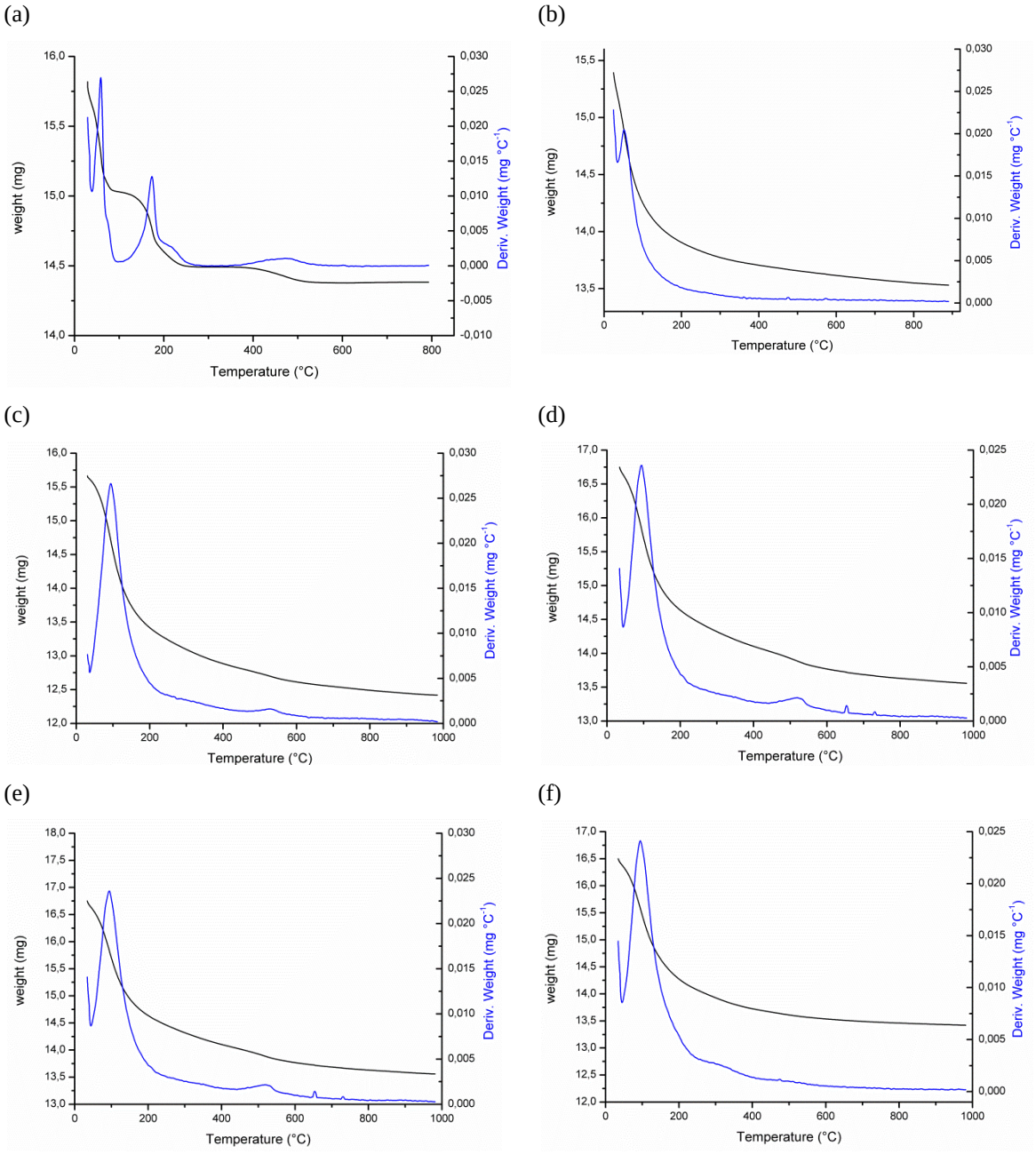

Figure S6. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of: (a) H_3PW; (b) silica-alumina; (c) 15 wt.%, (d) 20 wt.%, (e) 30 wt.% and (f) 40 wt.% of H_3PW supported on SiO_2-Al_2O_3. Samples subjected to synthetic air (80.0 ± 0.5% N_2 and 20.0 ± 0.5% O_2) flow of 100 mL min^{-1}, and heating rate of 10 °C min^{-1}.

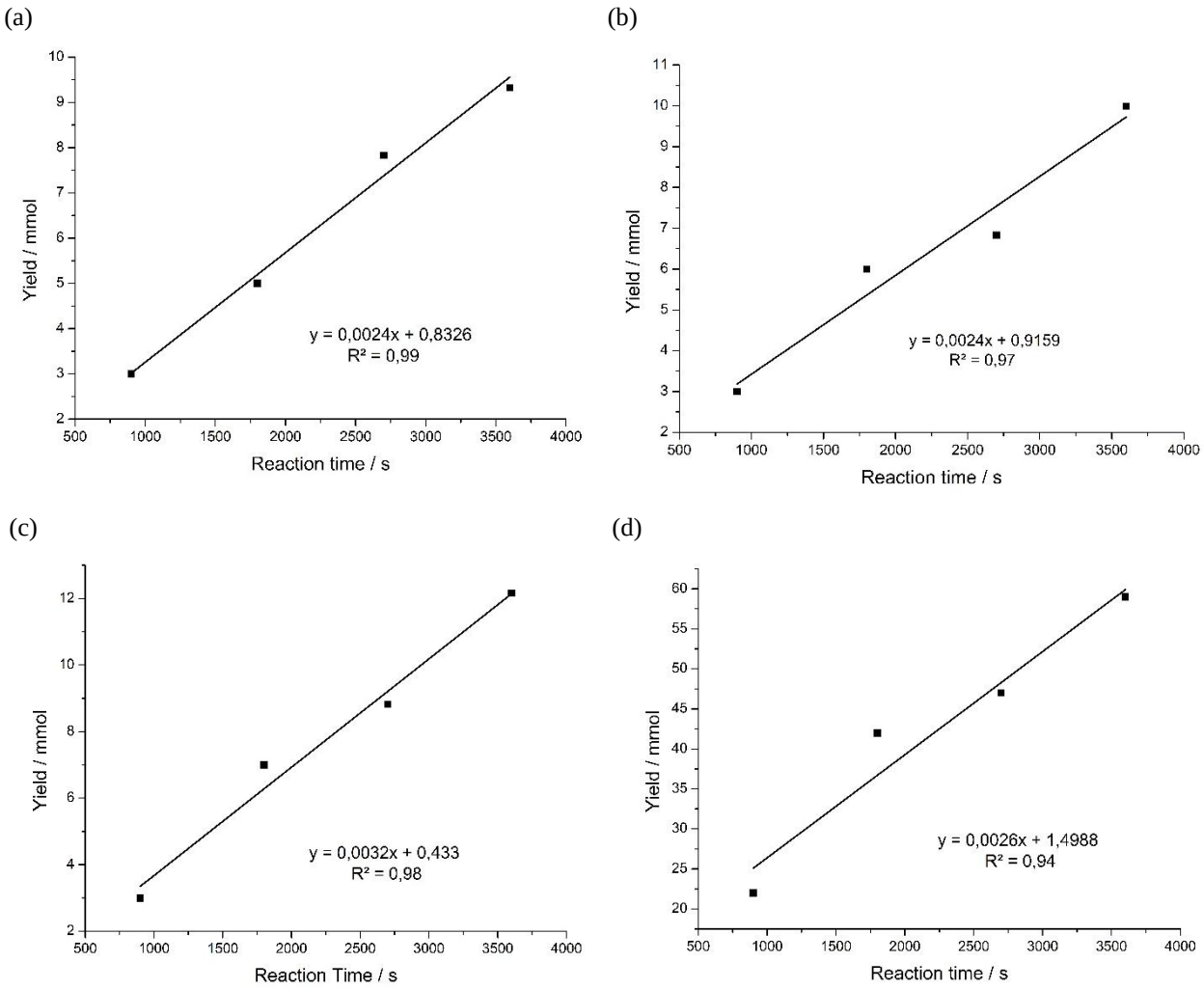

Figure S7. Yield to ethyl acetate formation at reaction times of 15, 30, 45 and 60 min for calculation of the turnover frequency (TOF) of: (a) 15 wt.%, (b) 20 wt.%, (c) 30 wt.% and (d) 40 wt.% of H_3PW supported on SiO_2-Al_2O_3.

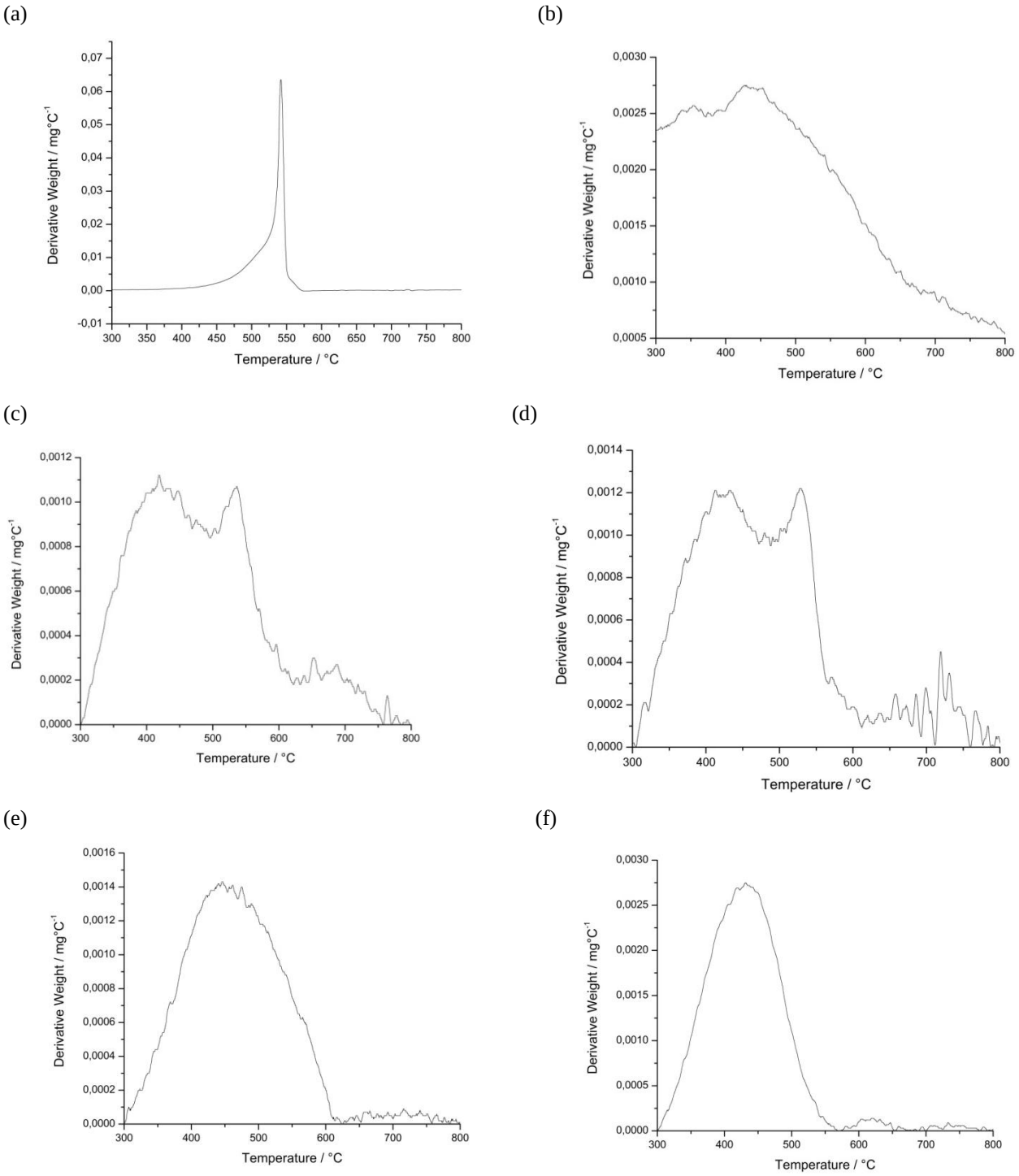

Figure S8. TPD (temperature programmed desorption)/DTG curves of catalysts with pyridine: (a) H_3PW, (b) SiO_2-Al_2O_3, (c) 15 wt.%, (d) 20 wt.%, (e) 30 wt.% and (f) 40 wt.% of H_3PW supported on SiO_2-Al_2O_3. Samples subjected to N_2 (99.999%), flow of 110 mL min^{-1}, and heating rate of 10 °C min^{-1}.

Table S1. Amount of acid sites for x wt.% H_3PW/SiO_2-Al_2O_3 catalysts, according to the range of temperature desorption of pyridine

	Amount of acid sites / (mmol g^{-1})			
	x wt.% H_3PW			
Temperature range / °C	15	20	30	40
300-400	0.070	0.102	0.101	0.108
400-500	0.124	0.126	0.135	0.224
500-600	0.077	0.059	0.063	0.041
300-600	0.271	0.287	0.299	0.373

Table S2. Amount of desorbed pyridine for x wt.% H_3PW/SiO_2-Al_2O_3 catalysts distributed cumulatively according to temperature range of desorption

	Amount of desorbed pyridine / %			
	x wt.% H_3PW			
Temperature range / °C	15	20	30	40
300-400	25.8	35.5	33.8	28.9
300-500	71.6	66.0	78.9	89.0
300-600	100	100	100	100

Details of experimental procedure for quantification of acid sites by TPD/TG

Acidity can be obtained by TG/DTG data by following desorption of a basic probe (e.g., pyridine) in a programmed temperature experiment (TPD/TG). The total number of acid sites (nPy) is determined by quantitative analysis of TG/DTG curves of the catalysts before (Catalyst) and after pyridine adsorption (Catalyst-Py), according to equation below:

$$n_{Py}(mmol) = \frac{\overbrace{\left(m_{600}/(m_{total} - m_{300})\right)}^{Catalyst-Py} - \overbrace{\left(m_{600}/(m_{total} - m_{300})\right)}^{Catalyst}}{MM_{Py}} 1000$$

First, it is determined the difference between the total mass (m_{total}) of the catalyst (containing pyridine) and the mass loss (m_{300}) between room temperature (25 °C) and 300 °C (i.e., the range of temperature where there are losses of water and any remaining physically adsorbed pyridine). This difference is related to the anhydrous catalyst with pyridine chemically adsorbed. Then, the mass loss (m_{600}) between 300 and 600 °C is normalized to a gram, dividing this mass (m_{600}) by that difference ($m_{total} - m_{300}$). Accordingly, the same method is applied to the catalyst without pyridine (i.e., pure catalyst before pyridine adsorption experiment). Thus, the subtraction of the normalized masses (Catalyst-Py − Catalyst) gives the adsorbed pyridine on the solid sample. Finally, the mass is converted to mmol of pyridine (nPy) dividing by the molar mass of pyridine (MM_{Py}) and multiplying by 1000.