

## Supporting Information

### Role of Lewis and Brønsted acid sites in the resorcinol tert-butylation over heteropolyacid-based catalysts.

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## Section 1. Experimental section

Percentages of Brønsted and Lewis sites calculation

First, the intensities were normalized ( $A_n$ ) with respect to those of a standard wafer of 20 mg and  

$$A_n = A_e * \frac{m_w}{(S_w) * m_w}$$
 using the following expression:

where  $A_e$  is the measured absorbance of the band considered,  $S_w$  is the cross section of the wafer ( $m^2$ ), and  $m_w$  is the weight of the wafer (mg).

**Table S1: Frequency ranges for pyridine bonded to Lewis and Brønsted sites of oxides.**

Pyridine bonded to Brønsted sites ( $\text{cm}^{-1}$ )	Pyridine bonded to Lewis sites ( $\text{cm}^{-1}$ )	References
1540	1600-1633	Parry et. Al, Journal of Catalysis 2, 371-379 (1963)
1540	1580-1632	Busca, Catalysis Today 41, 191-206 (1998)
1541	1600-1626	C. Morterra et al. Journal of the Chemical Society 75, 271 (1979)

Then, the quantification of the Brønsted acidity out of the total acidity was done using the formula:  

$$\frac{A_{nB}}{A_{nB} + A_{nL}} * 100$$

$$B\% = 100 - L\%$$

where  $A_{nB}$  is the normalized intensity of the band assigned to pyridine bonded to Brønsted sites and  $A_{nL}$  is the normalized intensity of the band assigned to Pyridine bonded to Lewis sites (see Table S1).

The acid sites density was calculated using the formula  

$$C_s = \frac{A_n S_w}{\zeta S_{BET}}$$

where  $C_s$  is the surface density of acid sites ( $\mu\text{mol}/\text{m}^2$ ),  $S_w$  is the cross section of the wafer,  $\zeta$  is the molar extinction coefficient of pyridine onto Lewis and Brønsted sites ( $\zeta_L = 1.5 \text{ cm}/\mu\text{mol}$  and  $\zeta_B = 1.67 \text{ m}/\mu\text{mol}$ ). The extinction coefficients values were taken from the literature.

Total mole of acid sites calculation

The total moles of acid sites were calculated as follows:

*Total moles of acid sites(mol)*

$$= \text{Surface density of strong Bronsted sites} \left( \frac{\text{mol}}{\text{m}^2} \right) * \text{Catalyst surface} (S_{BET}, \frac{\text{m}^2}{\text{g}}) * \text{g of Catalyst used in the reactor (g)}$$

## Mass Balance

An internal standard (IS) is a compound that is similar in physical and chemical characteristics to the sample being analysed. It must be inert to the sample and must not react with the sample or any solvent used to dilute or prepare it for the analysis.

The response factor (RF) is defined as the ratio between the response of the detector to a compound (i) and the concentration of that compound being analysed:

$$\text{response factor } RF_i = \frac{\text{peak area}_i}{\text{concentration}_i}$$

Relative response factor (RRF) is defined as the ratio between response factors of the compound and of the internal standard

$$\text{relative response factor } RRF_i = \frac{RF_i}{RF_{is}}$$

The compound concentration can be calculated using the formula:

$$C_i = \text{peak area}_i \left( \frac{C_{is}}{\text{peak area}_{is}} \right) \left( \frac{1}{RRF_i} \right)$$

Relative response factors:

RRFresorcinol	0.76
RRF4TBR	1.10
RRF46DTBR	3.71
RRFRmTBE	1.00
RRF2TBR	1.00
RRFunkown1	1.00
RRFunkown2	1.00

## Section 2. Catalysts physico-chemical characterization

**Table S2.** HPW wt. % for the SiO<sub>2</sub>/HPW, TiO<sub>2</sub>/HPW and ZrO<sub>2</sub>/HPW catalysts.

Catalyst	Nominal HPW mass engaged (g)	Nominal HPW mass engaged (%)	Effective HPW wt.%
SiO <sub>2</sub>	0	0	0
SiO <sub>2</sub> /HPW8	0.505	10	8
SiO <sub>2</sub> /HPW17	1.022	20	17
SiO <sub>2</sub> /HPW25	1.752	30	25
SiO <sub>2</sub> /HPW31	2.725	40	31
SiO <sub>2</sub> /HPW51	5.530	80	51
TiO <sub>2</sub>	0	0	0
TiO <sub>2</sub> /HPW9	0.588	10	9
TiO <sub>2</sub> /HPW17	1.063	20	17
TiO <sub>2</sub> /HPW21	1.606	30	21
TiO <sub>2</sub> /HPW29	2.129	40	29
TiO <sub>2</sub> /HPW41	4.239	80	41
ZrO <sub>2</sub>	0	0	0
ZrO <sub>2</sub> /HPW7	0.575	10	7
ZrO <sub>2</sub> /HPW20	1.171	20	20
ZrO <sub>2</sub> /HPW24	1.745	30	24
ZrO <sub>2</sub> /HPW29	2.303	40	29

**Table S3. TiO<sub>2</sub> (Anatase) and ZrO<sub>2</sub> (Monoclinic and tetragonal) crystal size calculated using the Scherrer equation.**

Catalyst	Anatase crystallite size (nm)
TiO <sub>2</sub>	53
TiO <sub>2</sub> /HPW9	39
TiO <sub>2</sub> /HPW17	39
TiO <sub>2</sub> /HPW21	43
TiO <sub>2</sub> /HPW29	35
TiO <sub>2</sub> /HPW41	26
	Zirconia monoclinic (28.2°)
ZrO <sub>2</sub>	39
ZrO <sub>2</sub> /HPW7	53
ZrO <sub>2</sub> /HPW20	71
ZrO <sub>2</sub> /HPW24	61
ZrO <sub>2</sub> /HPW29	39
	Zirconia tetragonal (30.2°)
ZrO <sub>2</sub>	25
ZrO <sub>2</sub> /HPW7	34
ZrO <sub>2</sub> /HPW20	41
ZrO <sub>2</sub> /HPW24	37
ZrO <sub>2</sub> /HPW29	41

**Table S4. Specific surface area, pore volume and pore diameter of the SiO<sub>2</sub>/HPW, TiO<sub>2</sub>/HPW and ZrO<sub>2</sub>/HPW catalysts**

Catalyst	Surface area, BET (m <sup>2</sup> /g)	Pore volume, BJH (cm <sup>3</sup> /g)	Pore diameter, BJH (nm)
SiO <sub>2</sub>	901	0.31	2.6
SiO <sub>2</sub> /HPW8	699	0.21	2.5
SiO <sub>2</sub> /HPW17	635	0.34	2.9
SiO <sub>2</sub> /HPW25	277	0.21	2.8
SiO <sub>2</sub> /HPW31	310	0.14	2.4
SiO <sub>2</sub> /HPW51	85	0.09	3.8
TiO <sub>2</sub>	15	0.05	6.3
TiO <sub>2</sub> /HPW9	44	0.09	6.6
TiO <sub>2</sub> /HPW17	55	0.12	6.1
TiO <sub>2</sub> /HPW21	65	0.08	4.3
TiO <sub>2</sub> /HPW29	67	0.08	3.9
TiO <sub>2</sub> /HPW41	202	0.08	2.9
ZrO <sub>2</sub>	5	-	-
ZrO <sub>2</sub> /HPW7	6	-	-
ZrO <sub>2</sub> /HPW20	9	-	-
ZrO <sub>2</sub> /HPW24	16	-	-
ZrO <sub>2</sub> /HPW29	1.6	-	-

**Table S5. Pyridine adsorption bands position and assignments**

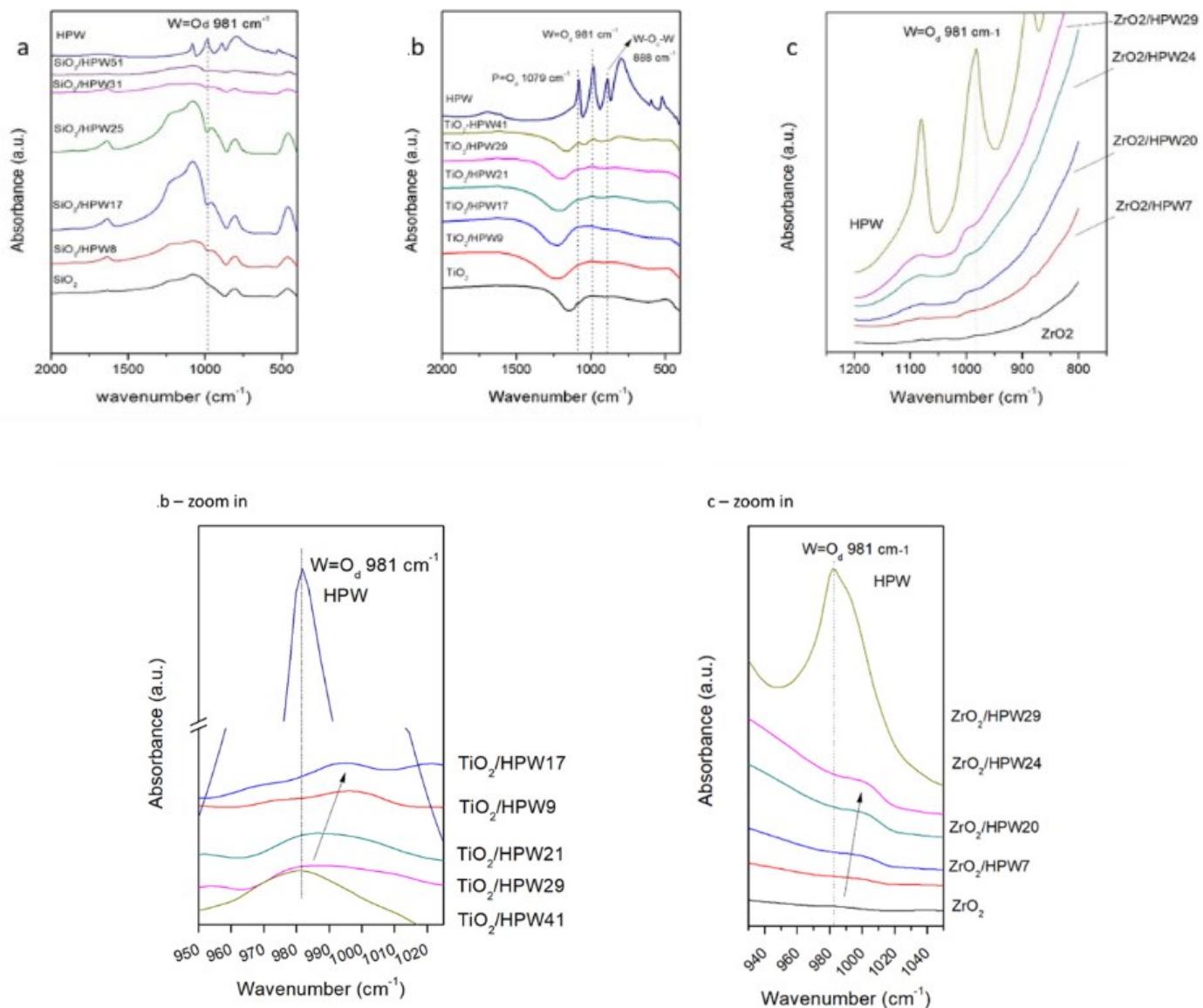
Wavenumber, cm <sup>-1</sup>	Assignment	References
1450	Lewis, L	[10], [5], [11]
1490	Weak Brønsted, WB	
1540	Brønsted, B	
1600	Weak Lewis, WL	
1613	Lewis, L	
1637	Brønsted, B	

**Table S6. Tungsten (W) and phosphorous (P) total moles present in the samples and tungsten to phosphorous ratio calculation**

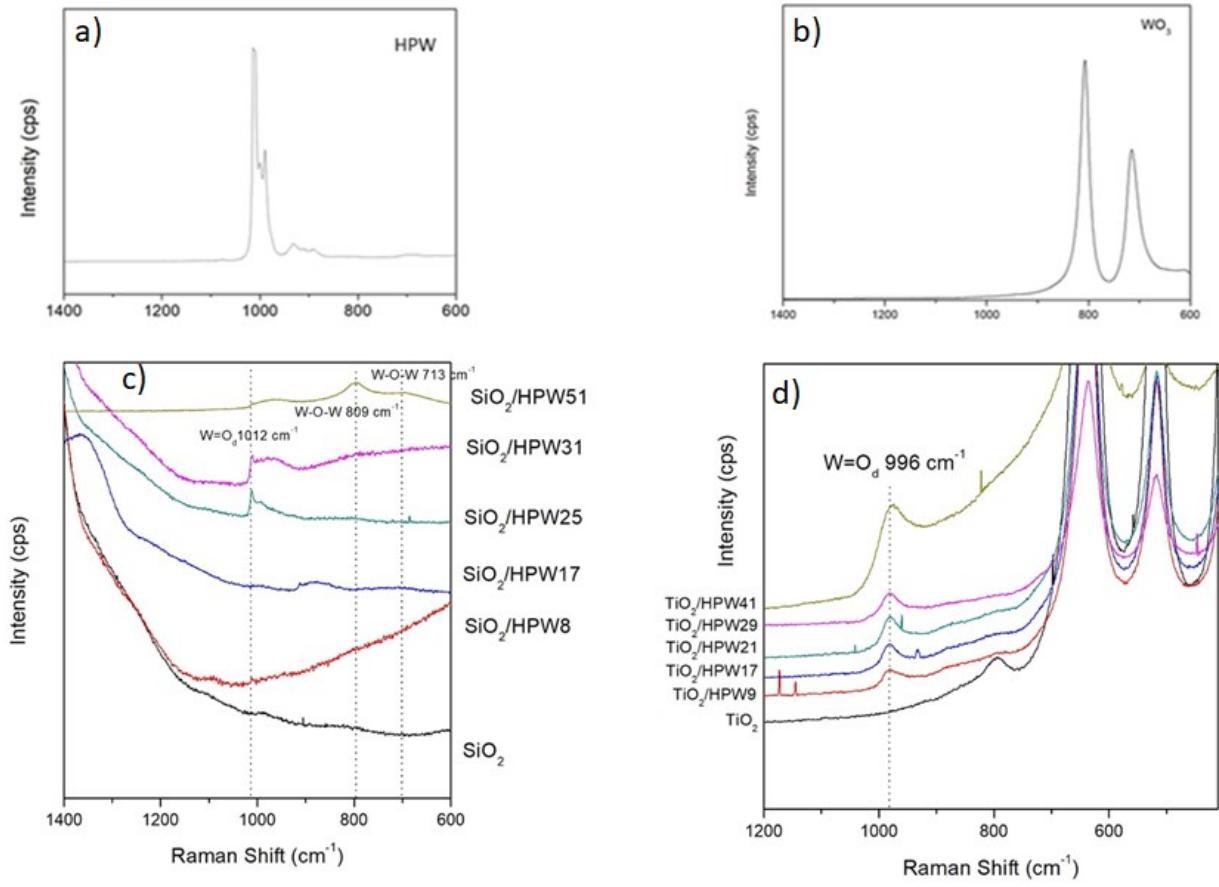
Samples	W (total moles)	P (total moles)	W/P (ratio)
SiO <sub>2</sub>	-	-	-
SiO <sub>2</sub> /HPW8	1.03E-04	8.96E-06	12.14
SiO <sub>2</sub> /HPW17	3.55E-05	2.36E-06	12.19
SiO <sub>2</sub> /HPW25	4.10E-05	3.52E-06	12.68
SiO <sub>2</sub> /HPW31	6.58E-05	4.46E-06	12.40
SiO <sub>2</sub> /HPW51	1.82E-05	1.19E-06	13.44
TiO <sub>2</sub>	-	-	-
TiO <sub>2</sub> /HPW9	1.46E-05	1.35E-06	12.26
TiO <sub>2</sub> /HPW17	2.77E-05	2.91E-06	11.70
TiO <sub>2</sub> /HPW21	4.24E-05	3.23E-06	12.02
TiO <sub>2</sub> /HPW29	5.49E-05	5.30E-06	12.30
TiO <sub>2</sub> /HPW41	1.08E-04	8.51E-06	12.13

**Table S7. Resorcinol conversion obtained using  $\text{SiO}_2/\text{HPW}$ ,  $\text{TiO}_2/\text{HPW}$  and  $\text{ZrO}_2/\text{HPW}$  catalysts in the resorcinol alkylation with MTBE.**

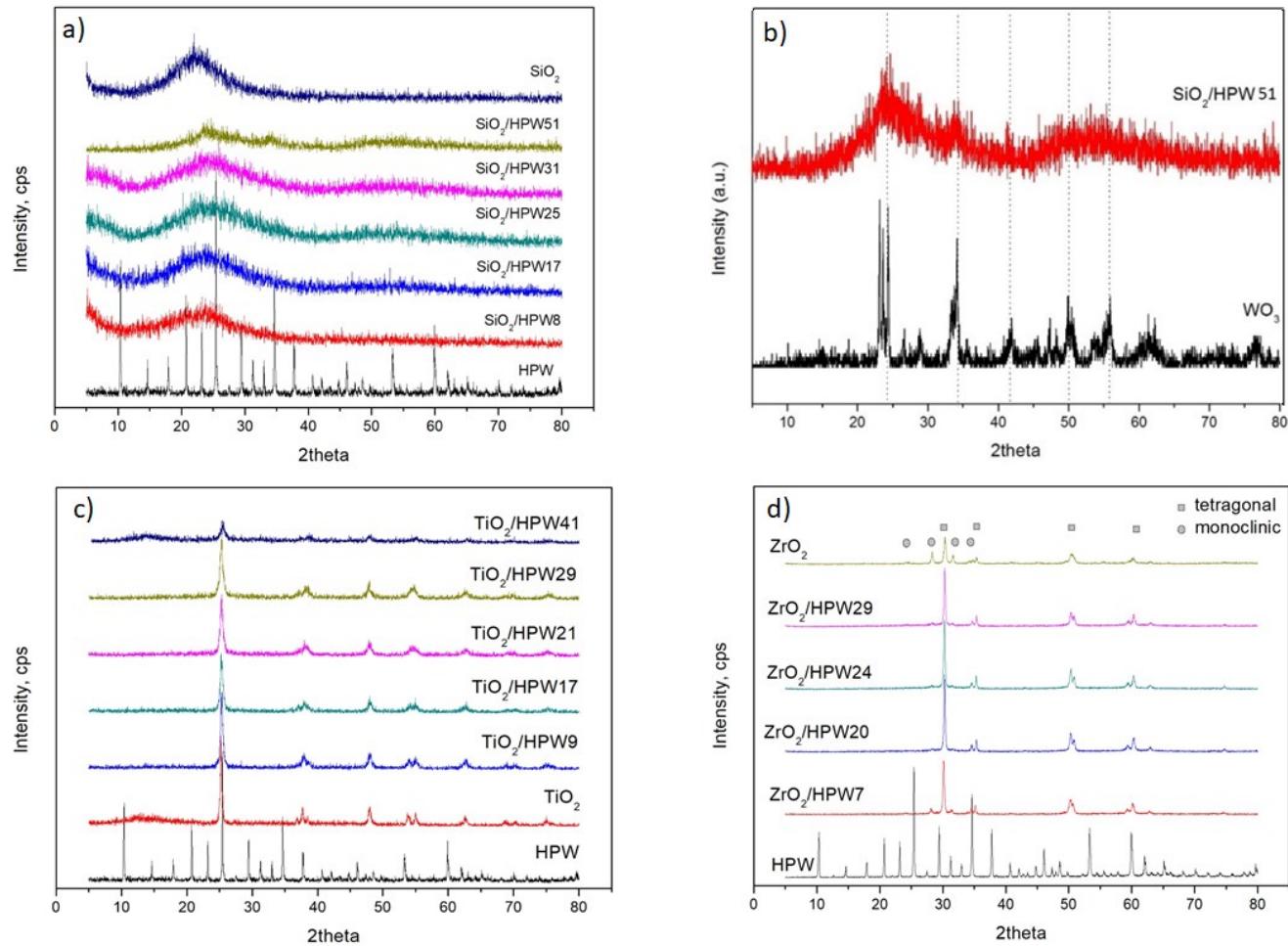
Catalyst	Resorcinol conversion, %
$\text{SiO}_2$	0
$\text{SiO}_2/\text{HPW}8$	8
$\text{SiO}_2/\text{HPW}17$	13
$\text{SiO}_2/\text{HPW}25$	20
$\text{SiO}_2/\text{HPW}31$	16
$\text{SiO}_2/\text{HPW}51$	21
<hr/>	
$\text{TiO}_2$	0
$\text{TiO}_2/\text{HPW}9$	15
$\text{TiO}_2/\text{HPW}17$	10
$\text{TiO}_2/\text{HPW}21$	21
$\text{TiO}_2/\text{HPW}29$	30
$\text{TiO}_2/\text{HPW}41$	22
<hr/>	
$\text{ZrO}_2$	0
$\text{ZrO}_2/\text{HPW}7$	0
$\text{ZrO}_2/\text{HPW}20$	0
$\text{ZrO}_2/\text{HPW}24$	0
$\text{ZrO}_2/\text{HPW}29$	0



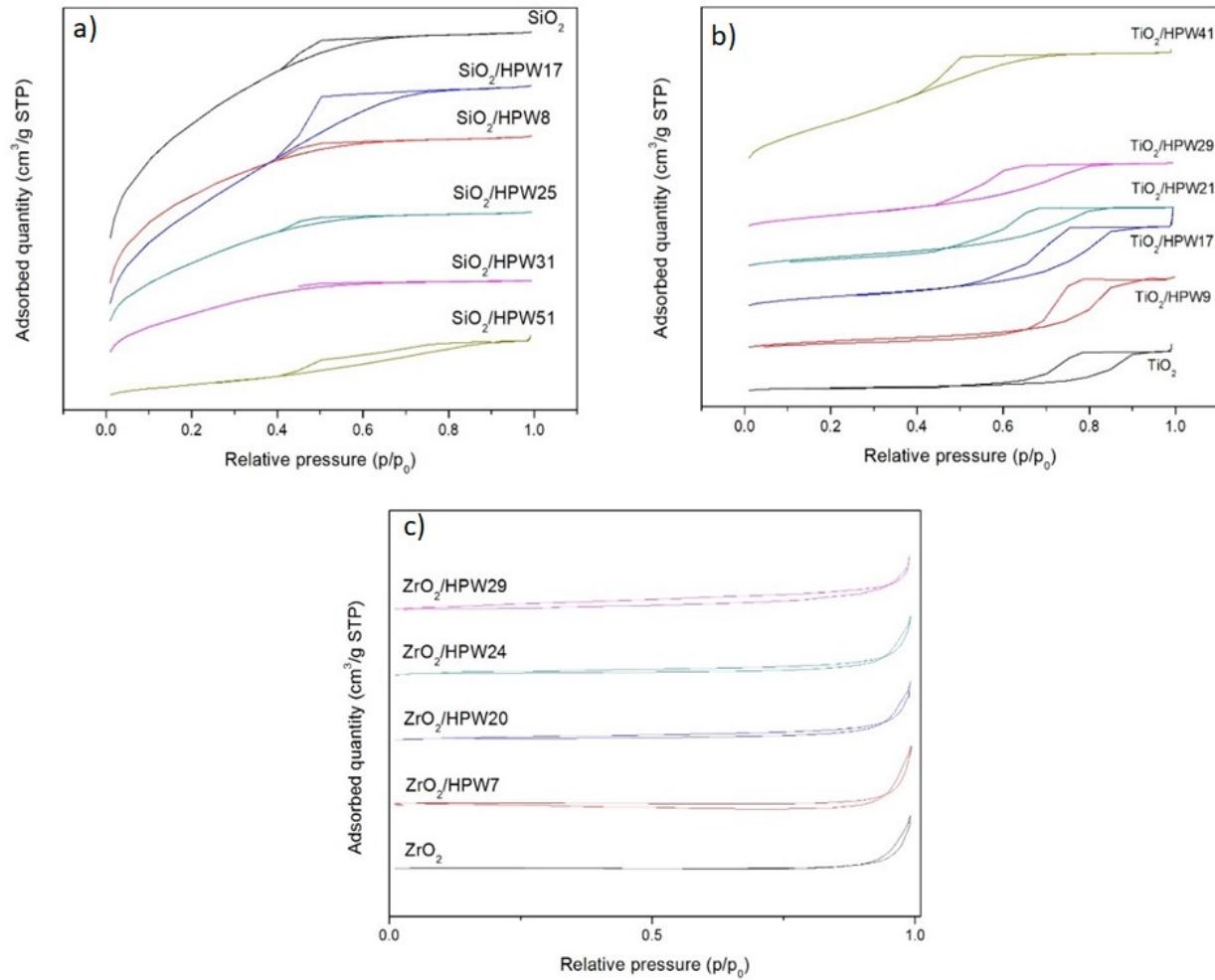
**Figure S1.** FT-IR spectra of the SiO<sub>2</sub>/HPW catalysts (a), of TiO<sub>2</sub>/HPW catalysts (b) and of ZrO<sub>2</sub>/HPW catalysts (c). A zoom of Figures b and c is given for the sake of clarity.



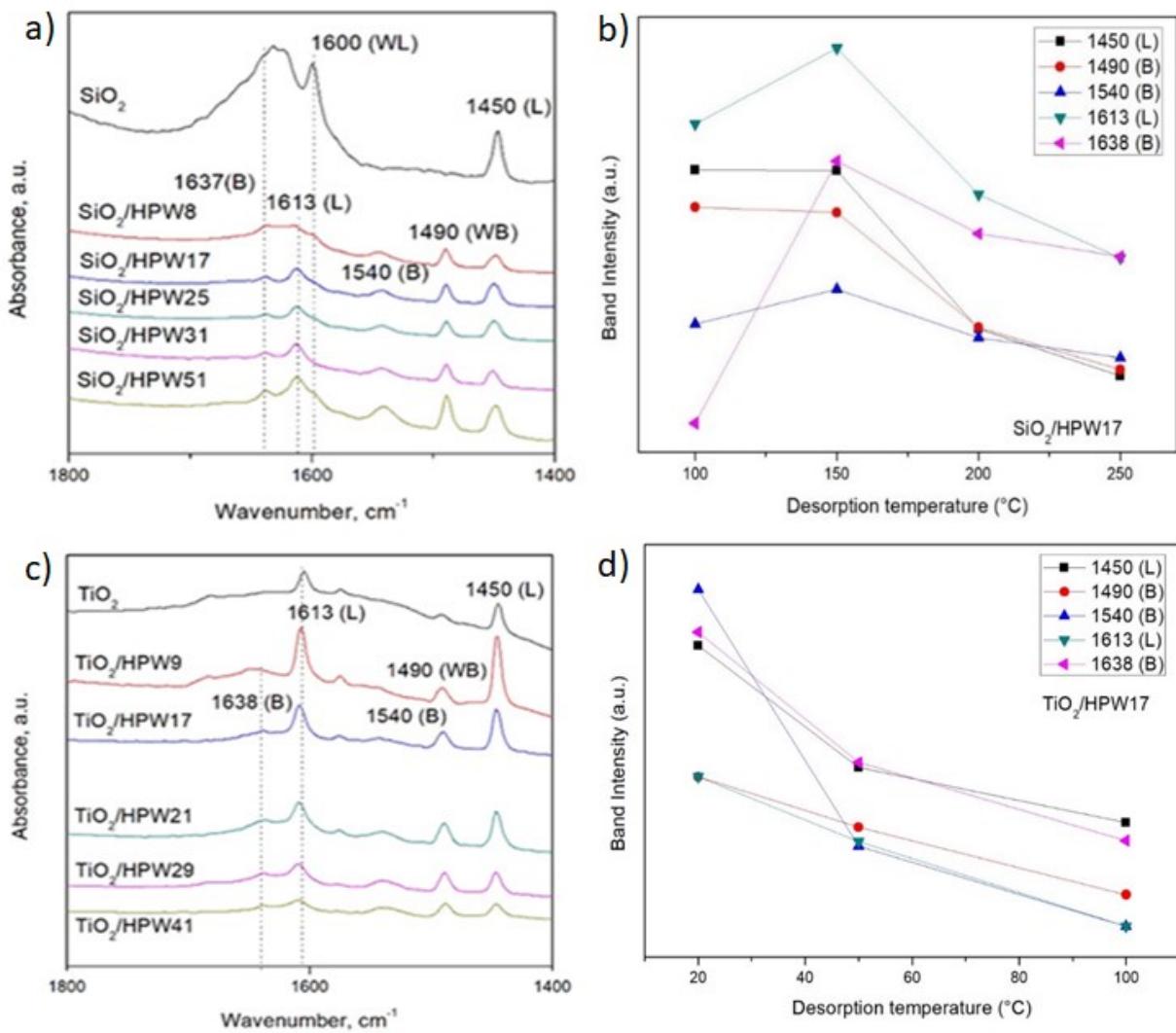
**Figure S2.** Raman spectra of the a) HPW, b)  $\text{WO}_3$  c)  $\text{SiO}_2/\text{HPW}$  and d)  $\text{TiO}_2/\text{HPW}$  catalysts.



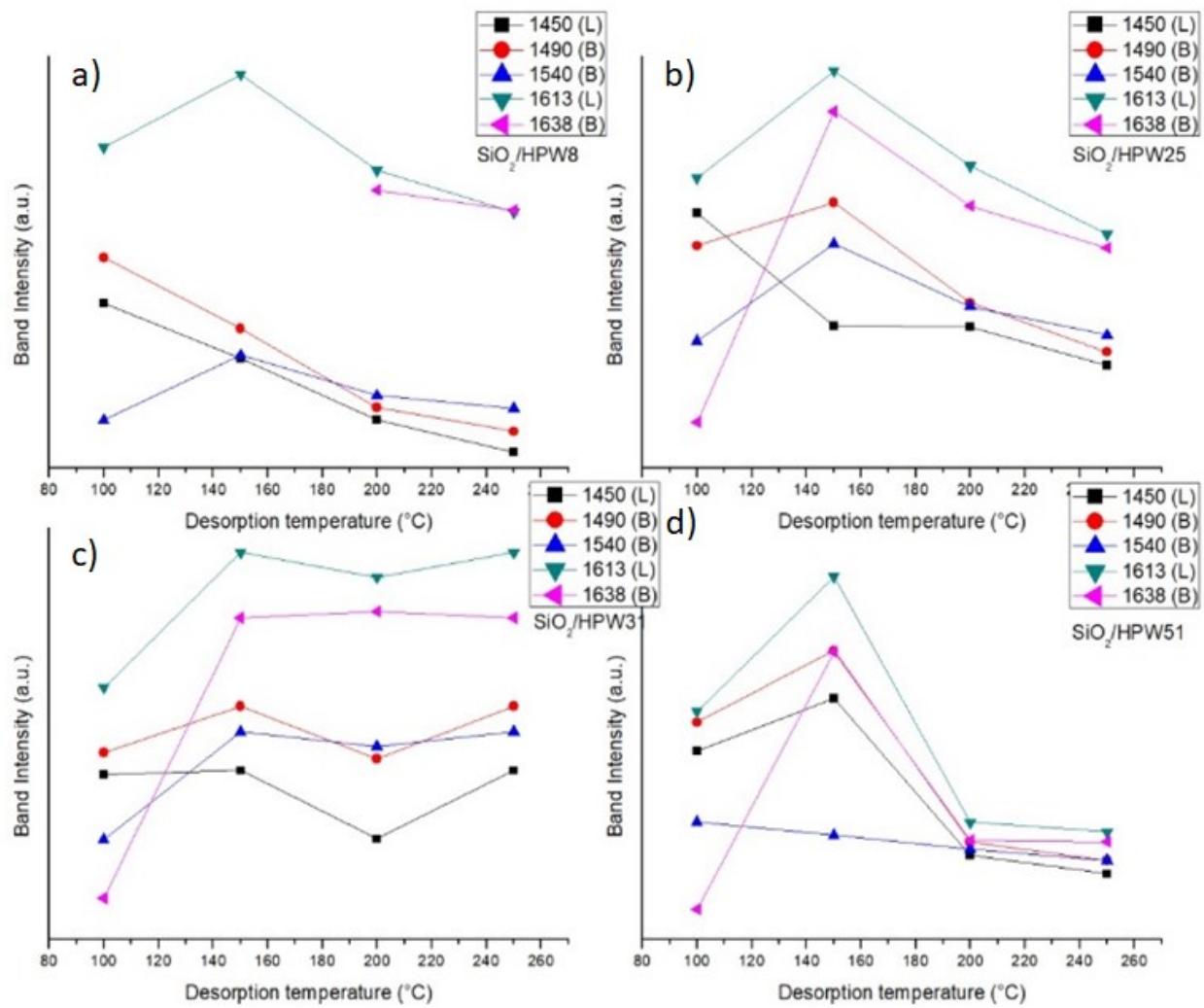
**Figure S3. Powder XRD patterns of a)  $\text{SiO}_2/\text{HPW}$  catalysts. b)  $\text{SiO}_2/\text{HPW}51$  and tungsten oxide ( $\text{WO}_3$ ), c)  $\text{TiO}_2/\text{HPW}$  catalysts and d)  $\text{ZrO}_2/\text{HPW}$  catalysts.**



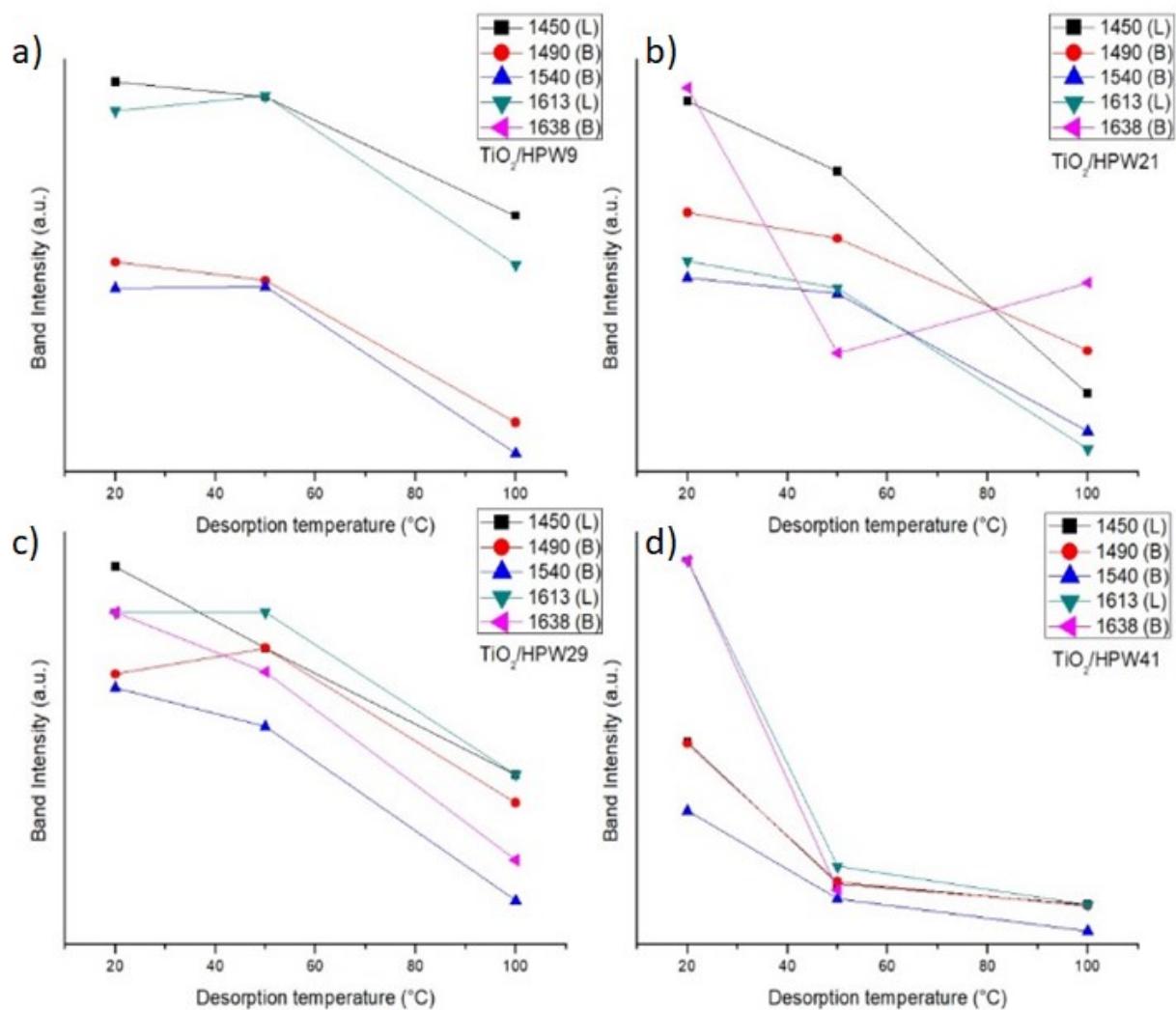
**Figure S4. Nitrogen adsorption isotherms for a) SiO<sub>2</sub>/HPW catalysts. b) SiO<sub>2</sub>/HPW51 and tungsten oxide, c) TiO<sub>2</sub>/HPW catalysts) ZrO<sub>2</sub>/HPW catalysts. The curves are shifted on the y-axis for the sake of clarity.**



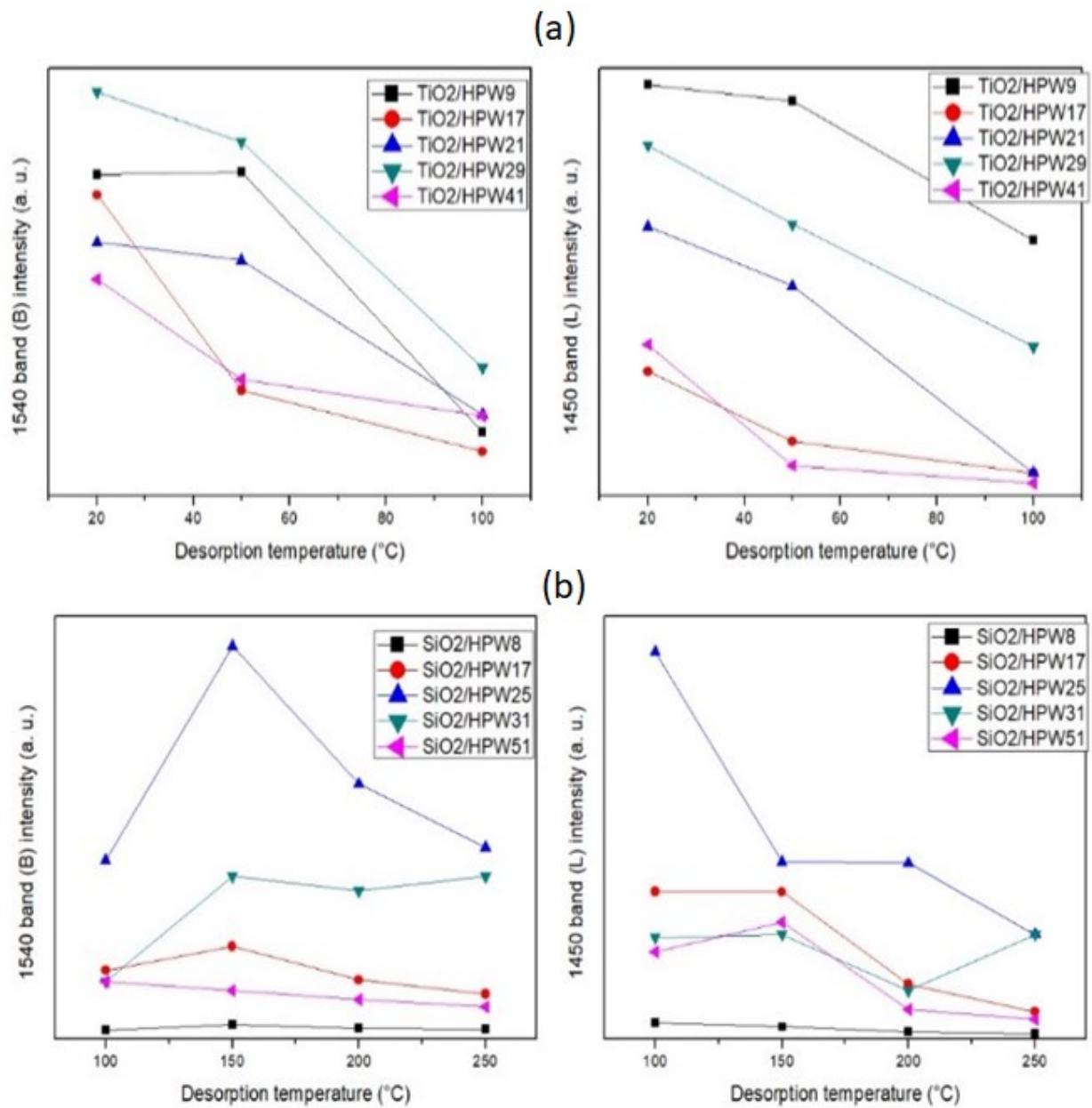
**Figure S5. Comparative IR spectra of adsorbed pyridine onto  $\text{SiO}_2/\text{HPW}$  catalysts (a) and  $\text{TiO}_2/\text{HPW}$  catalysts. Bands intensity variation of pyridine bonded to Lewis and Brønsted acid sites during desorption at different temperatures for the catalyst  $\text{SiO}_2/\text{HPW}17$  (b) and  $\text{TiO}_2/\text{HPW}17$  (d).**



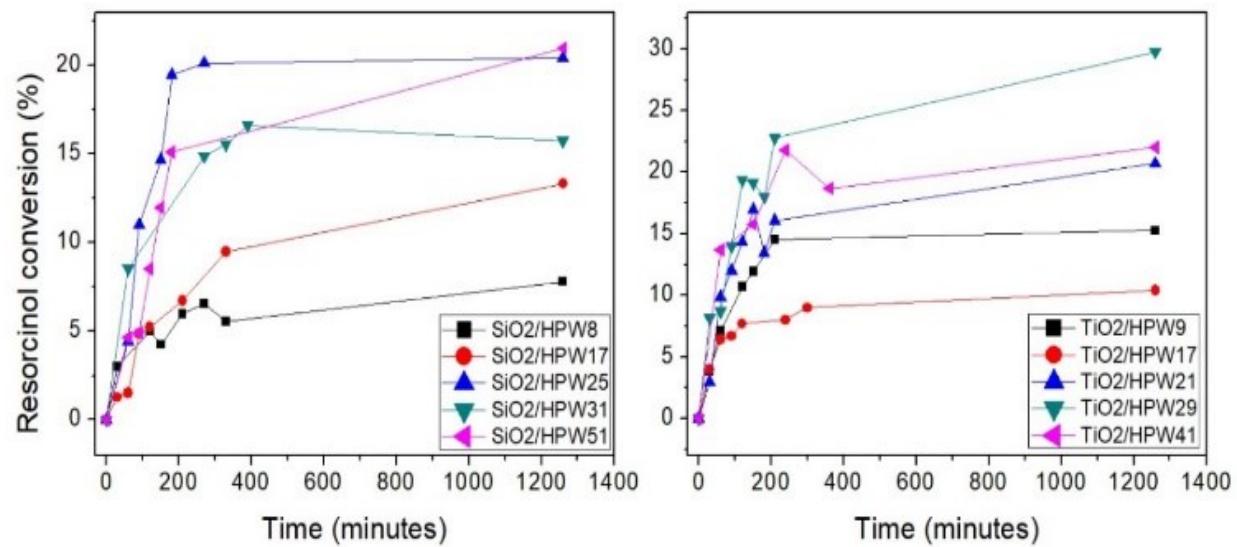
**Figure S6. Band intensity variation of pyridine bonded to Lewis and Brønsted acid sites during desorption at different temperatures for the catalysts  $\text{SiO}_2/\text{HPW}$ .**



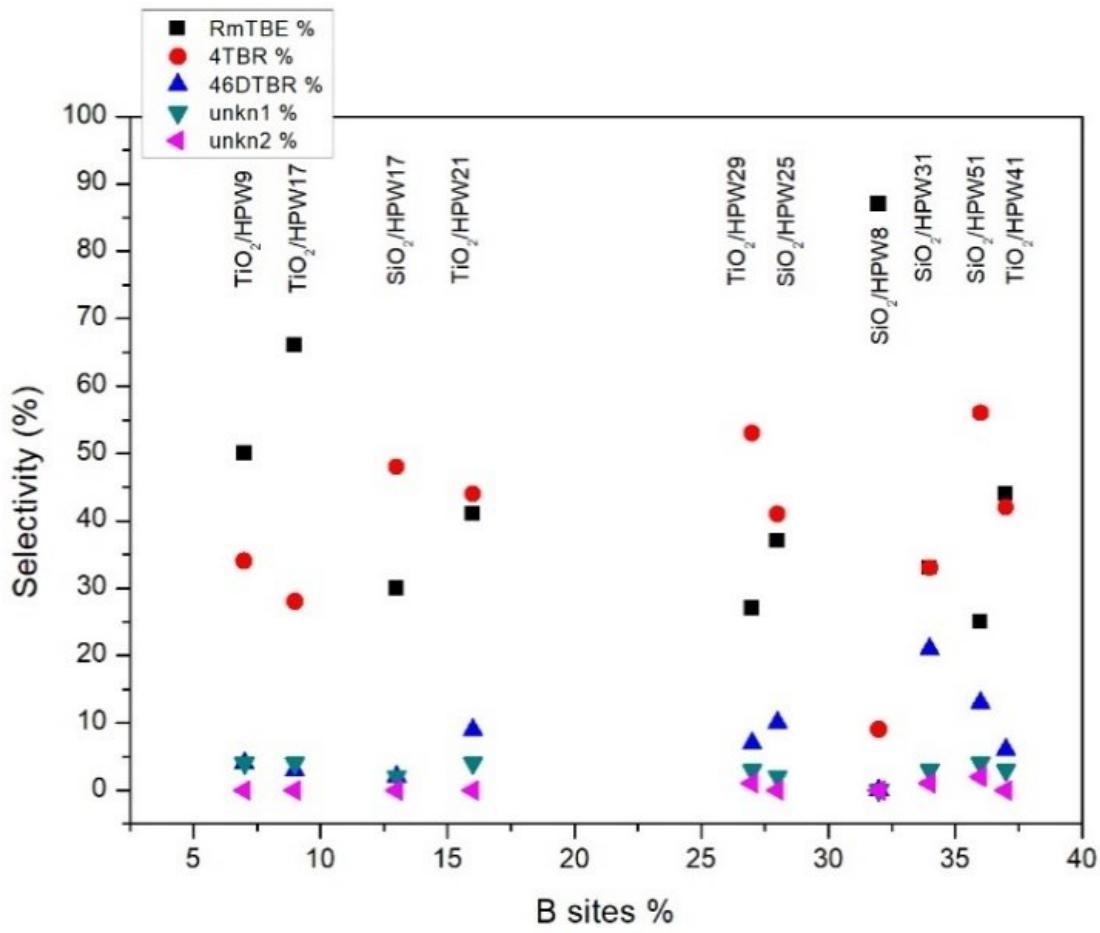
**Figure S7.** Band intensity variation of pyridine bonded to Lewis and Brønsted acid sites during desorption at different temperatures for the catalysts  $\text{TiO}_2/\text{HPW}$ .



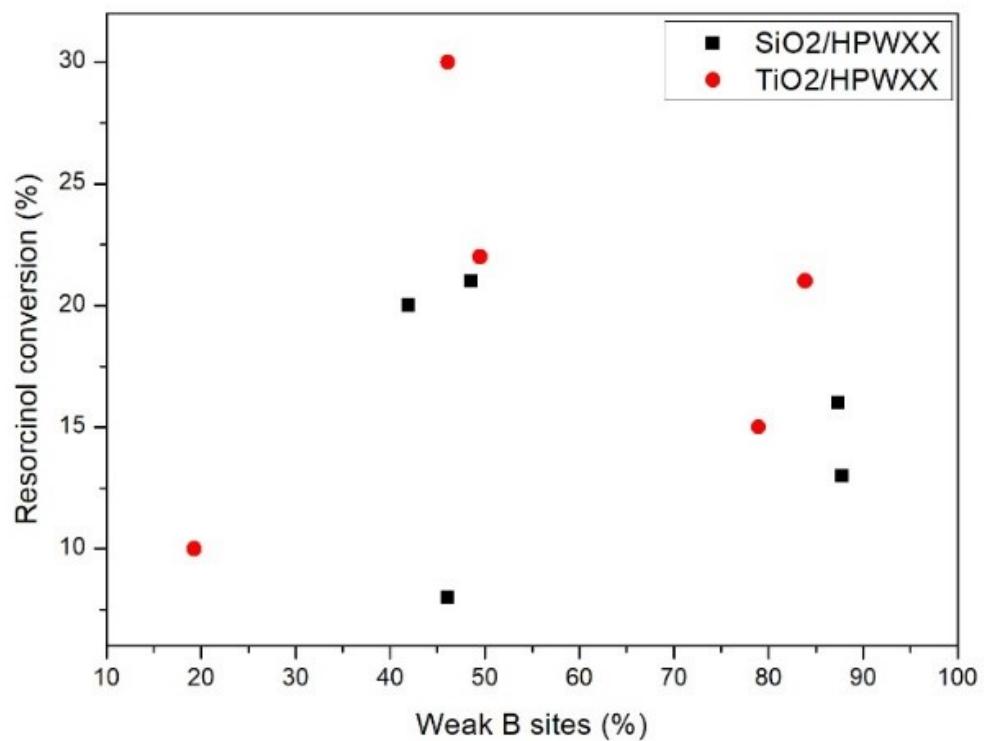
**Figure S8.** Bands intensity variation of pyridine bonded to Lewis ( $1450\text{ cm}^{-1}$ ) and Brønsted ( $1540\text{ cm}^{-1}$ ) acid sites during desorption at different temperatures for the catalysts (a) TiO<sub>2</sub>/HPW and (b) SiO<sub>2</sub>/HPW.



**Figure S9.** Resorcinol conversion reported as a function of time for the SiO<sub>2</sub>/HPW and TiO<sub>2</sub>/HPW catalysts (liquid phase, 60 °C, autogenic pressure).



**Figure S10. Reaction selectivity as a function of the B % of acid strong sites (calculated using the band at  $1540\text{ cm}^{-1}$ ).**



**Figure S11.** Correlation between conversion and weak B sites: in general, the resorcinol conversion was found to increase and then to decrease with the increasing number of strong B sites.

