

## SUPPLEMENTARY MATERIAL

### LIST OF CONTENTS

- Table S1. NH<sub>3</sub> - TPD results of all catalysts.
- Figure S1. <sup>31</sup>P MAS NMR of HPW@SBA-15 and HPW/SBA-15.
- Figure S2. DTA data of HPW catalysts.
- Figure S3. DTA data of HSiW catalysts.
- Figure S4. Diffuse reflectance UV-vis spectra of supported HPW catalysts.
- Figure S5. Diffuse reflectance UV-vis spectra of supported HSiW catalysts.
- Figure S6. Low and wide-angle XRD patterns of supported HPW catalysts.
- Figure S7. Low and wide-angle XRD patterns of supported HSiW catalysts.
- Figure S8. Nitrogen adsorption-desorption isotherms of supported HPW catalysts.
- Figure S9. Nitrogen adsorption-desorption isotherms of supported HSiW catalysts.
- Figure S10. Pore size distribution of supported HPW catalysts.
- Figure S11. Pore size distribution of supported HSiW catalysts.
- Figure S12. Evolution of the proportions of the four branched C<sub>6</sub> isomers as a function of the conversion for HSiW/SBA-15, HPW/SBA-15 and HPW@SBA-15.
- Figure S13. NH<sub>3</sub>-TPD profiles of pure HPW and HSiW.
- Figure S14. NH<sub>3</sub>-TPD profile of SBA-15.
- Figure S15. NH<sub>3</sub>-TPD profile of HPA hybrid catalysts.
- Figure S16. NH<sub>3</sub>-TPD profile of HPW/SiO<sub>2</sub>.
- Figure S17. Infrared and GC-MS profiles for NH<sub>3</sub> desorption from HPW/SBA-15.
- Figure S18. Infrared and GC-MS profiles for NH<sub>3</sub> desorption from HPW@SBA-15.
- Figure S19. Infrared and GC-MS profiles for NH<sub>3</sub> desorption from HSiW/SBA-15.
- Figure S20. Infrared and GC-MS profiles for NH<sub>3</sub> desorption from HSiW@SBA-15.
- Figure S21. Differential heat of ammonia adsorption on SBA-15 as a function of the ammonia coverage.
- Figure S22. Amount of ammonia adsorbed on the four catalysts as a function of added pressure.
- Figure S23. Amount of ammonia adsorbed on SBA-15 as a function of pressure.
- Figure S24. Infrared spectra of pyridine desorption from HPW/SBA-15.
- Figure S25. Infrared spectra of pyridine desorption from HPW@SBA-15.
- Figure S26. Infrared spectra of pyridine desorption from HSiW/SBA-15.
- Figure S27. Infrared spectra of pyridine desorption from HSiW@SBA-15.

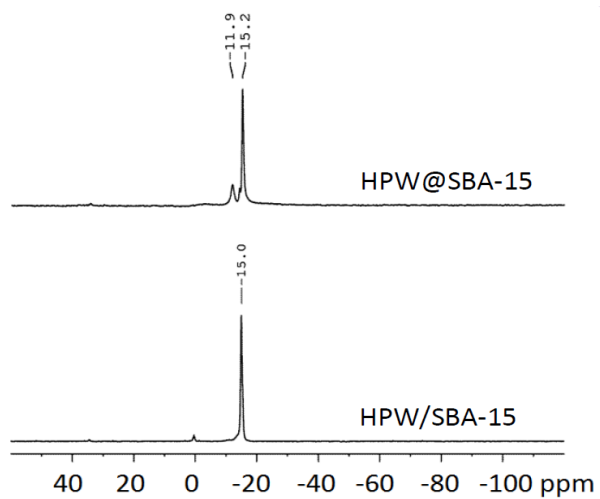


Figure S1

$^{31}\text{P}$  MAS NMR of HPW@SBA-15 and HPW/SBA-15.

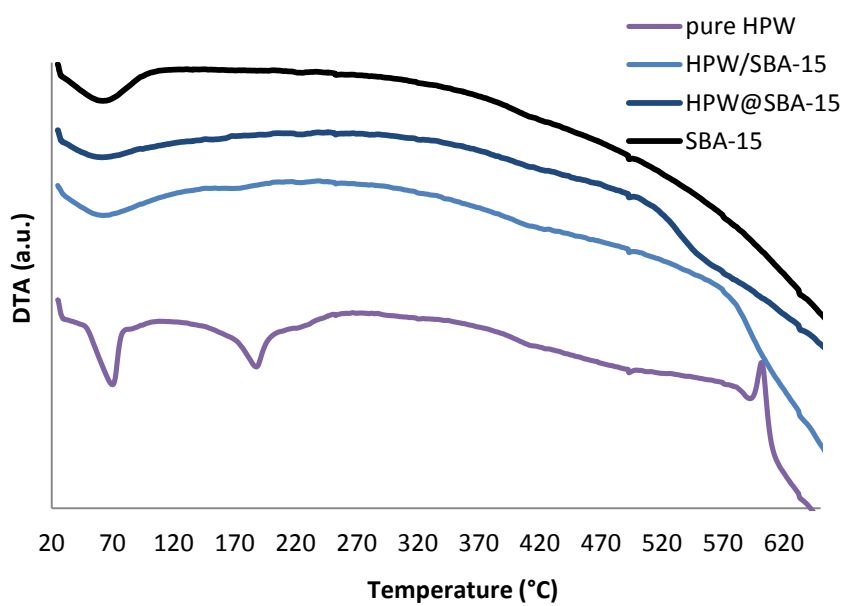


Figure S2

DTA data of HPW catalysts.

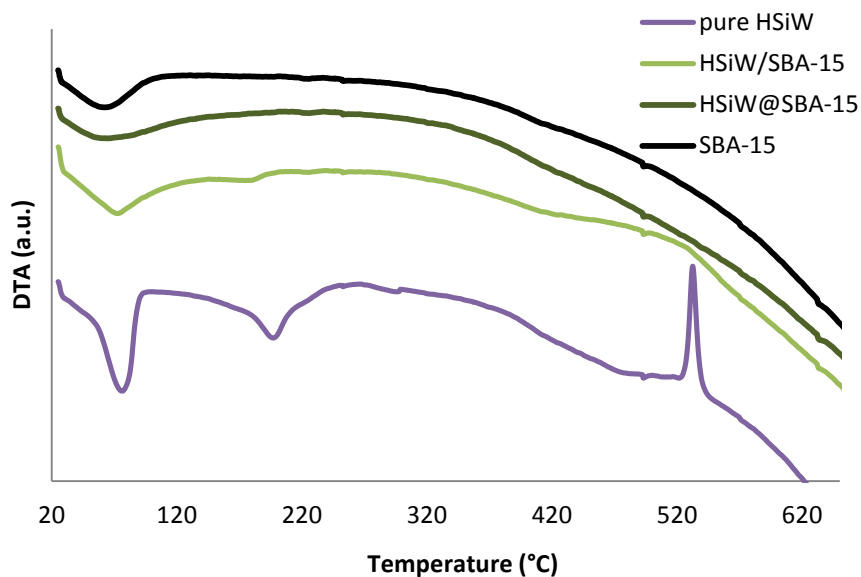


Figure S3

DTA data of HSiW catalysts.

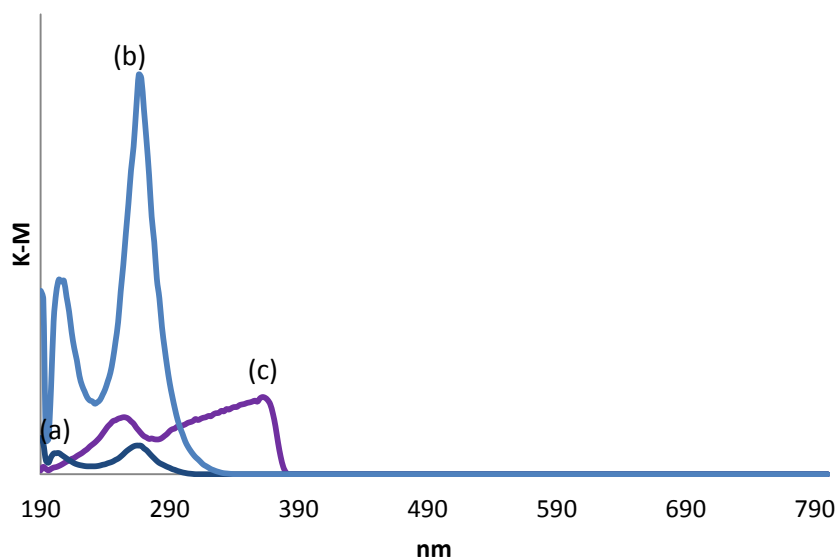


Figure S4

Diffuse reflectance UV-vis spectra of supported HPW catalysts (a) HPW/SBA-15, (b) HPW@SBA-15 and (c) pure HPW.

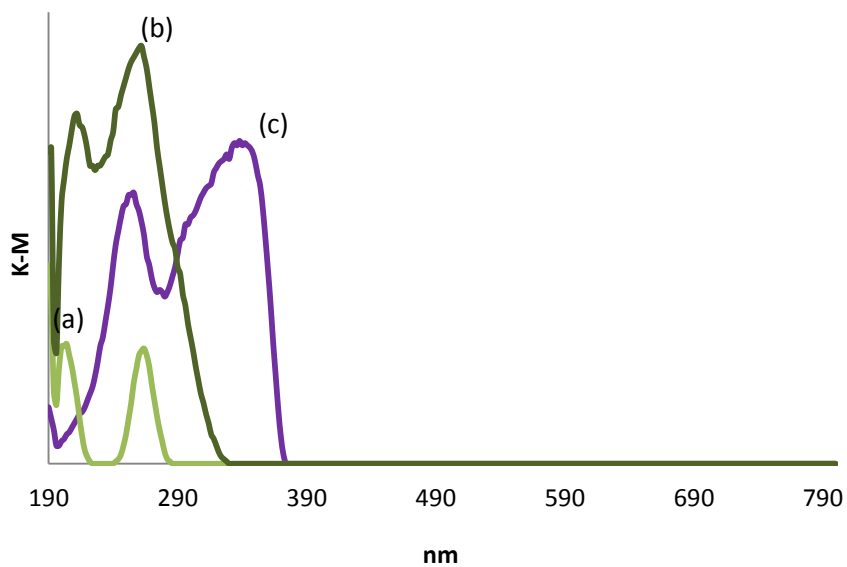


Figure S5

Diffuse reflectance UV-vis spectra of supported HSiW catalysts (a) HSiW/SBA-15, (b) HSiW@SBA-15 and (c) pure HSiW.

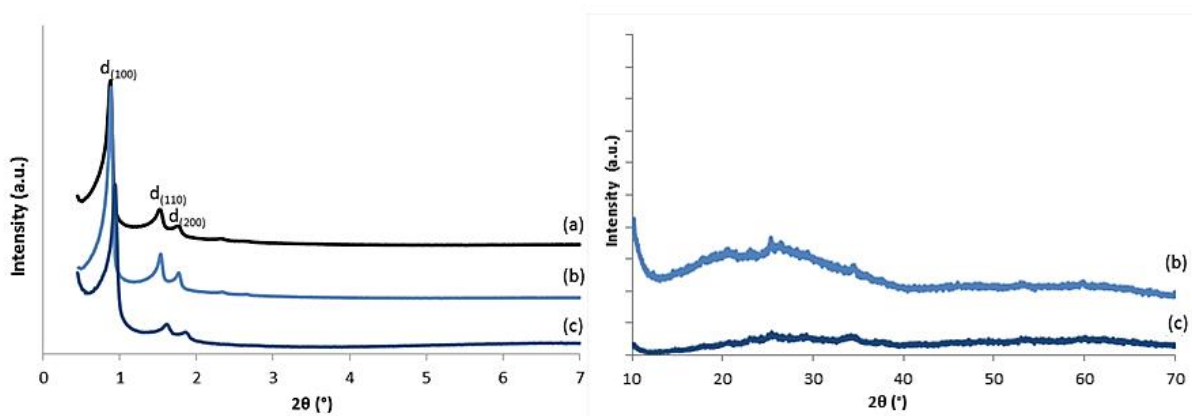


Figure S6

Low and wide-angle XRD patterns of supported HPW catalysts (a) SBA-15, (b) HPW/SBA-15 and (c) HPW@SBA-15.

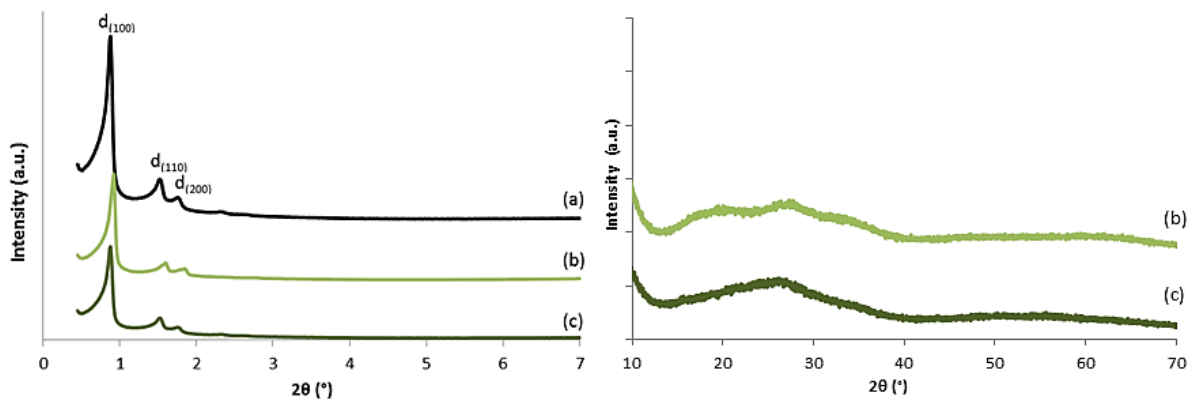


Figure S7

Low and wide-angle XRD patterns of supported HSiW catalysts (a) SBA-15, (b) HSiW/SBA-15 and (c) HSiW@SBA-15.

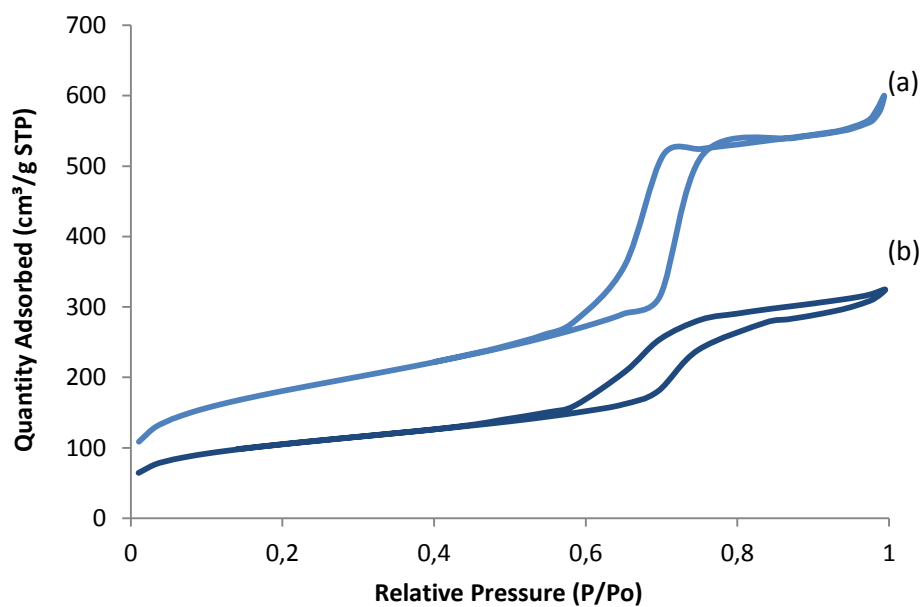


Figure S8

Nitrogen adsorption-desorption isotherms of supported HPW catalysts (a) HPW/SBA-15 and (b) HPW@SBA-15.

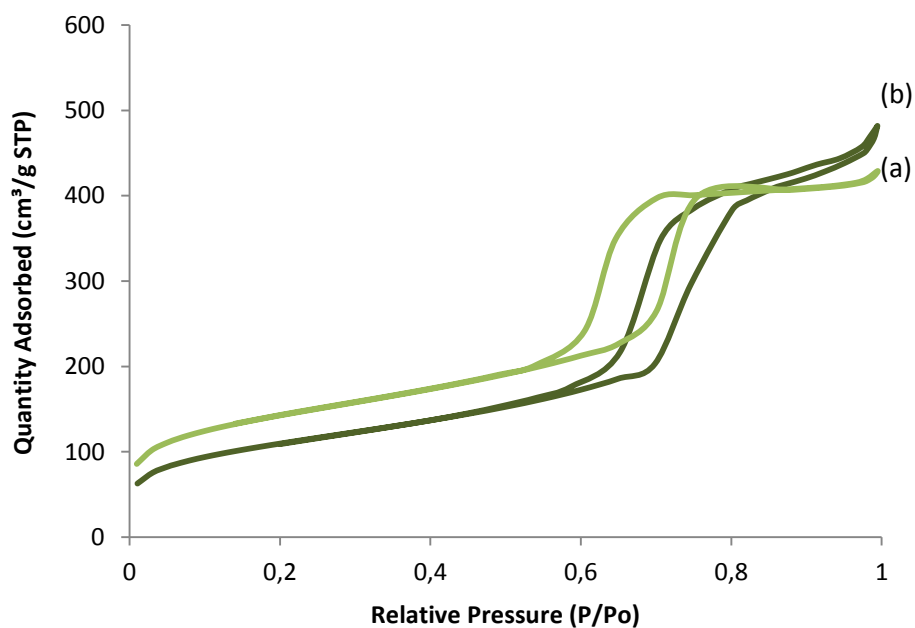


Figure S9.

Nitrogen adsorption-desorption isotherms of supported HSiW catalysts (a) HSiW/SBA-15 and (b) HSiW@SBA-15.

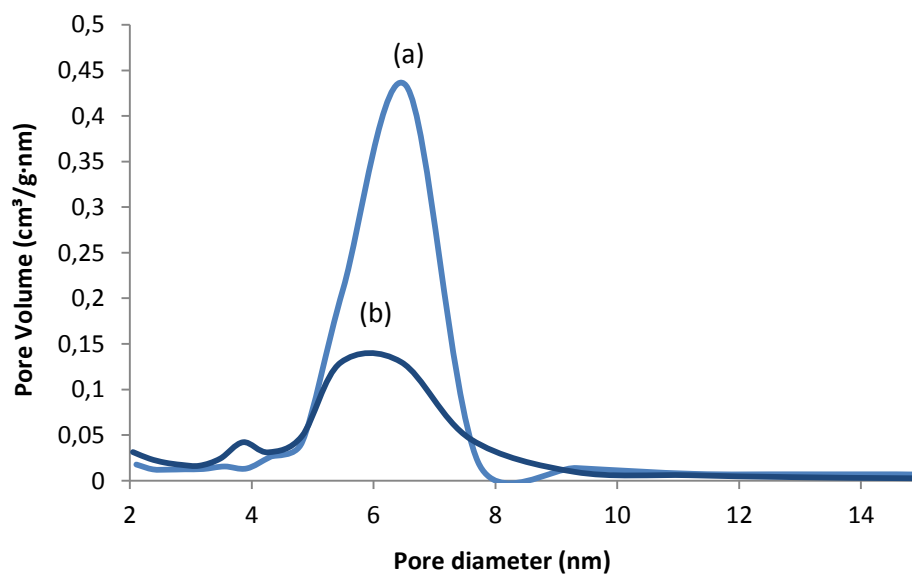


Figure S10

Pore size distribution of supported HPW catalysts (a) HPW/SBA-15 and (b) HPW@SBA-15.

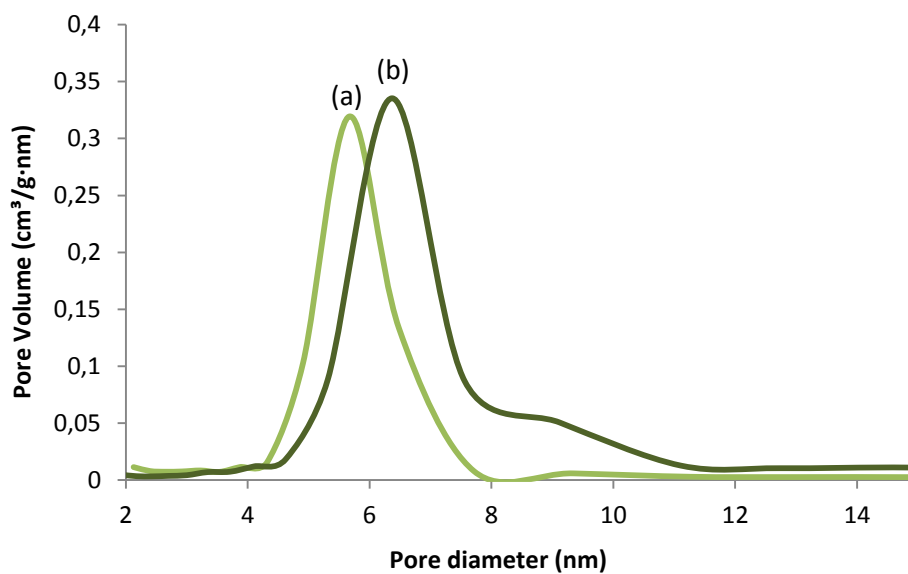


Figure S11

Pore size distribution of supported HSiW catalysts (a) HSiW/SBA-15 and (b) HSiW@SBA-15.

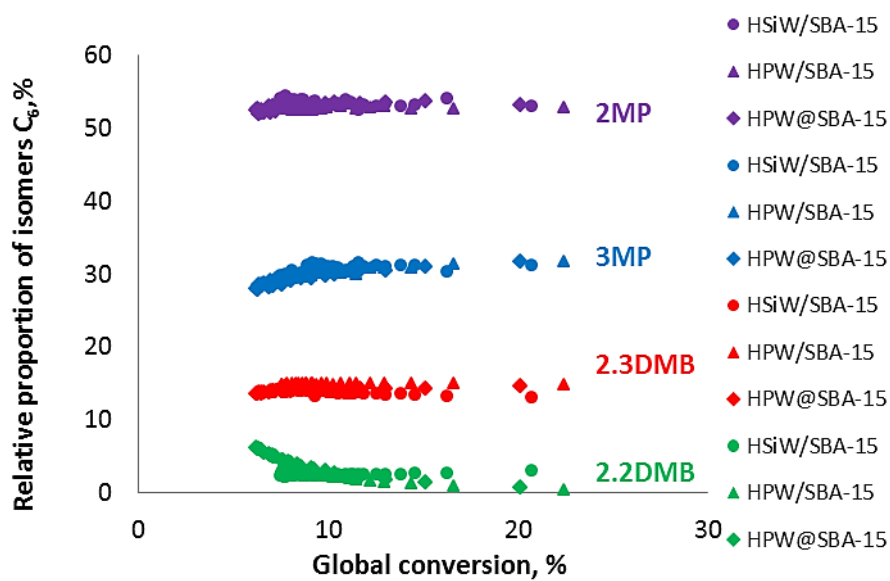


Figure S12

Evolution of the proportions of the four branched C<sub>6</sub> isomers as a function of the conversion for HSiW/SBA-15, HPW/SBA-15, and HPW@SBA-15.

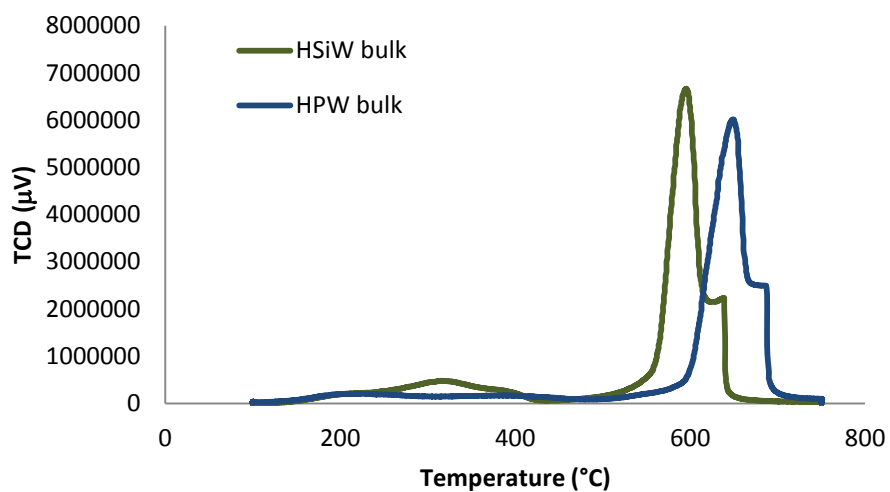


Figure S13

NH<sub>3</sub>-TPD profiles of pure HPW and HSiW.

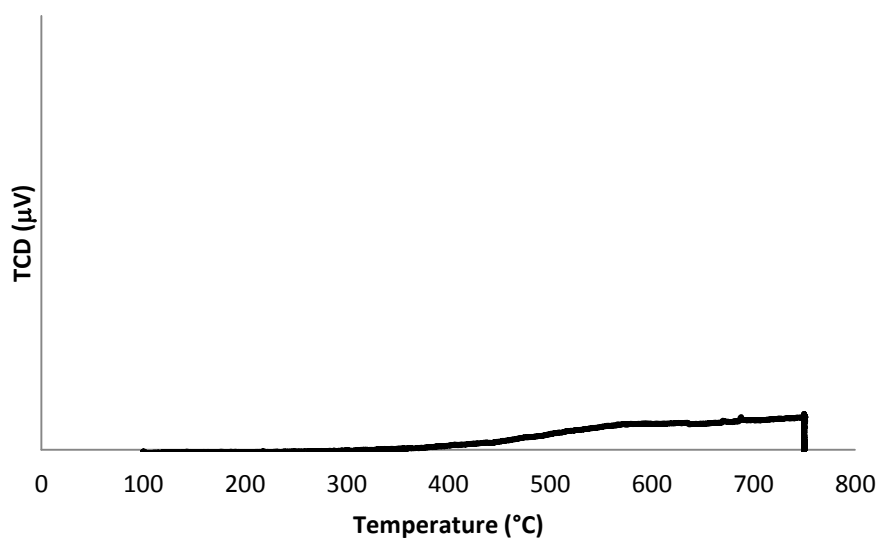


Figure S14

NH<sub>3</sub>-TPD profile of SBA-15.

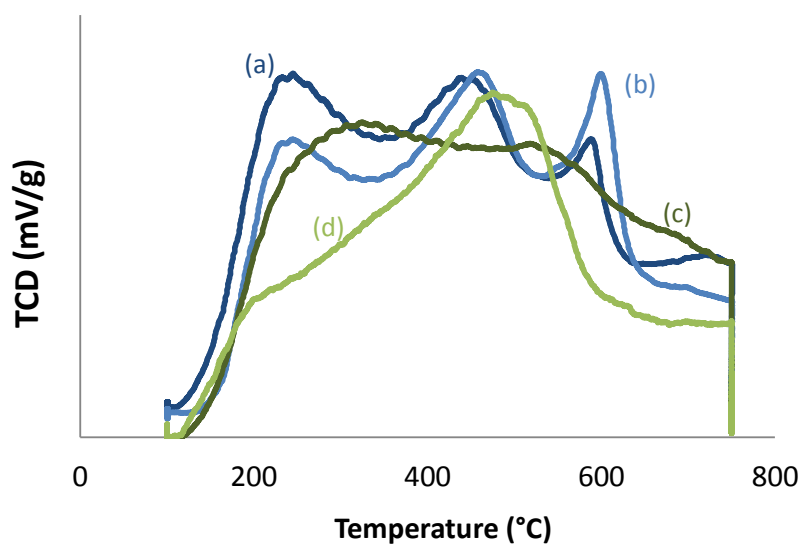


Figure S15

NH<sub>3</sub>-TPD profiles of (a) HPW@SBA-15, (b) HPW/SBA-15, (c) HSiW@SBA-15 and (d) HSiW/SBA-15.

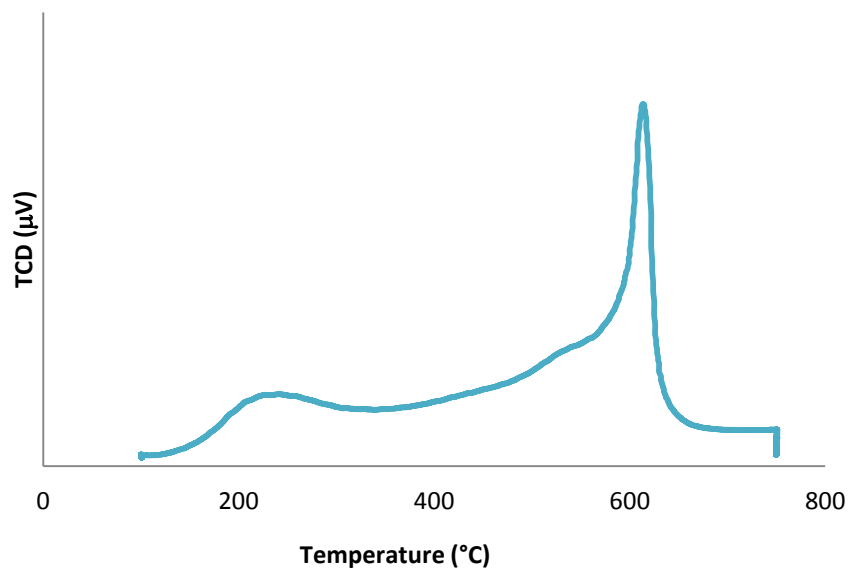


Figure S16

NH<sub>3</sub>-TPD profile of HPW/SiO<sub>2</sub>.

Table S1  
NH<sub>3</sub>-TPD results for all catalysts

Catalysts	wt% W	mmol NH <sub>3</sub> /g	mmol /g HPA	mol /mol HPA
SBA-15	-	0.3	-	-
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	76.6	1.5	1.5	4.3
HPW@SBA-15	27.7	1.9	0.7	2.0
HPW/SBA-15	24.7	2.5	0.8	2.3
HPW/SiO <sub>2</sub>	27.0	1.0	0.4	1.0
HSiW/SBA-15	24.6	2.3	0.7	2.1
HSiW@SBA-15	22.6	2.0	0.6	1.7

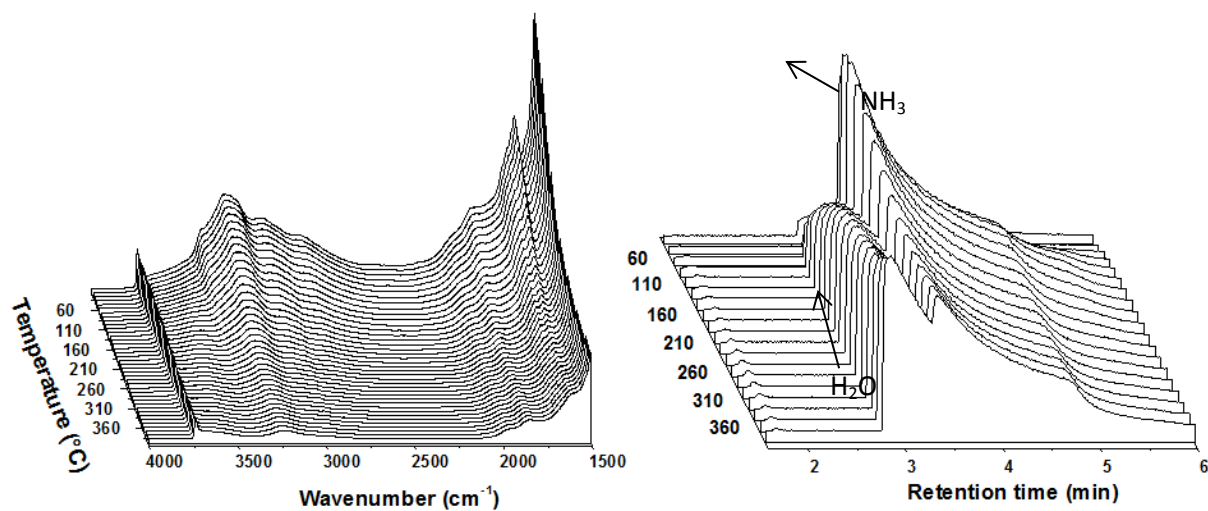


Figure S17

Infrared and GC-MS profiles for  $\text{NH}_3$  desorption from HPW/SBA-15.

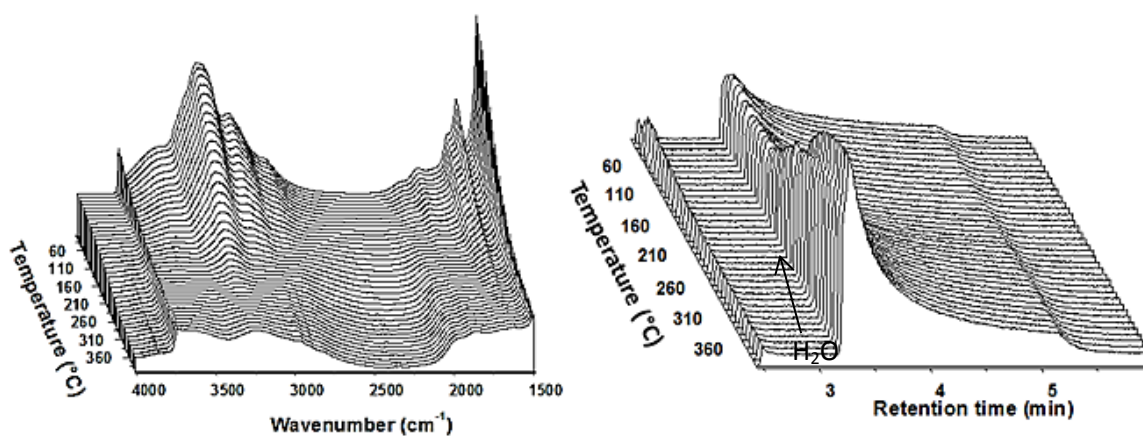


Figure S18

Infrared and GC-MS profiles for  $\text{NH}_3$  desorption from HPW@SBA-15.

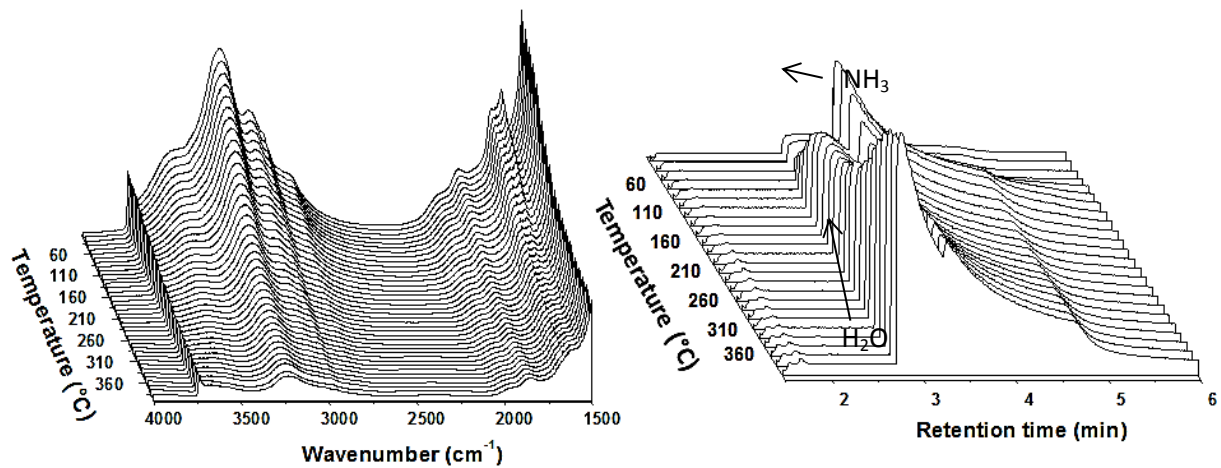


Figure S19

Infrared and GC-MS profiles for  $\text{NH}_3$  desorption from HSiW/SBA-15.

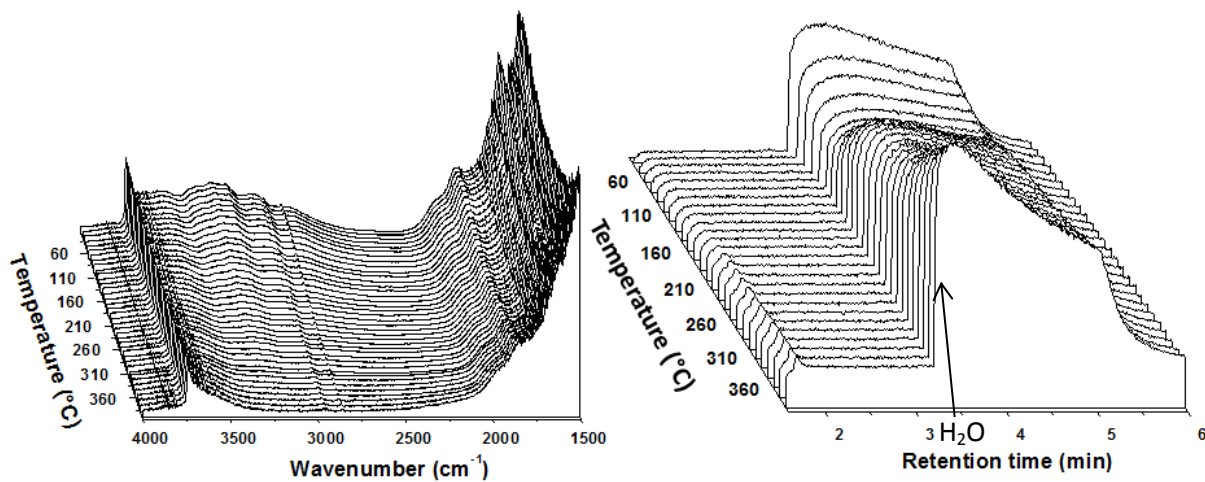


Figure S20

Infrared and GC-MS profiles for  $\text{NH}_3$  desorption from HSiW@SBA-15.

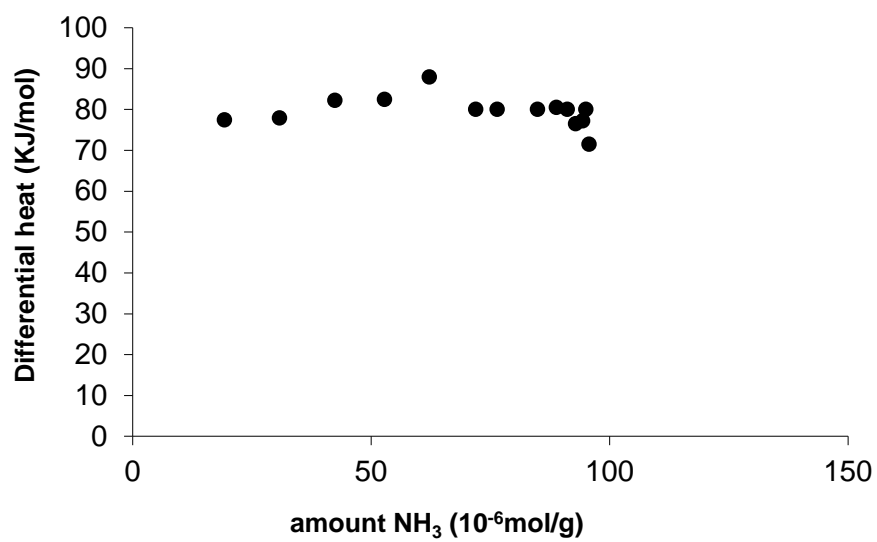


Figure S21

Differential heat of ammonia adsorption on SBA-15 as a function of the ammonia coverage.

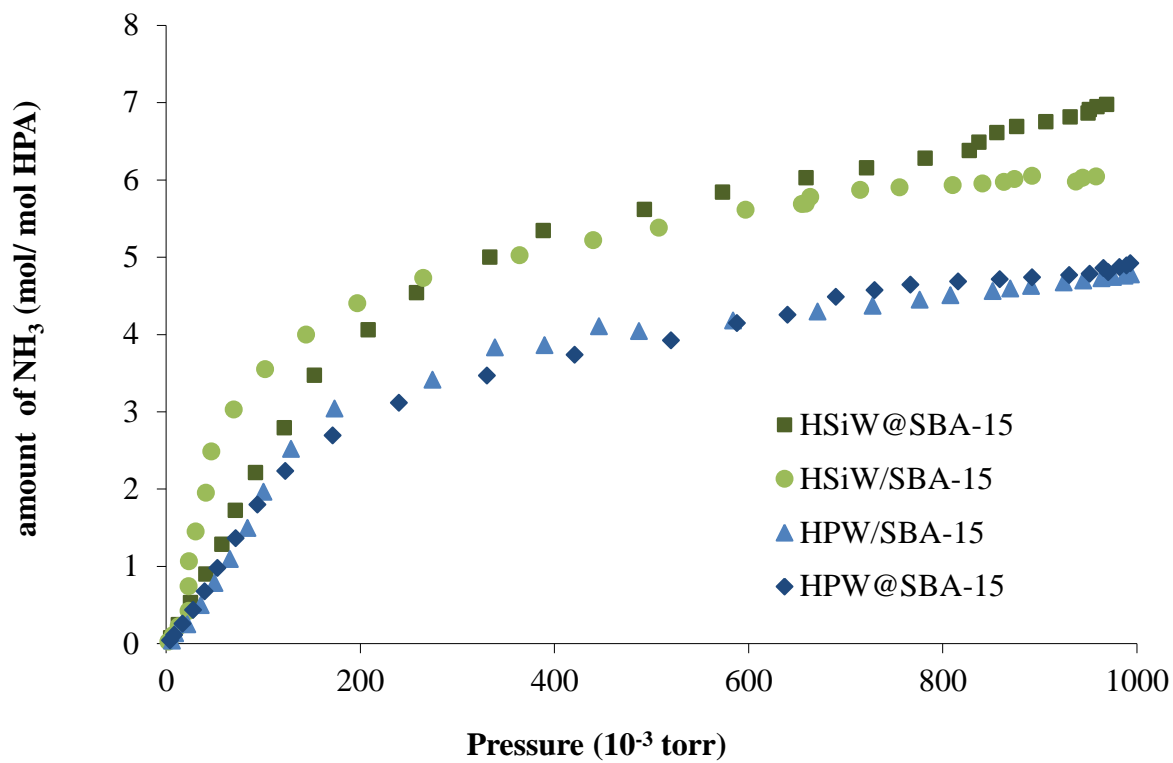


Figure S22

Amount of ammonia adsorbed on the four catalysts as a function of added pressure.

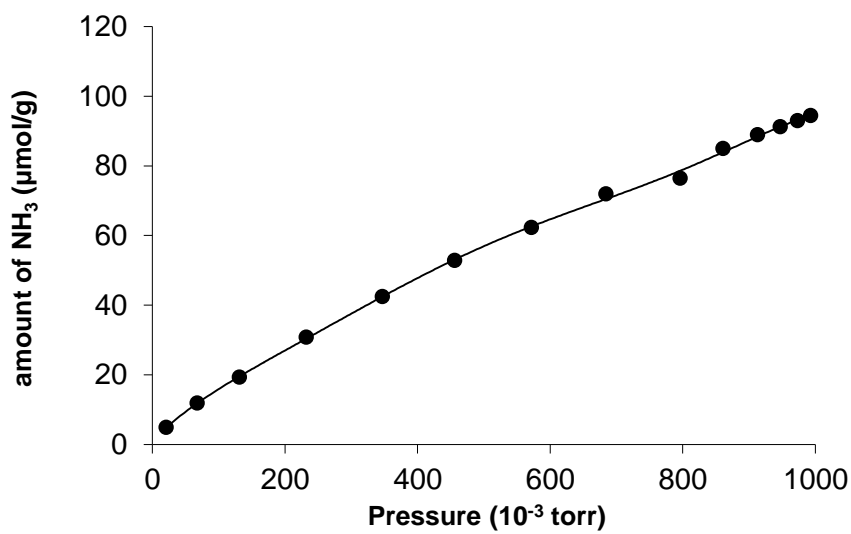


Figure S23

Amount of ammonia adsorbed on SBA-15 as a function of pressure.

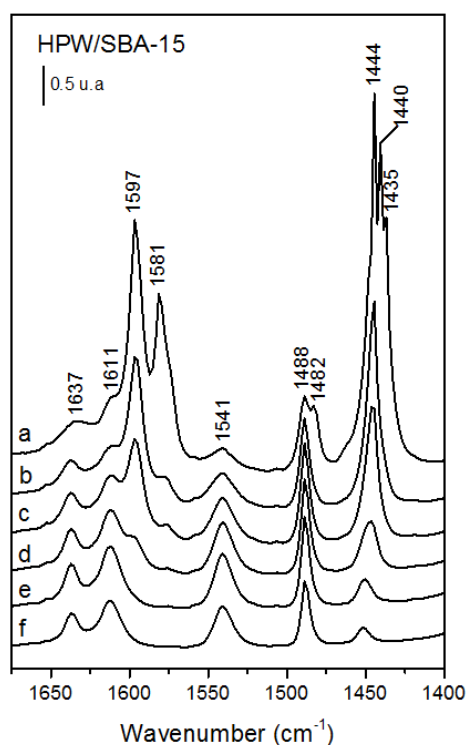


Figure S24

Infrared spectra of pyridine on HPW/SBA-15, (a) adsorption at room temperature and as a function of the desorption temperature (b) room temperature, (c) 50°C, (d) 100°C, (e) 150°C and (f) 200°C.

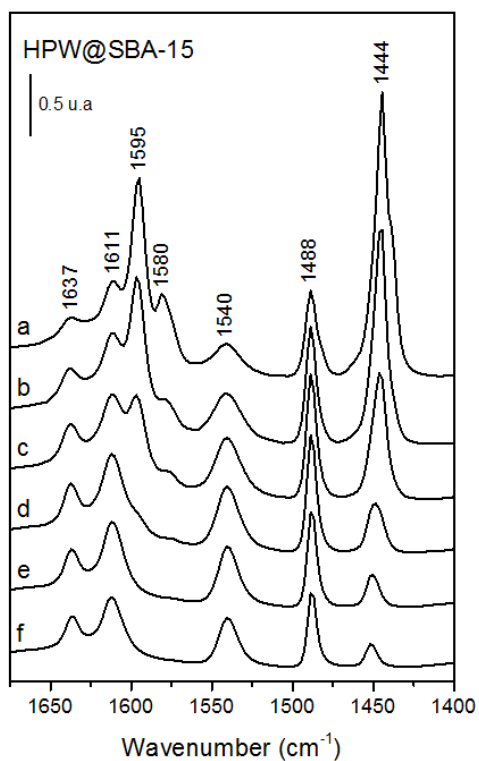


Figure S25

Infrared spectra of pyridine on HPW@SBA-15, (a) adsorption at room temperature and as a function of the desorption temperature (b) room temperature, (c) 50°C, (d) 100°C, (e) 150°C and (f) 200°C.

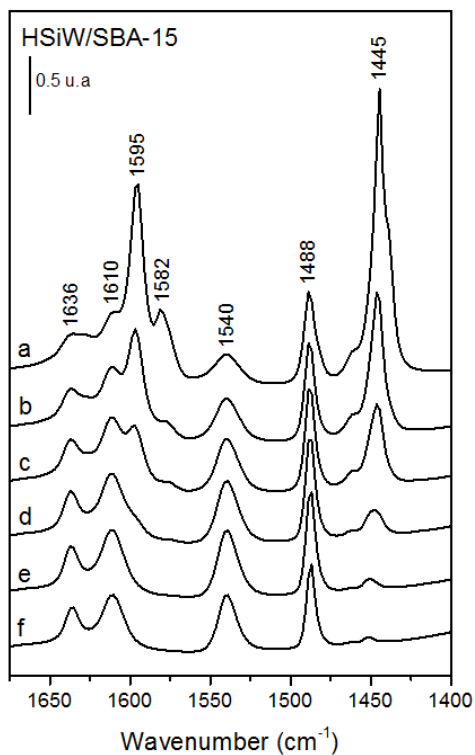


Figure S26

Infrared spectra of pyridine on HSiW/SBA-15, (a) adsorption at room temperature and as a function of the desorption temperature (b) room temperature, (c) 50°C, (d) 100°C, (e) 150°C and (f) 200°C.

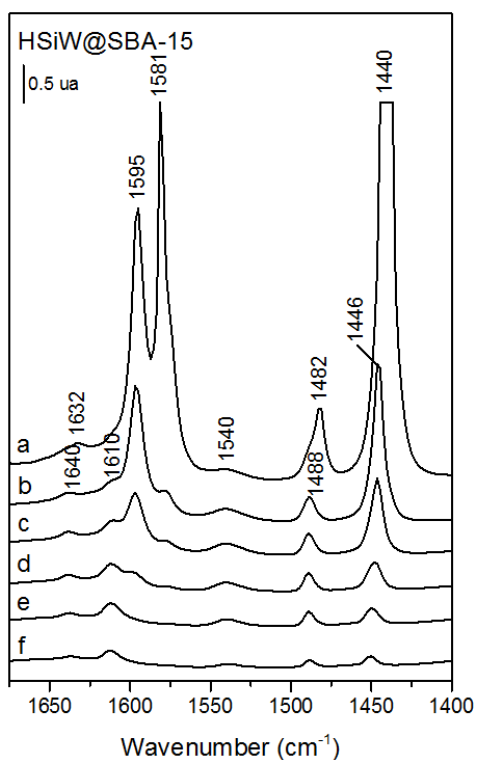


Figure S27

Infrared spectra of pyridine on HSiW@SBA-15, (a) adsorption at room temperature and as a function of the desorption temperature (b) room temperature, (c) 50°C, (d) 100°C, (e) 150°C and (f) 200°C.