Quantification of Acidic Sites of Nanoscopic Hydroxylated Magnesium Fluorides by FTIR and ^{15}N MAS NMR Spectroscopy

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Transposing of equation 4 for Figure 1

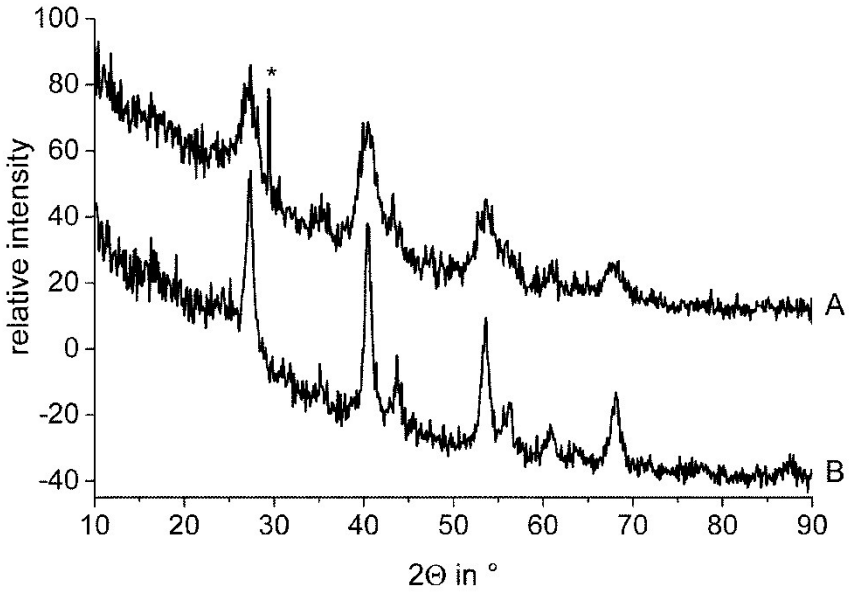
$$1 = \frac{\frac{dA_{LPy}}{dn}}{\varepsilon'_{LPy}} + \frac{\frac{dA_{BPy}}{dn}}{\varepsilon'_{BPy}} \qquad |*\varepsilon'_{LPy}*\varepsilon'_{BPy}$$

$$\varepsilon'_{BPy}*\varepsilon'_{LPy} = \frac{dA_{LPy}}{dn}*\varepsilon'_{BPy} + \frac{dA_{BPy}}{dn}*\varepsilon'_{LPy} \qquad |- \frac{dA_{LPy}}{dn}*\varepsilon'_{BPy}$$

$$\frac{dA_{BPy}}{dn}*\varepsilon'_{LPy} = \varepsilon'_{BPy}*\varepsilon'_{LPy} - \frac{dA_{LPy}}{dn}*\varepsilon'_{BPy}$$

$$\frac{dA_{BPy}}{dn}*\varepsilon'_{LPy} = \varepsilon'_{BPy}*(\varepsilon'_{LPy} - \frac{dA_{LPy}}{dn}) \qquad |/(\varepsilon'_{LPy} - \frac{dA_{LPy}}{dn})$$

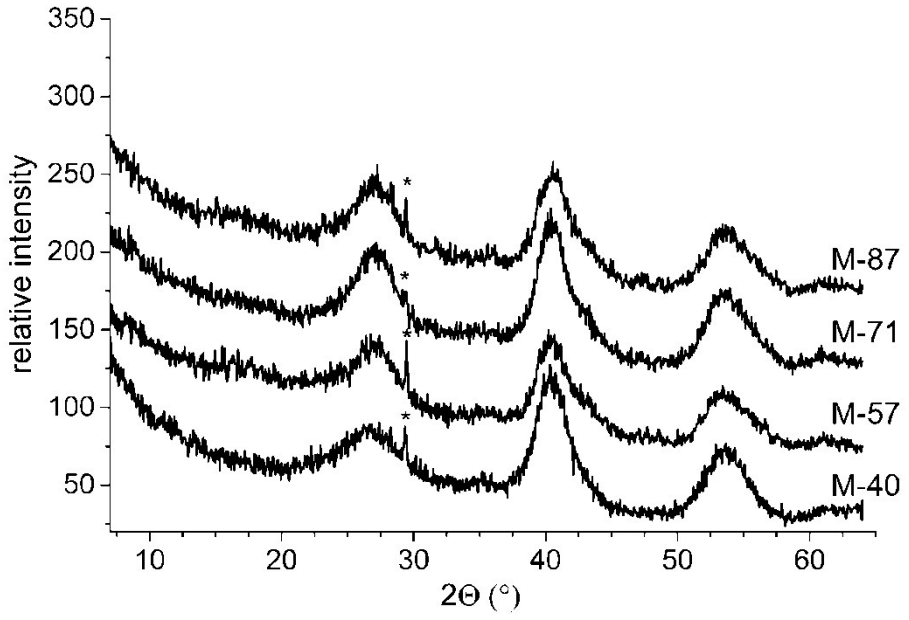
$$\varepsilon'_{BPy} = \frac{\frac{dA_{BPy}}{dn}*\varepsilon'_{LPy}}{\varepsilon'_{LPy} - \frac{dA_{LPy}}{dn}}$$



1

2 SI Figure 1: X-Ray powder diffraction patterns of a hydroxylated magnesium fluoride sample before (A) and
3 after it was calcinated at 300°C for 2 h (B). * indicate reflex of the sample holder.

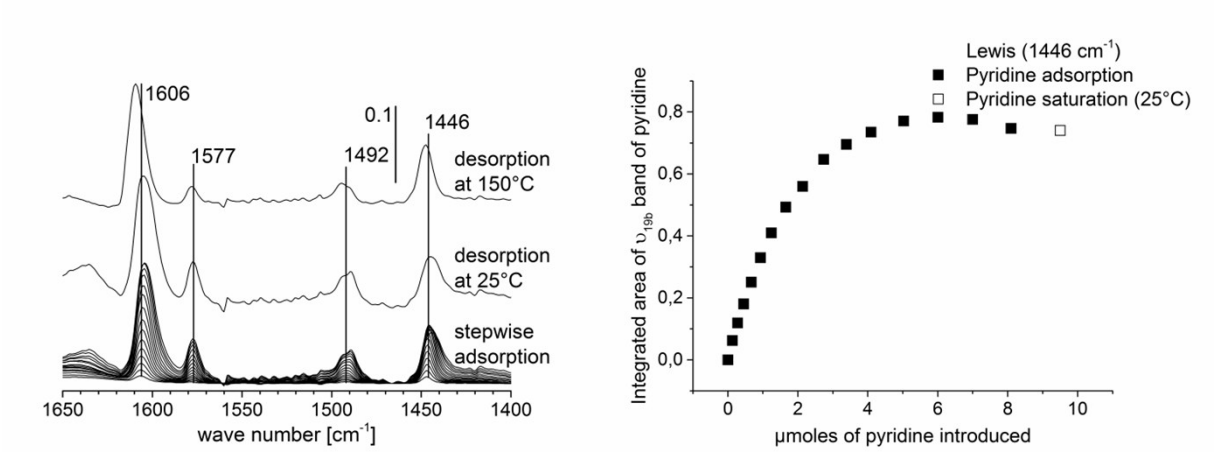
4



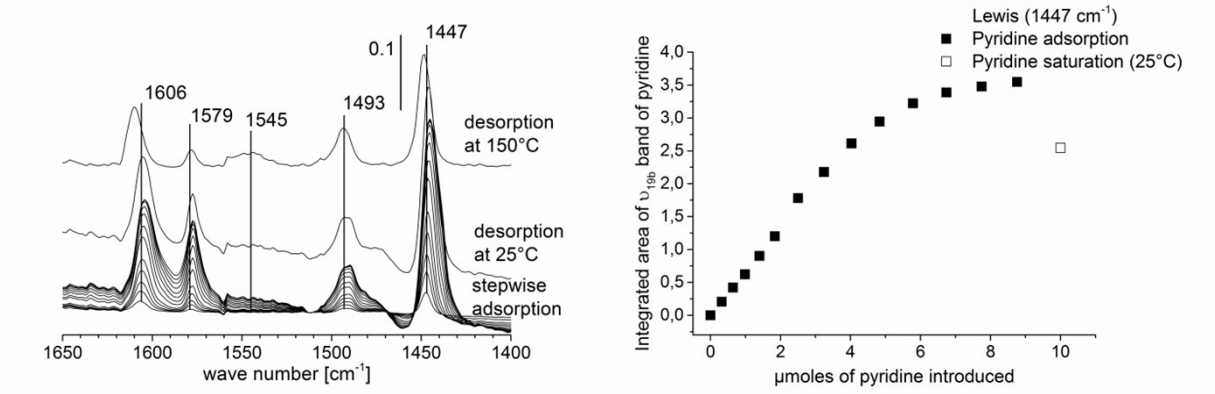
5

6 SI Figure 2: X-Ray powder diffraction patterns of the four hydroxylated magnesium fluoride samples. * indicate
7 reflex of the sample holder.

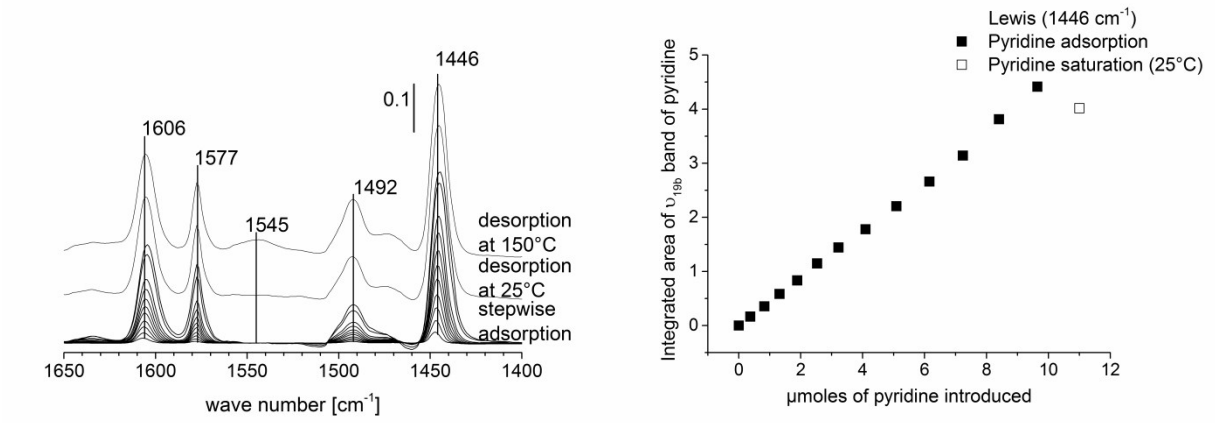
8



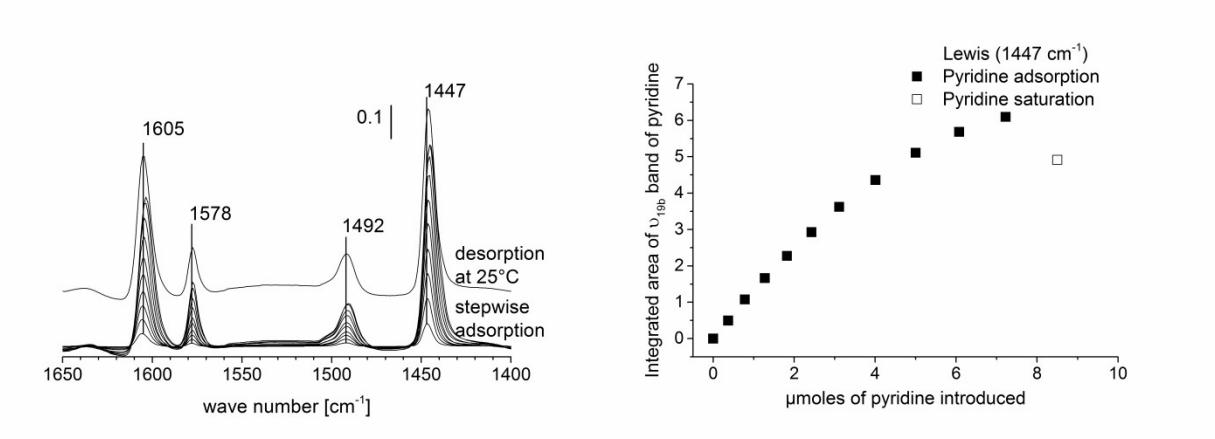
SI Figure 3. FTIR spectra after stepwise pyridine adsorption at ungrounded M-40 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1446 cm^{-1}. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



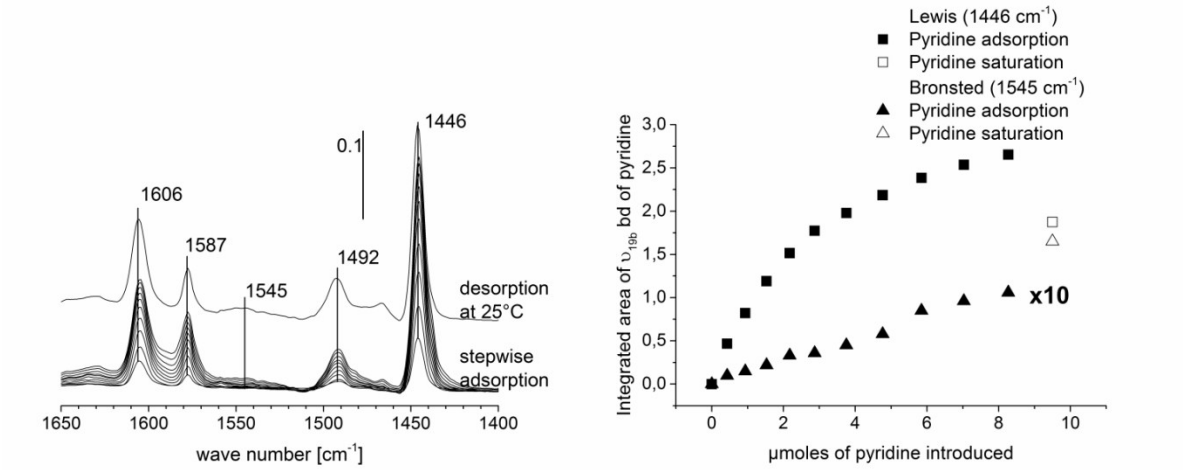
SI Figure 4. FTIR spectra after stepwise pyridine adsorption at ungrounded M-71 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1447 cm^{-1}. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



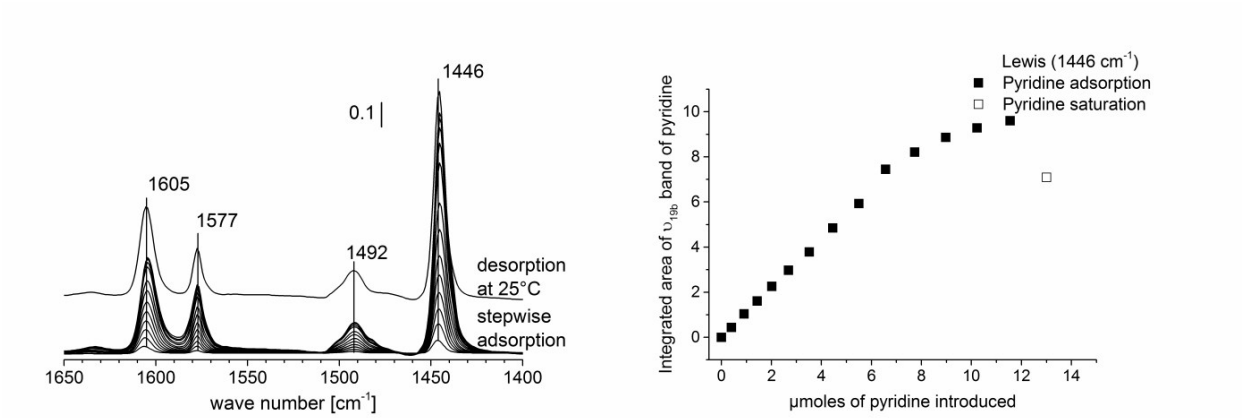
SI Figure 5. FTIR spectra after stepwise pyridine adsorption at ungrounded M-87 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1446 cm^{-1}. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



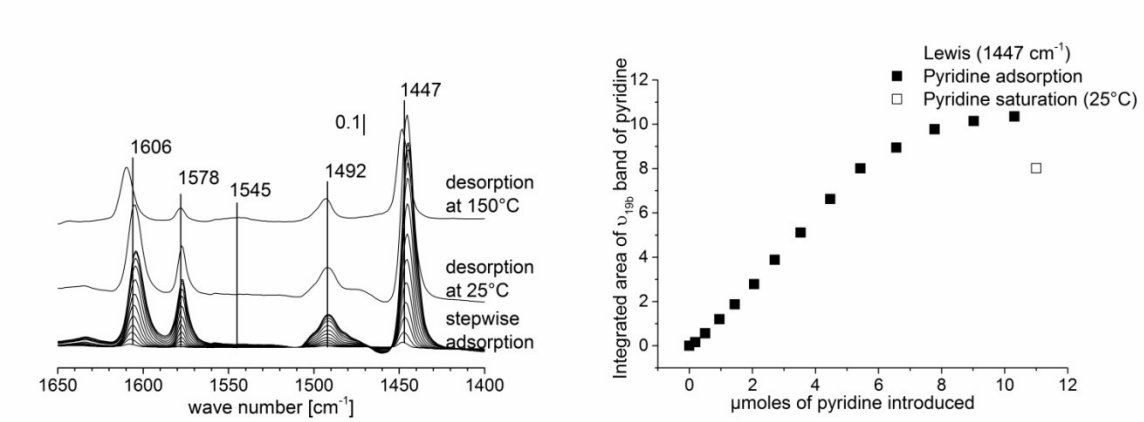
SI Figure 6. FTIR spectra after stepwise pyridine adsorption at grounded M-40 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1447 cm^{-1} versus pyridine introduced into the cell. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



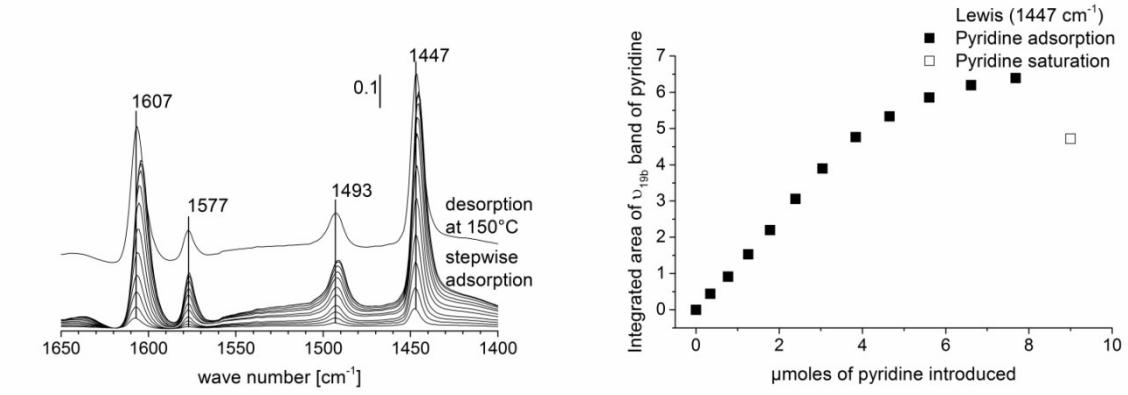
SI Figure 7. FTIR spectra after stepwise pyridine adsorption at grounded M-57 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1446 cm^{-1} and protonated pyridine at about 1545 cm^{-1}. In the intensity plot, the signal intensity of the protonated pyridine is multiplied by a factor of ten. Also shown are the integrated intensities of ν_{19b} band after saturation with pyridine (open symbol).



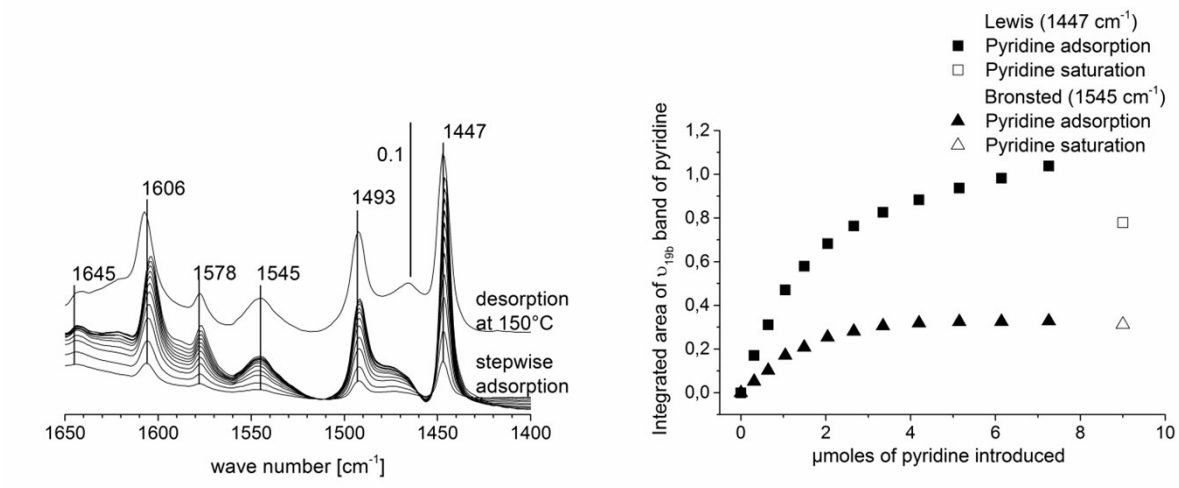
SI Figure 8. FTIR spectra after stepwise pyridine adsorption at grounded M-71 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1447 cm^{-1} versus pyridine introduced into the cell. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



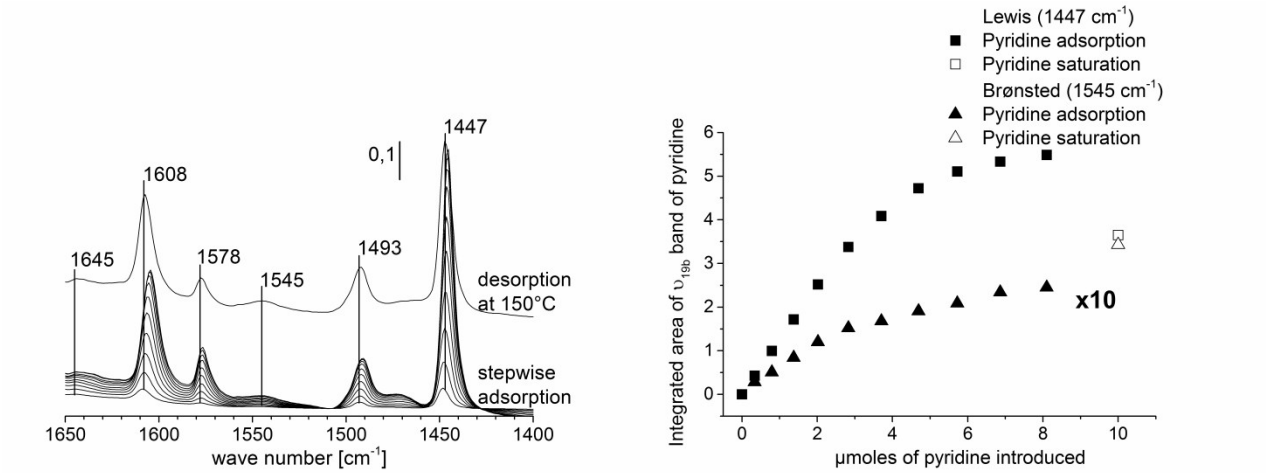
SI Figure 9. FTIR spectra after stepwise pyridine adsorption at grounded M-87 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1446 cm^{-1}. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



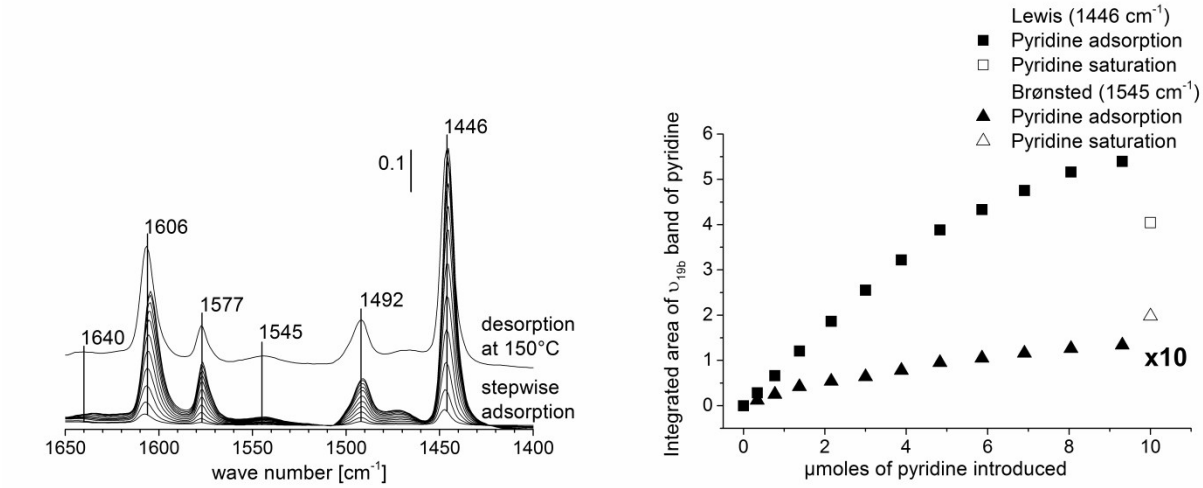
SI Figure 10. FTIR spectra after stepwise pyridine adsorption at 150°C at grounded M-40 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1447 cm^{-1}. Also shown is the integrated intensity of ν_{19b} band after saturation with pyridine (open symbol).



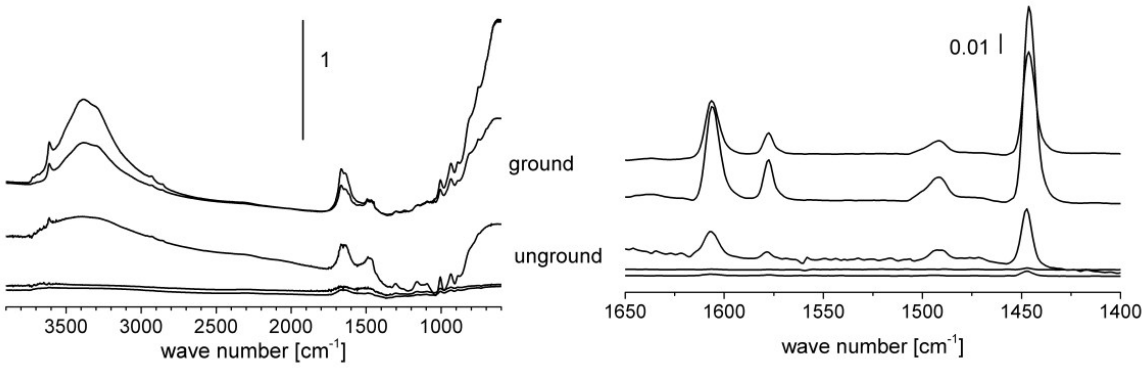
SI Figure 11. FTIR spectra after stepwise pyridine adsorption at 150°C at grounded M-57 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1447 cm^{-1} and protonated pyridine at about 1545 cm^{-1}. Also shown are the integrated intensities of ν_{19b} band after saturation with pyridine (open symbol).



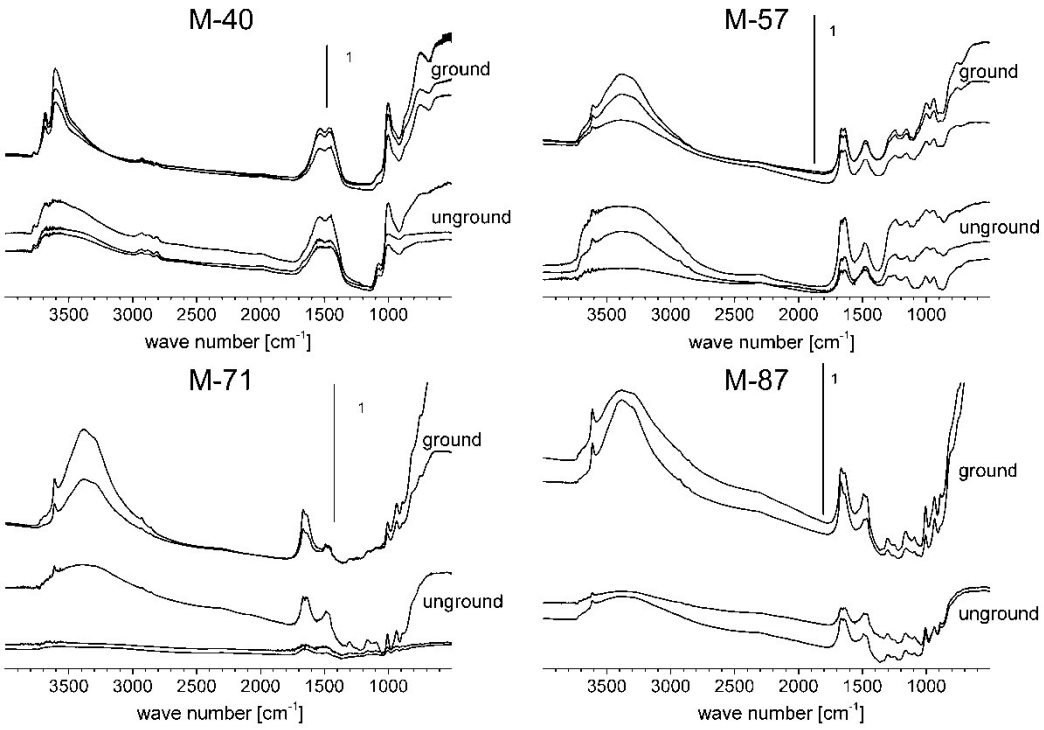
SI Figure 12. FTIR spectra after stepwise pyridine adsorption at 150°C at grounded M-71 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1447 cm^{-1} and 1545 cm^{-1}. In the intensity plot, the signal intensity of the protonated pyridine is multiplied by a factor of ten. Also shown are the integrated intensities of ν_{19b} band after saturation with pyridine (open symbol).



SI Figure 13. FTIR spectra after stepwise pyridine adsorption at 150°C at grounded M-87 and the integrated intensity of ν_{19b} band of coordinated pyridine at about 1446 cm^{-1} and 1545 cm^{-1}. In the intensity plot, the signal intensity of the protonated pyridine is multiplied by a factor of ten. Also shown are the integrated intensities of ν_{19b} band after saturation with pyridine (open symbol).



SI Figure 14: FTIR spectra of grounded and ungrounded samples of M-71 (left) and segment of FTIR difference spectra of the same samples, in which the characteristic bands of pyridine occur, after about 0.5 µmol of pyridine were adsorbed at 25°C (right).



SI Figure 15: FTIR spectra of several grounded and ungrounded samples of the four hydroxylated magnesium fluorides before pyridine adsorption.

SI Table 1: BET surface areas for the ungrounded and grounded sample M-40.

M-40	BET surface area [m^2/g]
ungrounded	282
Grounded	300