Environmental applications of zeolites: hydrophobic Sn-BEA as a selective gas sensor for exhaust fumes

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Supplementary information

S1. Sample characterisation

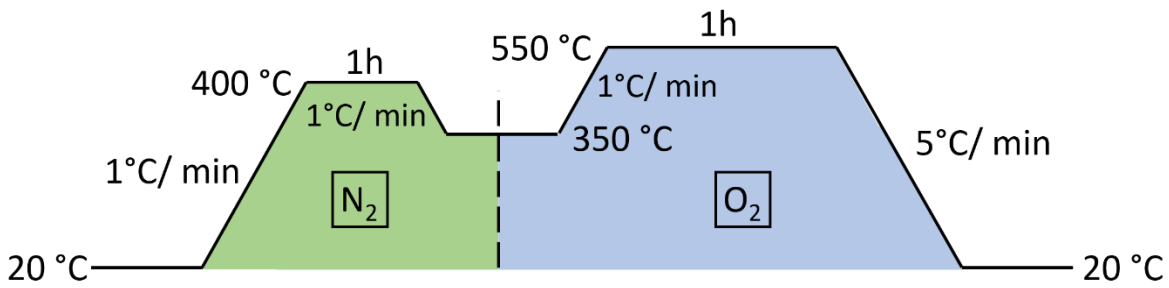

Figure **S1.** Sn-BEA calcination scheme.

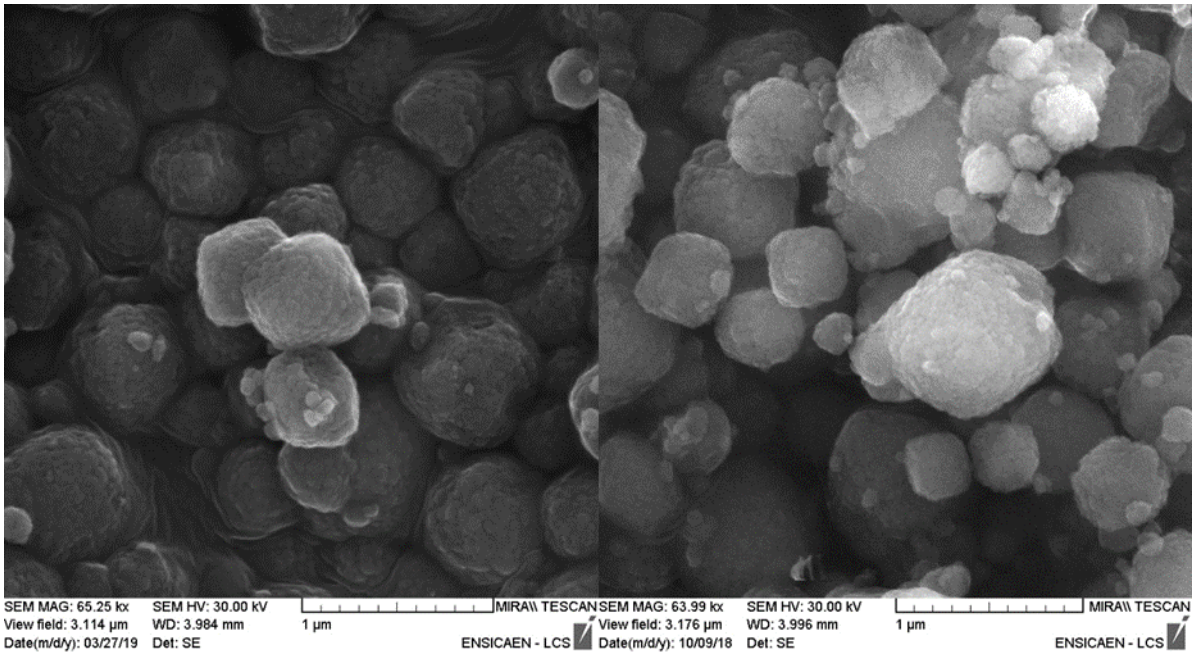

Figure **S2.** SEM micrographs of BEA (left) and DeAl-BEA (right) zeolites.

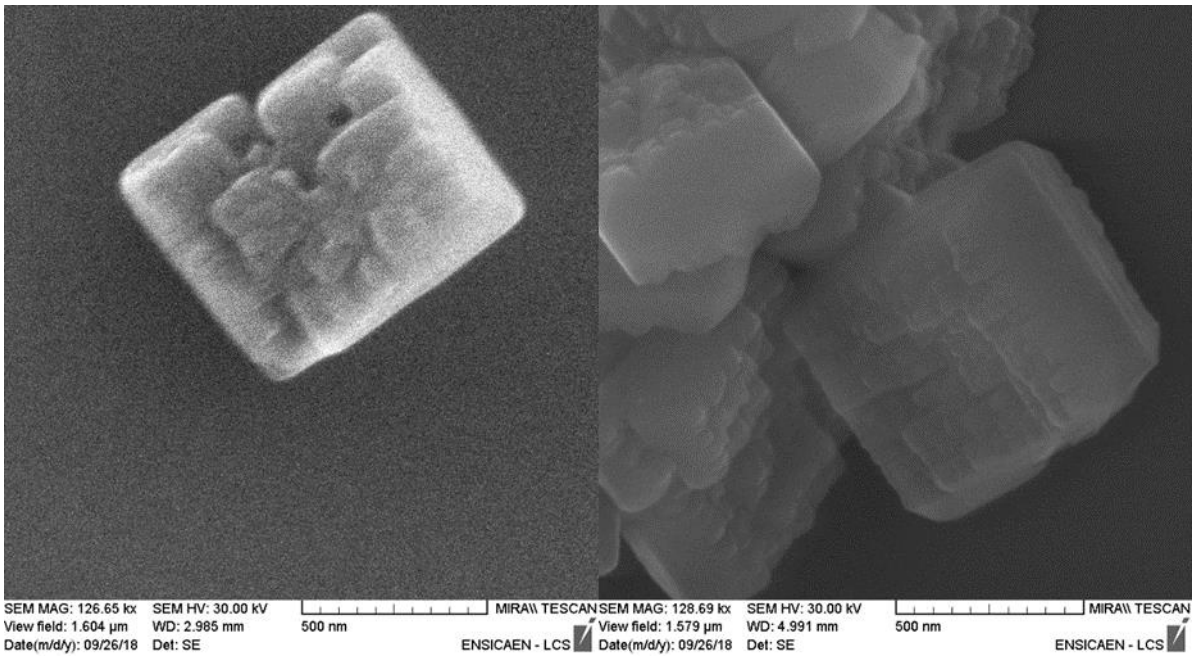

Figure **S3.** SEM micrographs of Sn-BEA zeolite.

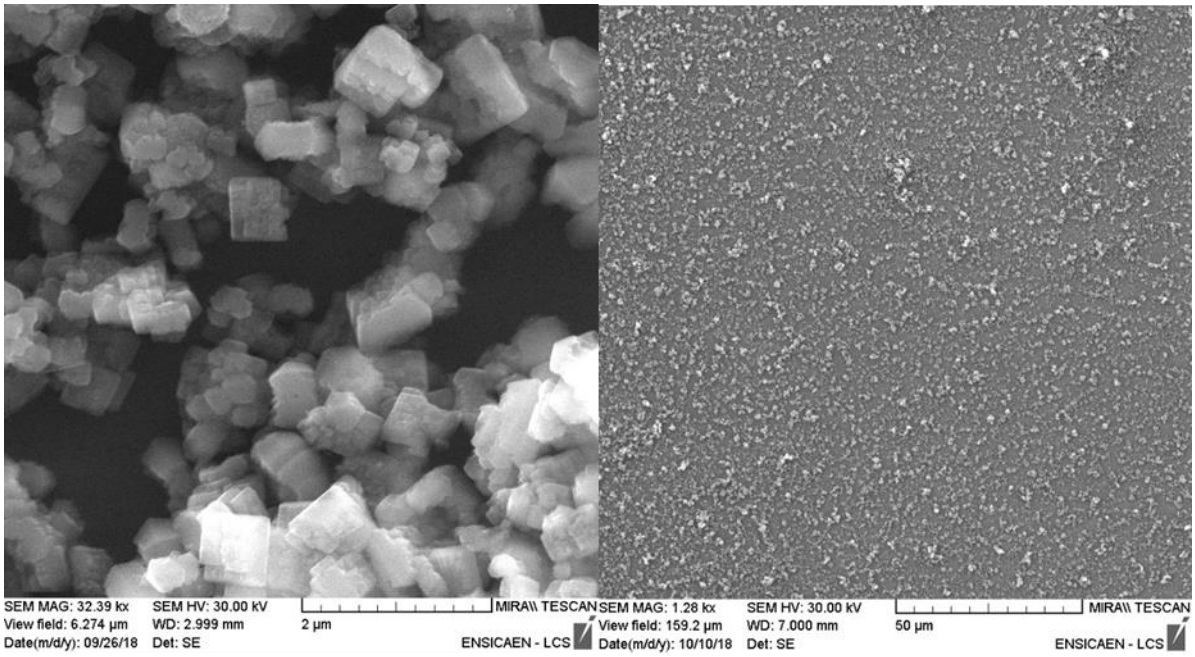

Figure **S4.** SEM micrographs of Sn-BEA powder (left) and Sn-BEA deposited on a silicon wafer (right).

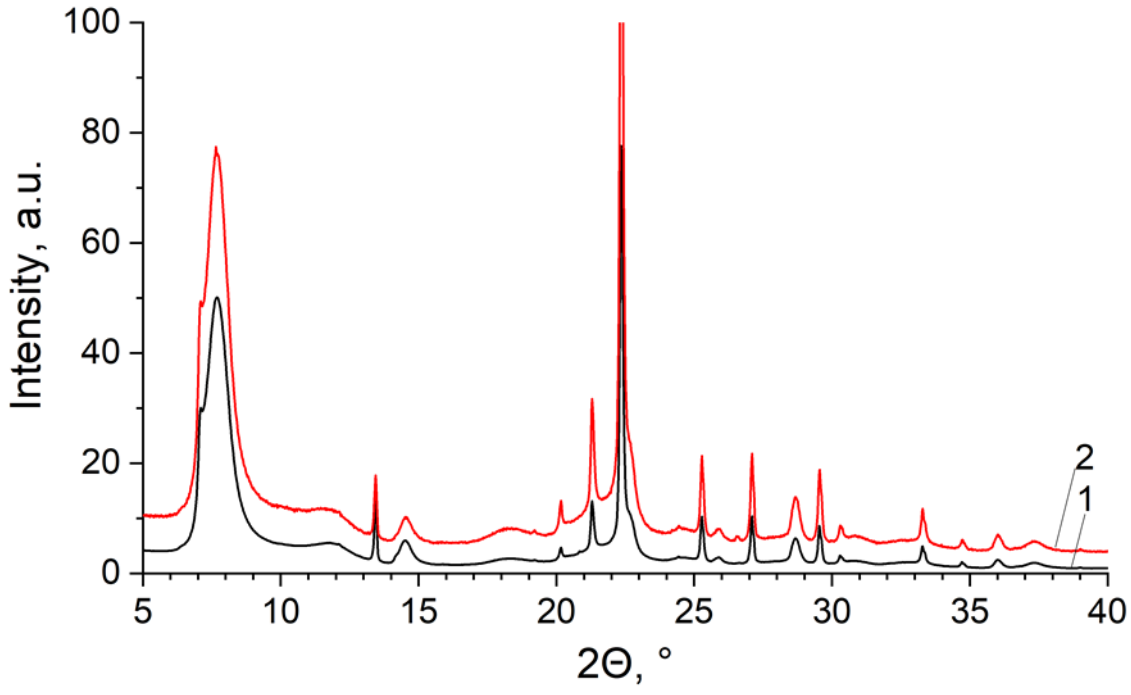

Figure **S5.** XRD patterns of Sn-BEA freshly prepared (1), Sn-BEA zeolites after 9 months (2).

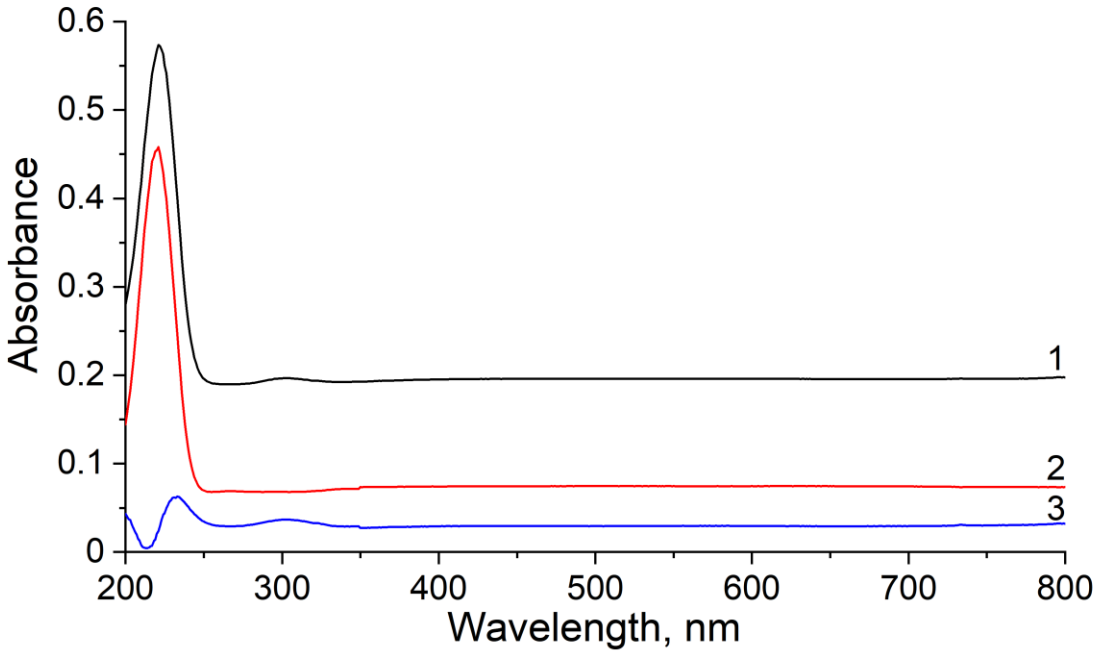

Figure **S6.** DRUV-VIS spectra of Sn-BEA(1) and DeAl-BEA (2) zeolites,

(1)-(2) difference spectrum (3).

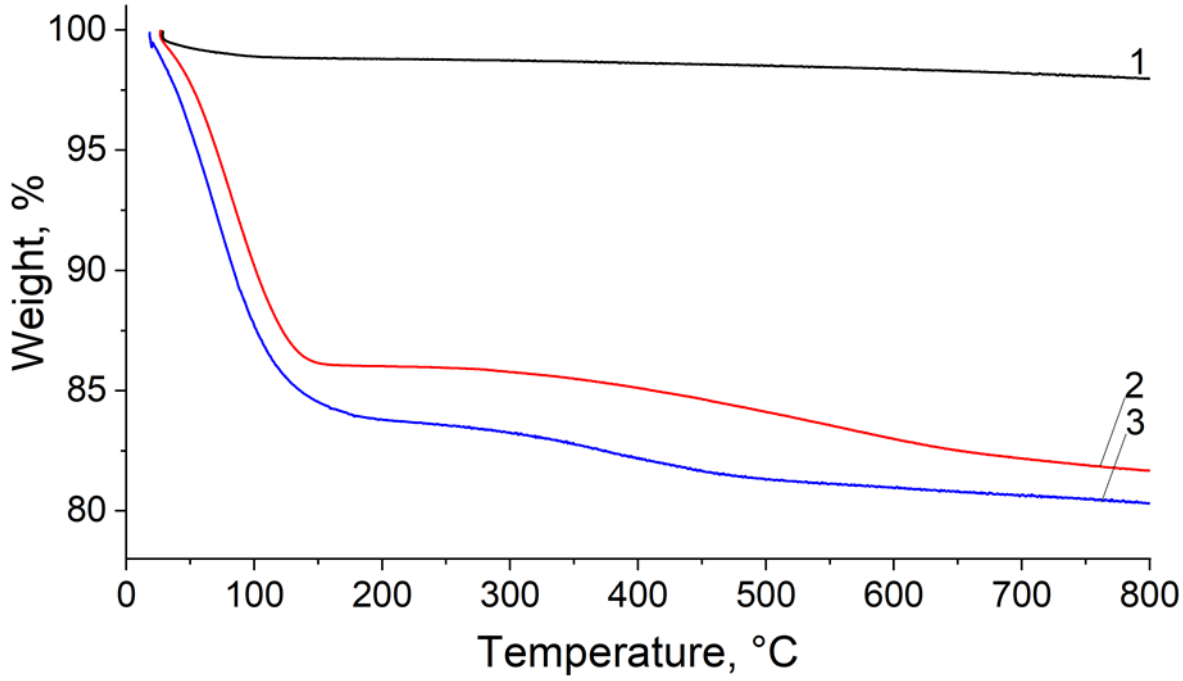

Figure **S7.** TG curves of Sn-BEA (1), DeAl-BEA (2) and BEA (3) zeolites.

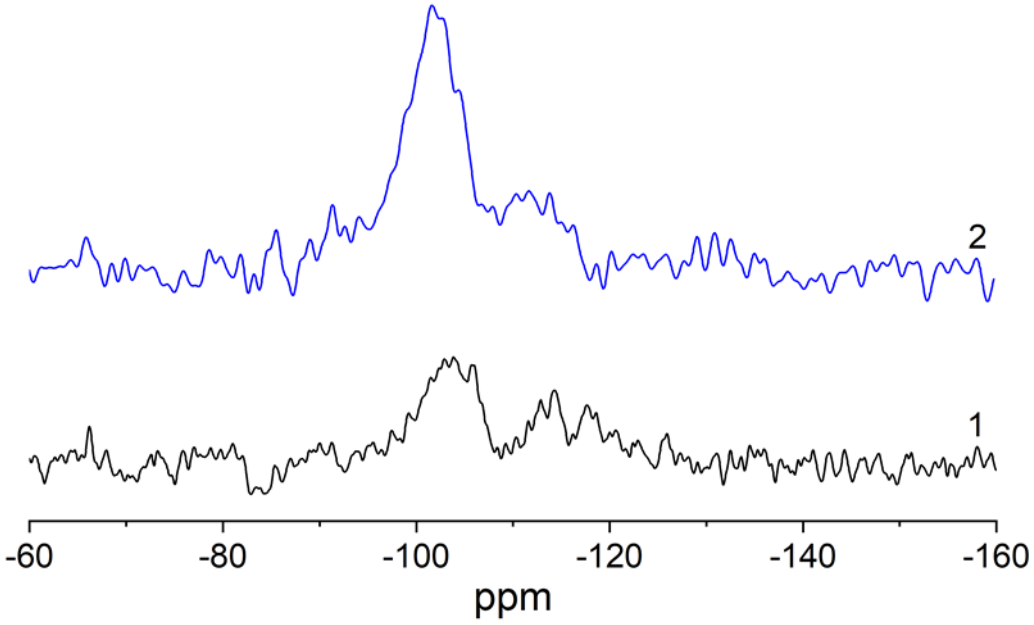

Figure **S8.** ^{29}Si-^{1}H CP MAS NMR spectra of Sn-BEA (1), and BEA (2) zeolites.

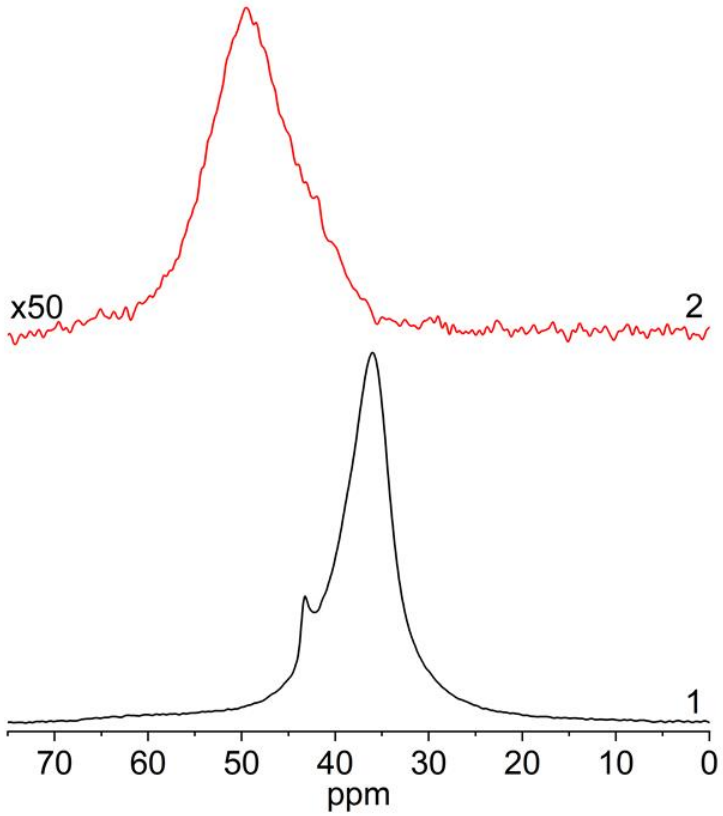

Figure **S9.** ^{31}P MAS NMR spectra of TMPO adsorbed on Sn-BEA (1) and DeAl-BEA (2, intensity is multiplied by a factor of 50) zeolites.

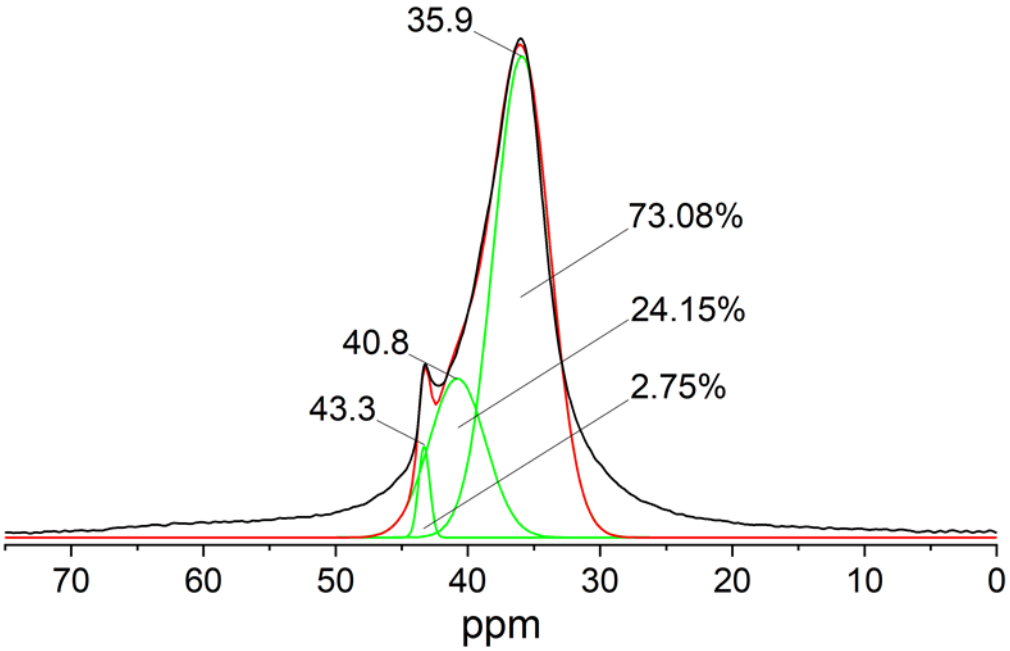

Figure **S10.** Deconvoluted ^{31}P MAS NMR spectrum of TMPO adsorbed on Sn-BEA (black), fitted cumulative peak (red) and single fitted peaks (green).

There is some discussion in the literature regarding the interpretation of the ^{31}P NMR spectra of TMPO adsorbed on zeolites. Indeed, according to [38,53] the peak around 43 ppm should be attributed to physisorbed TMPO. Lewis et al.,[38] who first reported characterisation of Sn-containing zeolites, stated that the physisorbed TMPO is represented by wide peaks (fwhm>9 ppm) and the bound TMPO has narrow peaks (fwhm <1.5 ppm). On the other hand, Dubray et al.[52] reported a different interpretation of adsorbed TMPO on Mo-containing MFI zeolites, describing the narrow peaks as physisorbed TMPO and the broad peaks as the molybdenum bound TMPO. Overall, the interpretation of TMPO spectra is not unambiguous.

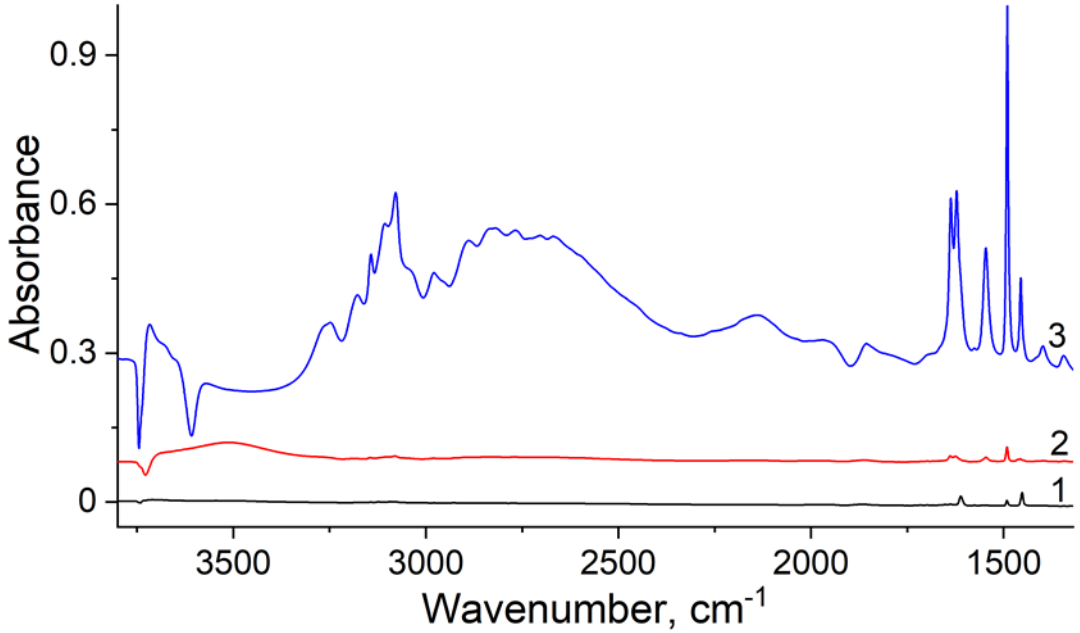

Figure **S11.** Difference FTIR spectra of Sn-BEA (1), DeAl-BEA (2) and BEA (3) following pyridine adsorption.

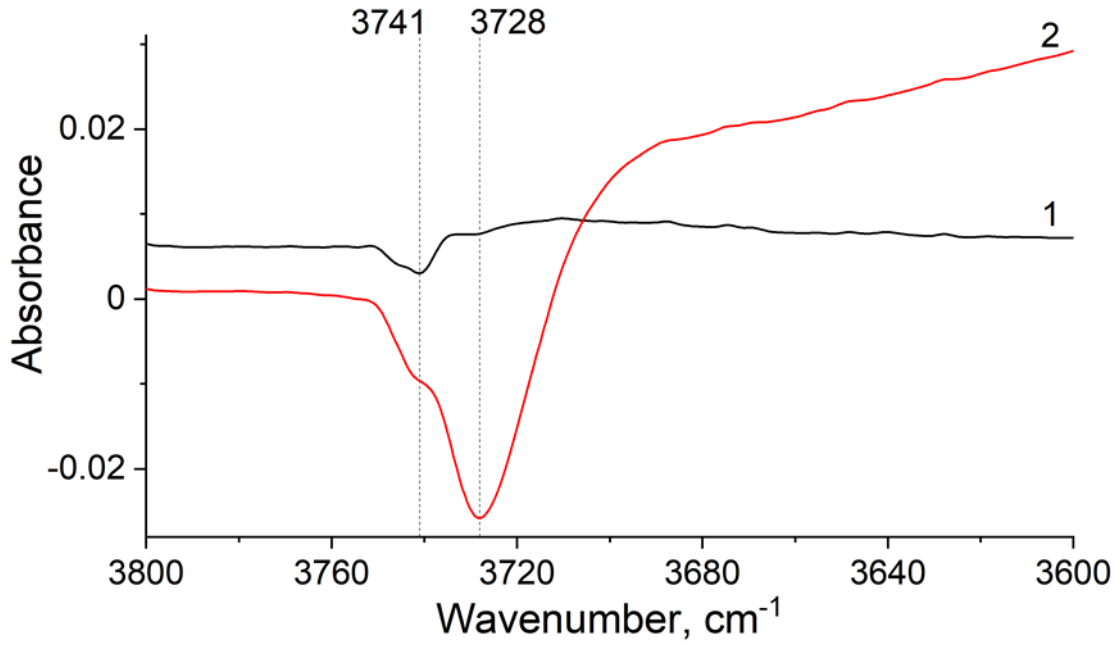

Figure **S12.** The OH-region of the difference FTIR spectra of Sn-BEA (1) and DeAl-BEA (2) zeolites following pyridine adsorption.

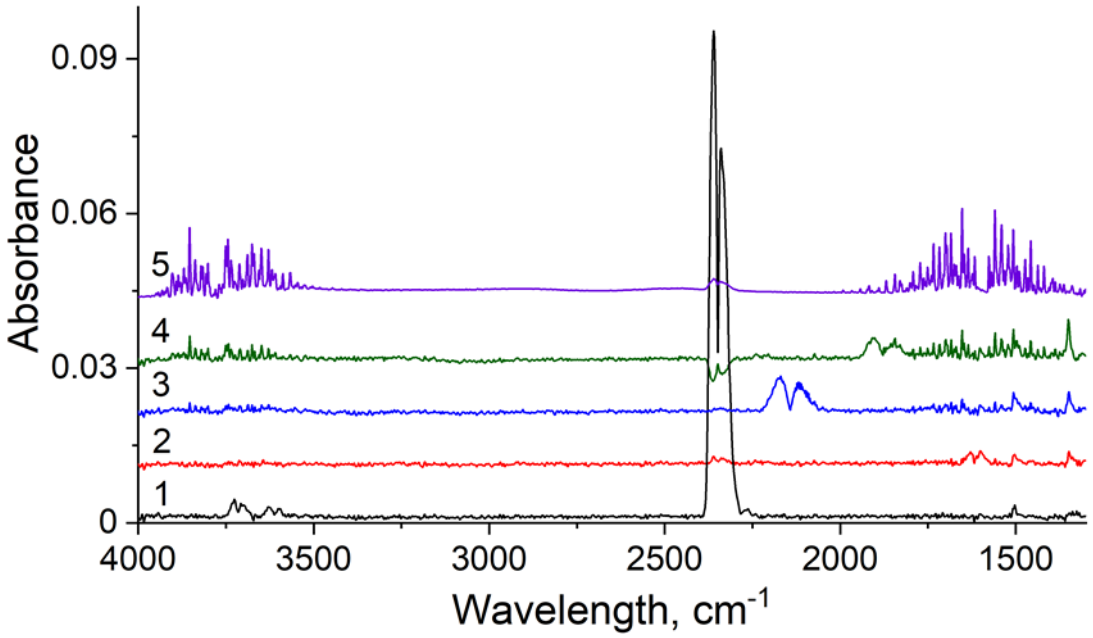

Figure **S13.** FTIR spectra of the selected exhaust gases, 5000 ppm of CO_2 (1), 1000 ppm of NO_2 (2), 5000 ppm of CO (3), 5000 ppm of NO (4), water vapour (5).

S2. FTIR difference spectra of CO, CO_2, NO, NO_2 detected by Sn-BEA and DeAl-BEA

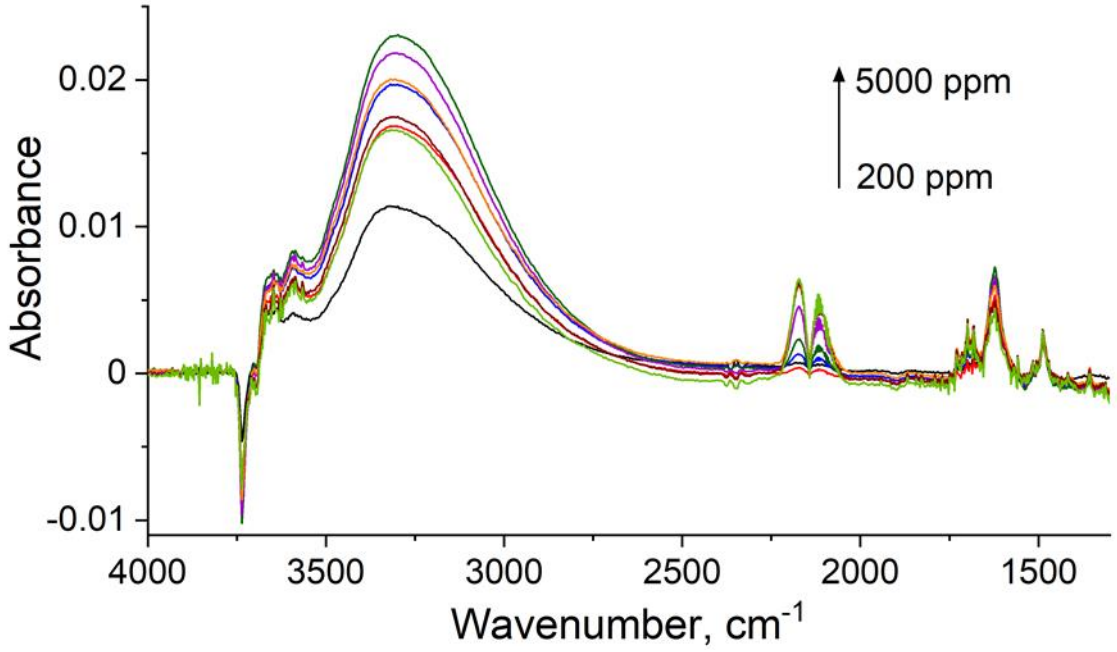

Figure **S14.** FTIR spectra of CO detected by Sn-BEA: 200 ppm (black), 400 ppm, 800 ppm, 1600 ppm, 3200 ppm, 4000 ppm, 4500 ppm, 5000 ppm.

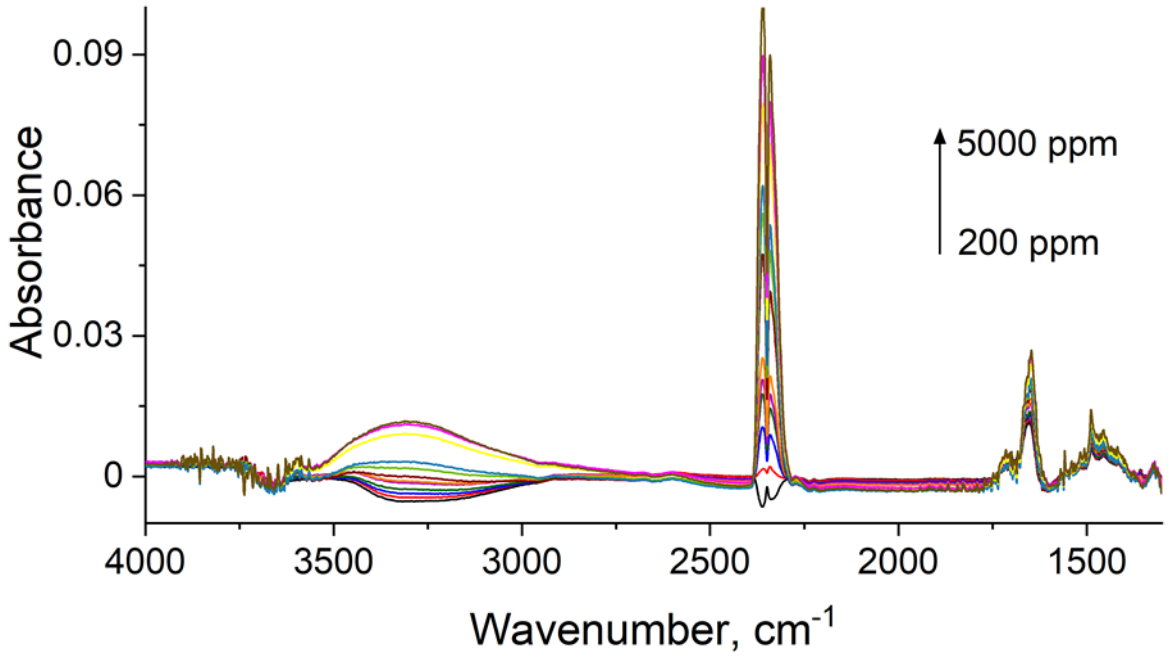

Figure **S15.** FTIR spectra of CO_2 detected by Sn-BEA: 200 ppm (black), 200-1000 ppm increments of 200 ppm, 1000-5000 ppm increments of 500 ppm.

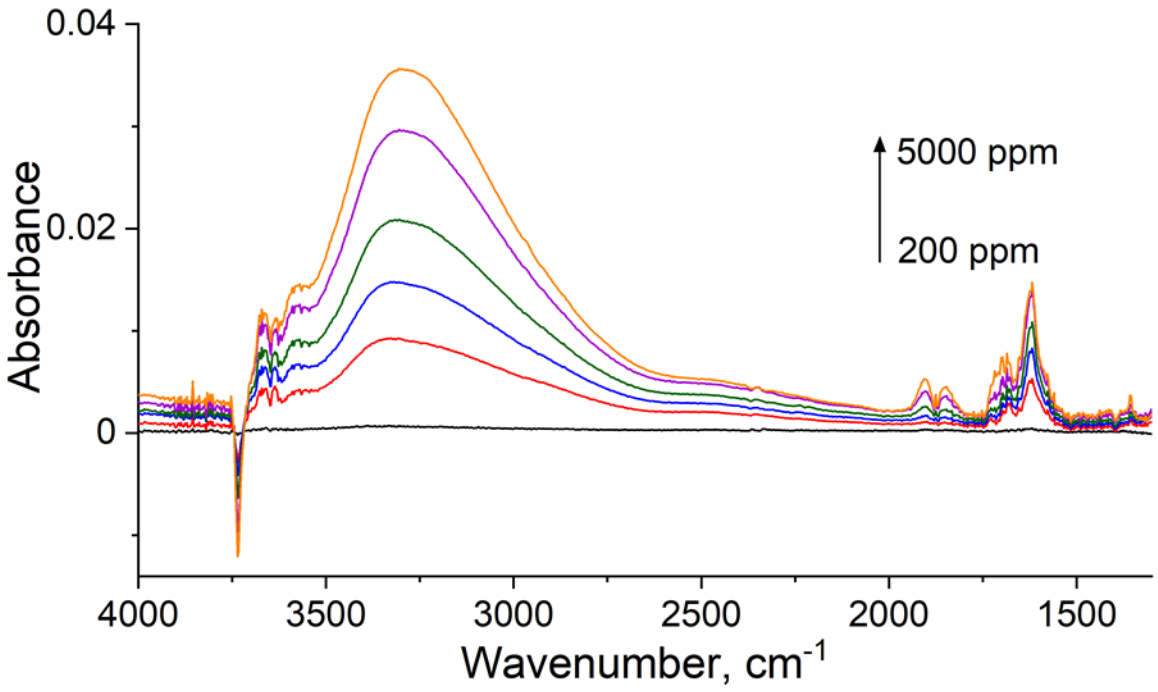

Figure **S16.** FTIR spectra of NO detected by Sn-BEA: 200 ppm (black), 400 ppm, 800 ppm, 1600 ppm, 3200 ppm, 5000 ppm.

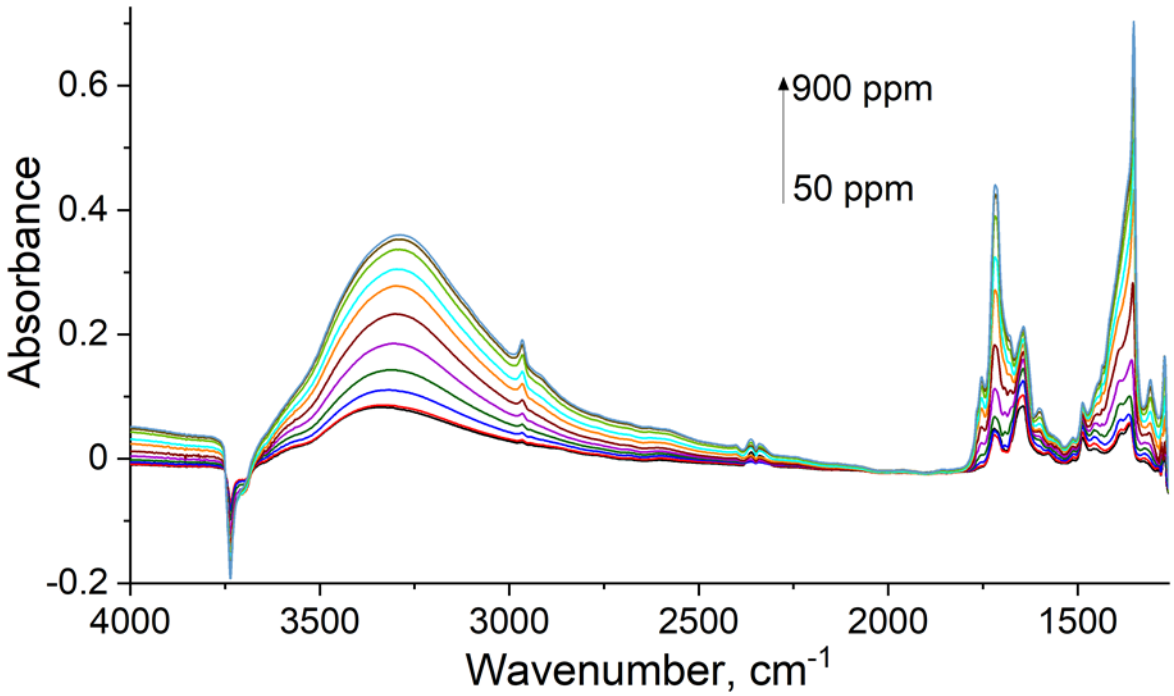

Figure **S17.** FTIR spectra of NO_2 detected by Sn-BEA: 50 ppm (black), 100-900 ppm increments of 100 ppm.

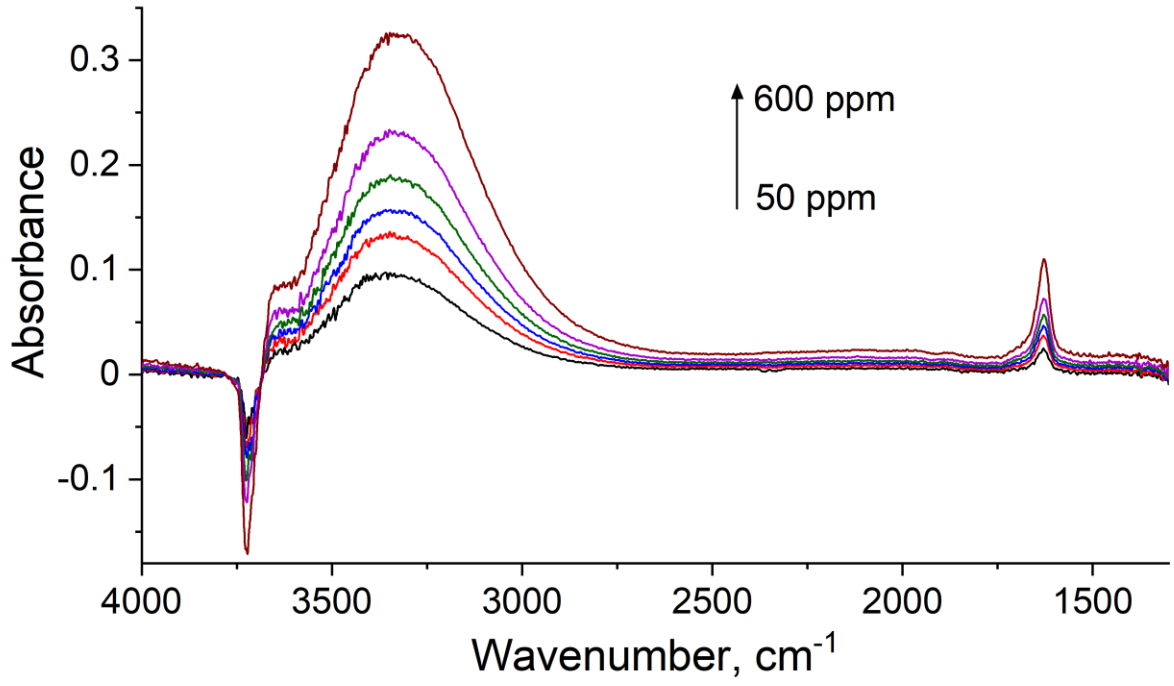

Figure **S18.** FTIR spectra of CO detected by DeAl-BEA: 50 ppm (black), 100 ppm, 200 ppm, 300 ppm, 400 ppm, 600 ppm.

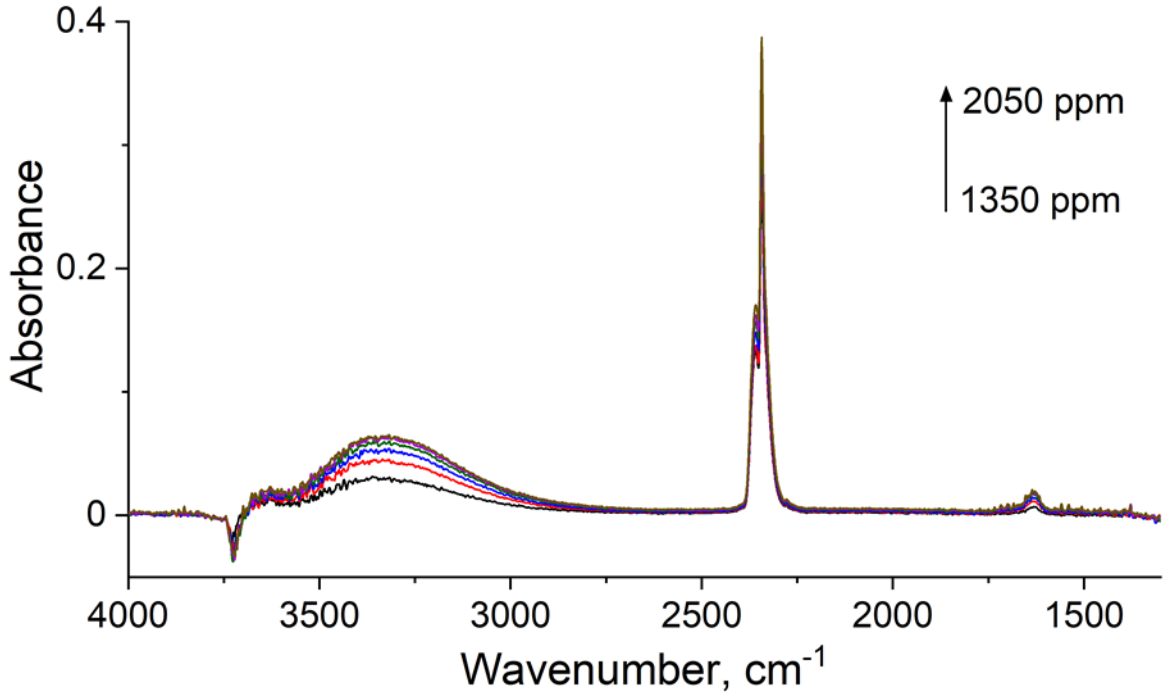

Figure **S19.** FTIR spectra of CO_2 detected by DeAl-BEA: 1350 ppm (black), increments of 150 ppm.

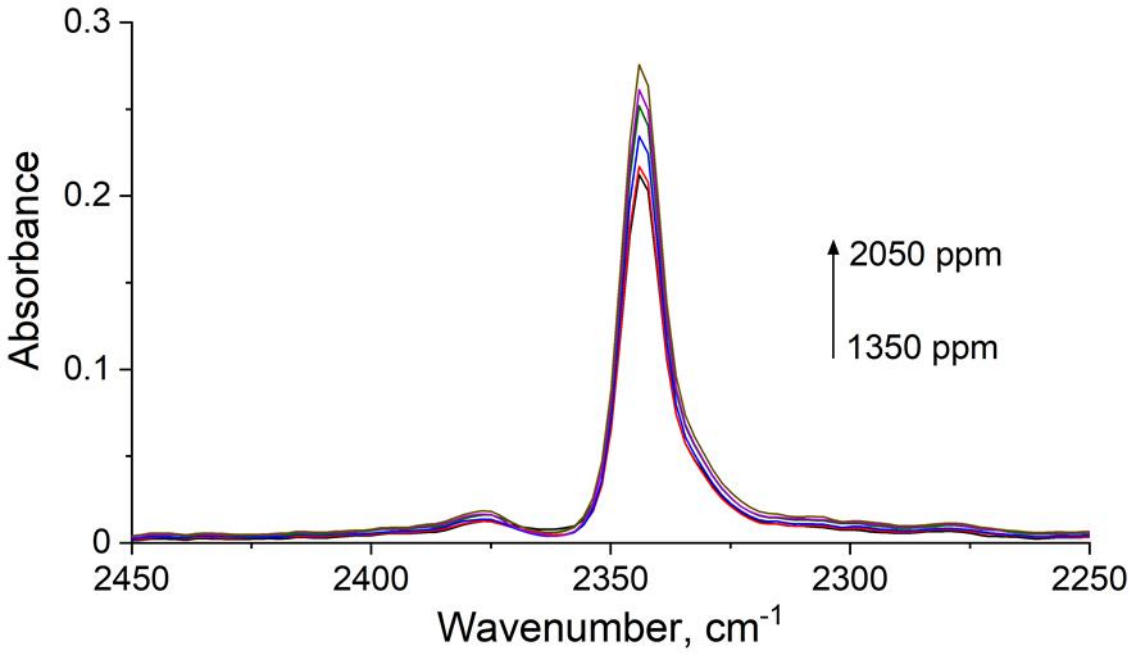

Figure **S20.** FTIR spectra of CO_2 detected by DeAl-BEA: zoomed in the 2450-2240 cm^{-1} region, 1350 ppm (black), increments of 150 ppm, CO_2 gas phase spectrum subtracted.

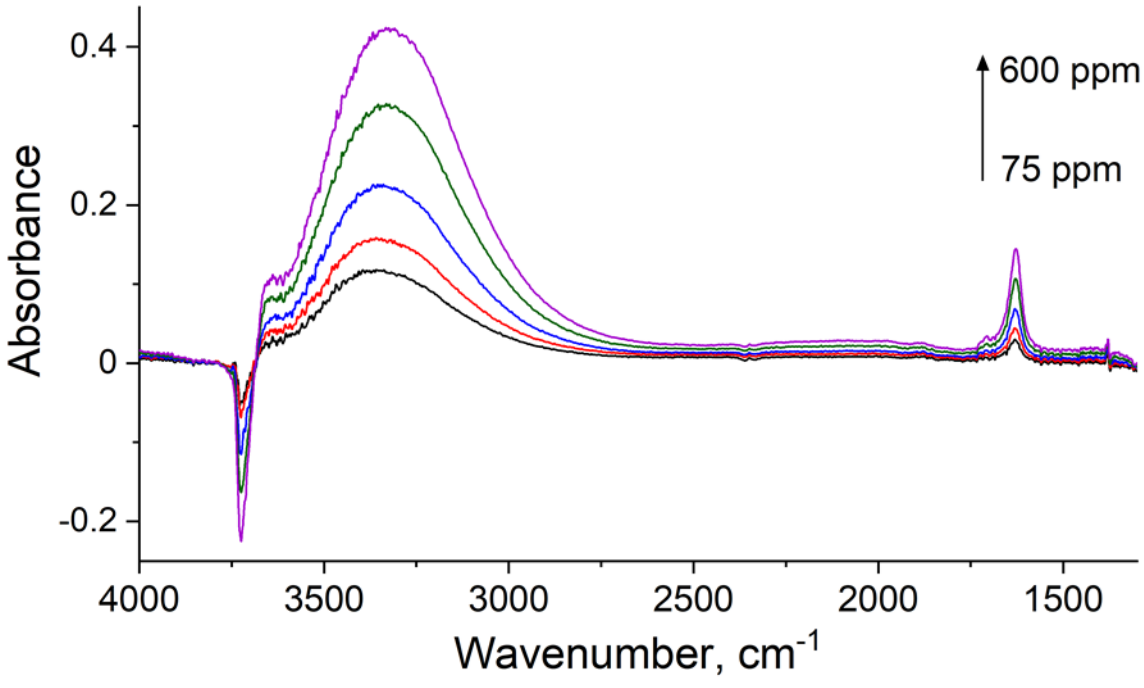

Figure **S21.** FTIR spectra NO detected by DeAl-BEA: 75 ppm (black), 100 ppm, 200 ppm, 400 ppm, 600 ppm.

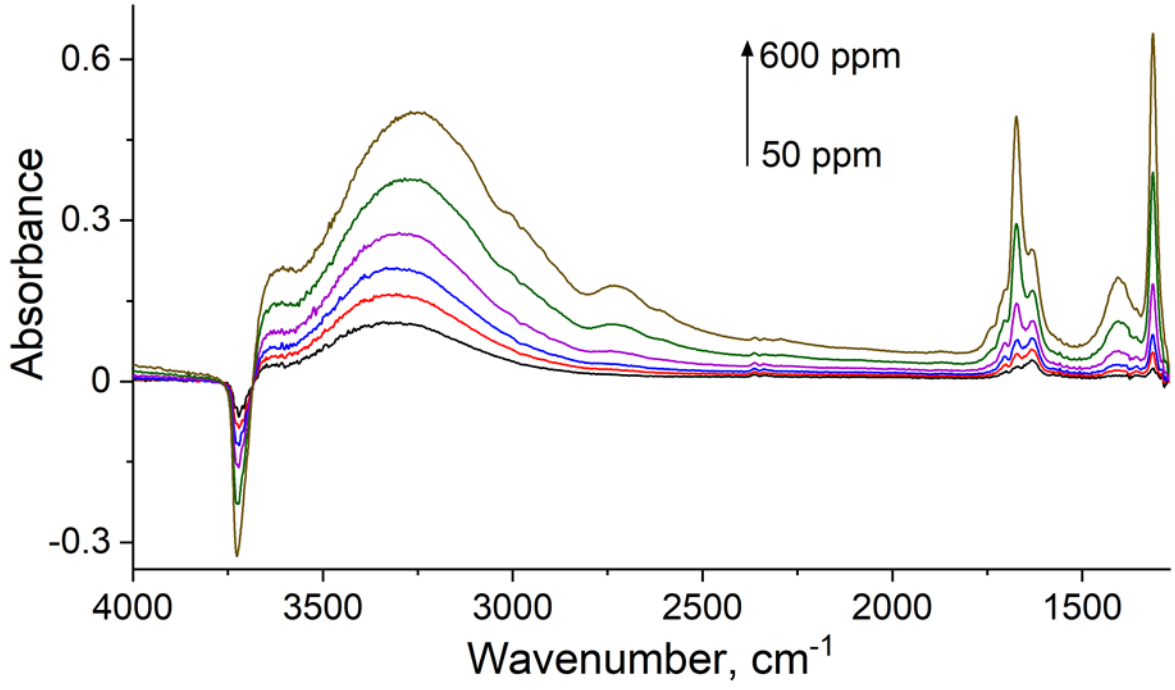

Figure **S22.** FTIR spectra of NO_2 detected by DeAl-BEA: 50 ppm (black), 75 ppm, 100 ppm, 200 ppm, 400 ppm, 600 ppm.

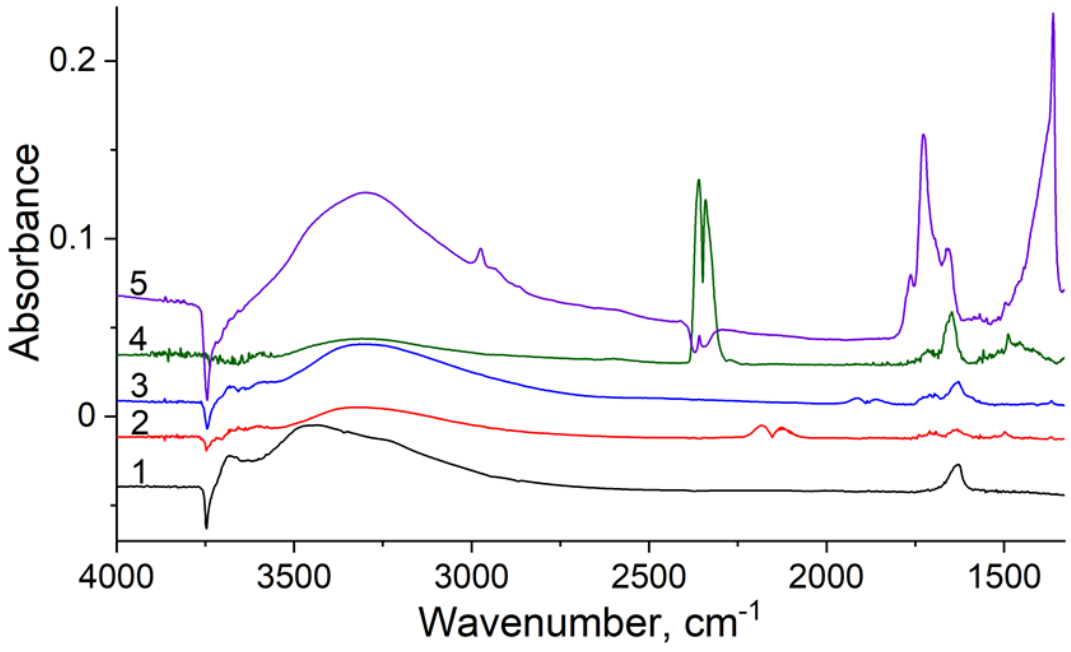

Figure **S23.** FTIR spectra of 5000 ppm of H_2O (1), 5000 ppm of CO (2), 5000 ppm of NO (3), 5000 ppm of CO_2 (4) and 900 ppm of NO_2 (5) adsorbed on Sn-BEA, all the spectra are offset and spectrum 1 is multiplied by a factor of 0.1 for clarity.

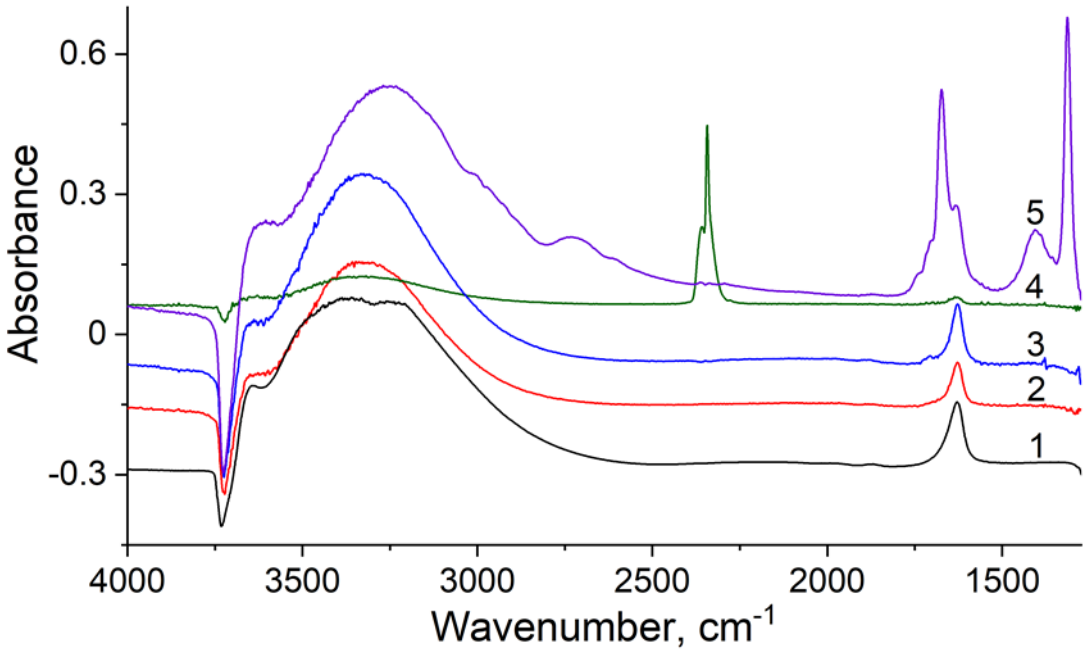

Figure **S24.** FTIR spectra of 5000 ppm of H_2O (1), 600 ppm of CO (2), 600 ppm of NO (3), 2050 ppm of CO_2 (4) and 600 ppm of NO_2 (5) adsorbed on DeAl-BEA, all the spectra are offset and spectrum 1 is multiplied by a factor of 0.1 for clarity.

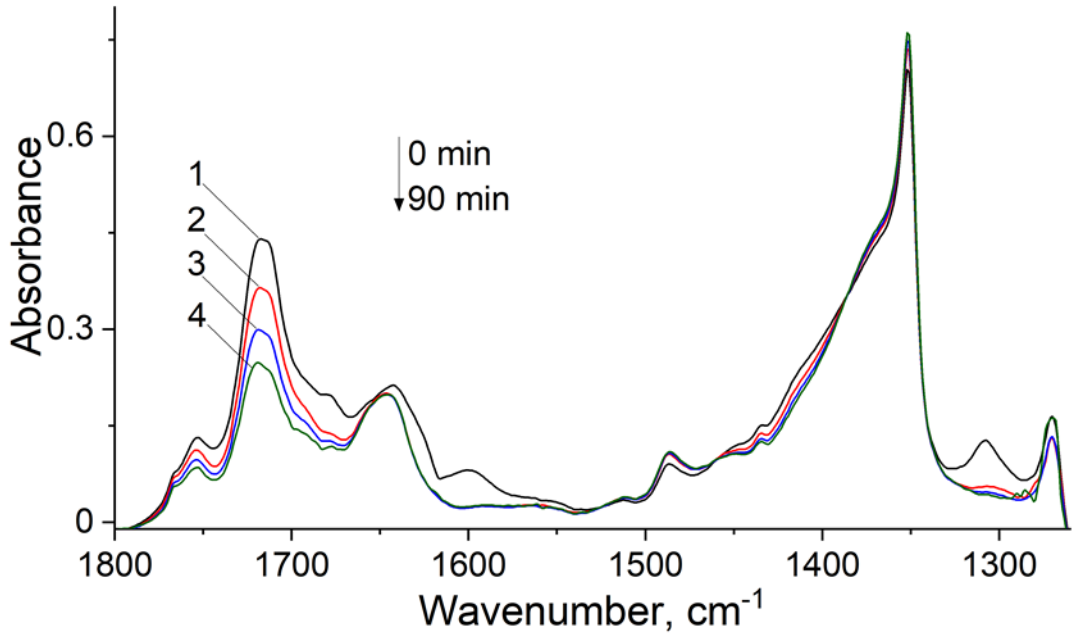

Figure **S25.** FTIR spectra of 900 ppm of NO_2 adsorbed on Sn-BEA (1), followed by desorption at room temperature for 30 min (2), 60 min (3) and 90 min (4).

References

38. Lewis, J. D., Ha, M., Luo, H., Faucher, A., Michaelis, V. K., Román-Leshkov, Y. & Románroman-Leshkov, Y. Distinguishing Active Site Identity in Sn-Beta Zeolites Using 31P MAS NMR of Adsorbed Trimethylphosphine Oxide. *ACS Catal.* **8,** 3076–3086 (2018).

53. Zheng, A., Liu, S.-B. & Deng, F. 31P NMR Chemical Shifts of Phosphorus Probes as Reliable and Practical Acidity Scales for Solid and Liquid Catalysts. *Chem. Rev.* **117,** 12475–12531 (2017).

52. Dubray, F., Moldovan, S., Kouvatas, C., Grand, J., Aquino, C., Barrier, N., Gilson, J.-P., Nesterenko, N., Minoux, D. & Mintova, S. Direct Evidence for Single Molybdenum Atoms Incorporated in the Framework of MFI Zeolite Nanocrystals. *J. Am. Chem. Soc.* **141,** 8689–8693 (2019).