NMR-Detected Host-Guest Proton Exchange as a Tool to Explore Surface/Volume Ratios and Fluid Filling of Internal and External Spaces of Porous Solids containing Surface-OH-Groups

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Supplementary Information

1. Sample Composition

The samples were initially characterized by the mass ratio $W = m_{\mathrm{MPz}}/m_{\mathrm{silica}}$, where m_{MPz} represents the mass in mg of 4-methylpyrazole (MPz) and m_{silica} the mass in mg of the silica used, MCM-41 or SBA-15. The molar ratios of the NH groups of MPz and of the SiOH groups of silica, $R = N_{\mathrm{NH}}/N_{\mathrm{OH}}$, were determined by ^{1}H MAS NMR as described in the main text. X_{NH} represents the mole fraction of the NH groups of MPz.

Table S1. Composition of 4-methylpyrazole (MPz) inside silica of the MCM-41 type and ^{1}H MAS Chemical Shifts δ at 398 K

$W = m_{\mathrm{MPz}}/m_{\mathrm{silica}}$	$R = N_{\mathrm{NH}}/N_{\mathrm{OH}}$	$X_{\mathrm{NH}} = R/(1+R)$	δ/ppm
0.000	0.00	0.00	1.7
0.006	0.01	0.01	1.9
0.010	0.05	0.05	3.3
0.014	0.02	0.02	2.7
0.019	0.04	0.04	3.2
0.020	0.08	0.07	3.9
0.029	0.10	0.09	4.1
0.039	0.18	0.15	4.8
0.049	0.19	0.16	5.4
0.058	0.18	0.15	5.6
0.066	0.32	0.24	6.7
0.078	0.22	0.18	6.1
0.085	0.30	0.23	6.9
0.097	0.25	0.20	6.7
0.114	0.24	0.19	7.1
0.131	0.37	0.27	6.9
0.203	0.48	0.32	8.0
0.211	0.41	0.29	7.8
0.221	0.50	0.33	8.3
0.240	0.41	0.29	8.2
0.264	0.61	0.38	8.2
0.293	0.60	0.37	7.8
0.335	0.54	0.35	8.5
0.379	0.68	0.40	9.0
0.427	1.02	0.50	9.5
0.446	1.28	0.56	10.1
			9.6
1.28	2.75	0.73	11.7
			11.8
			9.7
4.18	8.13	0.89	11.9
			12.0
$W = m_{\mathrm{MPz}}/m_{\mathrm{silica}}$	$R = N_{\mathrm{NH}}/N_{\mathrm{OH}}$	$X_{\mathrm{NH}} = R/(1+R)$	δ/ppm

Table S2. Composition of 4-methylpyrazole (MPz) inside silica of the SBA-15 type and ^{1}H MAS Chemical Shifts δ at 398 K

$W = m_{\mathrm{MPz}}/m_{\mathrm{silica}}$	$R = N_{\mathrm{NH}}/N_{\mathrm{OH}}$	$X_{\mathrm{NH}} = R/(1+R)$	δ/ppm
0.000	0.00	0.00	1.7
0.009	0.01	0.01	2.0
0.014	0.06	0.06	2.7
0.023	0.04	0.04	4.1
0.028	0.06	0.06	3.7
0.042	0.07	0.07	3.9
0.056	0.08	0.07	4.5
0.057	0.07	0.07	4.6
0.070	0.13	0.12	4.9
0.074	0.08	0.07	5.0
0.085	0.09	0.08	5.1
0.099	0.12	0.11	5.5
0.113	0.18	0.15	5.8
0.127	0.19	0.16	6.1
0.148	0.17	0.15	6.1
0.170	0.33	0.25	6.5
0.183	0.35	0.26	7.5
0.268	0.34	0.25	6.9
0.282	0.38	0.28	7.9
1.26	1.55	0.61	10.4 11.0
2.83	3.50	0.77	10.4 11.3 11.8

Figure S1. Selected single 90° pulse ^{1}H MAS NMR spectra at 398 K and 7 T of 4-methyl-*1H*-pyrazole in MCM-41.

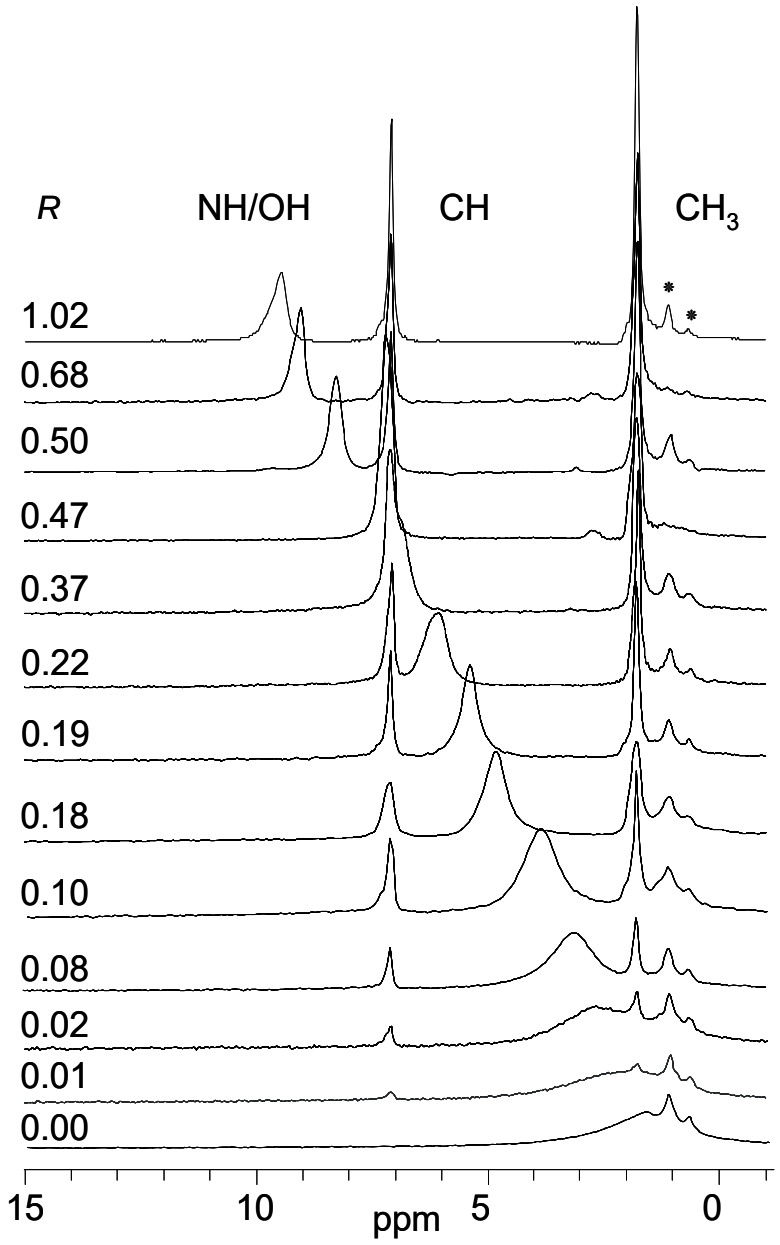

Figure S2. Selected single 90° pulse ^{1}H MAS NMR spectra at 398 K and 7 T of 4-methyl-*1H* -pyrazole in SBA-15.

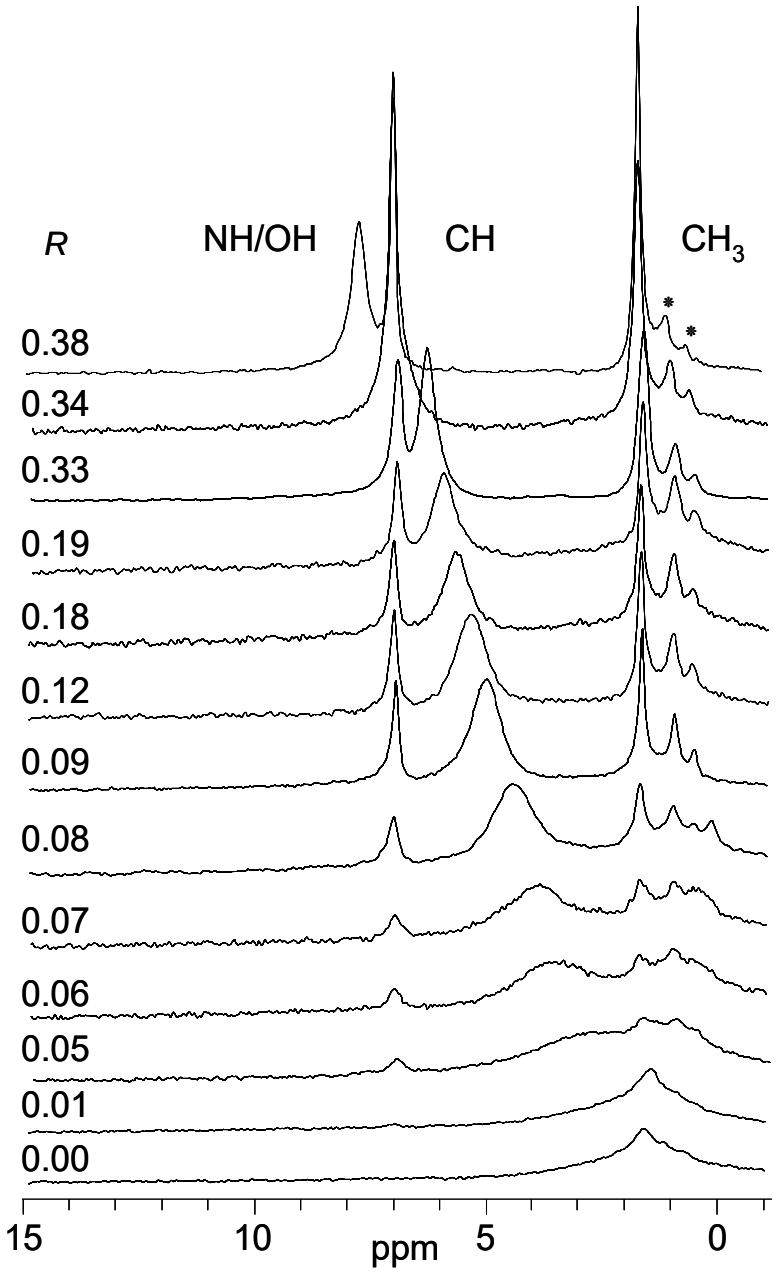

Figure S3. Density of neat 4-methyl-pyrazole at different temperatures according to the Data of Table 3.