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Enthalpy–Entropy Correlation for Hydrogen Adsorption on MOFs: Variable-Temperature FTIR Study of Hydrogen Adsorption on MIL-100(Cr) and MIL-101(Cr)

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The thermodynamics of hydrogen interaction with the coordinatively unsaturated Cr^{III} cationic sites in the metal–organic frameworks MIL-100(Cr) and MIL-101(Cr) was studied by variable-temperature infrared (VTIR) spectroscopy. Simultaneous measurement of the equilibrium pressure of hydrogen and the integrated IR absorbance over the temperature range 79–105 K led to the determination of the corresponding values of standard adsorption enthalpy (ΔH^0) and entropy (ΔS^0). For MIL-100(Cr) these values were ΔH^0 = –6.9 kJ mol^{-1} and ΔS^0 = –80 J mol^{-1} K^{-1}, whereas for MIL-101(Cr) the values ΔH^0 = –9.5 kJ mol^{-1} and ΔS^0 = –112 J mol^{-1} K^{-1} were obtained. These thermodynamic quantities show a positive correlation between ΔH^0 and ΔS^0, which is analyzed in the broader context of the corresponding data available for hydrogen adsorption on other two MOFs and also on several cation-exchanged zeolites. The implications for hydrogen storage and delivery by using MOFs are discussed.

Introduction

By and large, the search for materials capable of hydrogen storage by physical adsorption focuses mainly on porous carbons and metal–organic frameworks (MOFs).[1] The latter have the advantage of showing a large variety of chemical compositions and framework structure types, which, in principle, should facilitate the intelligent design of chemical synthesis of compounds aimed at optimizing hydrogen storage and delivery.[2–12] In general terms, MOFs are obtained by joining metal cations (or cationic clusters) with organic linkers, which results in structures (amenable to rational design) that show permanent porosity, large internal surface area and low density. While these are required properties for high gravimetric hydrogen uptake at low temperature,[13,14] a relatively high binding affinity for hydrogen is also needed when hydrogen storage at (or near) ambient temperature is sought. Strategies for increasing the gas–solid interaction energy include creation of coordinatively unsaturated (open) metal cation sites in the framework[15–18] and doping of (functionalized) MOFs with alkali or alkaline-earth metal cations.[19–23]

Extensive experimental work, summarized in several recent reviews,[24–28] shows that the adsorption enthalpy of molecular hydrogen on MOFs not having unsaturated metal cations tends to be in the range –4 to –6 kJ mol^{-1}, which is too small for relevant uptake near ambient temperature. However, when open metal cation centres can be generated by removal of coordinated solvent molecules that act as terminal ligands, ΔH^0 is significantly increased; values in the range –9 to –13 kJ mol^{-1} were reported in those cases.[6,29–34] While these larger ΔH^0 values are more promising, one should keep in mind that the thermodynamics of hydrogen uptake and release is actually ruled by the combined effect of adsorption enthalpy and entropy, and not by ΔH^0 alone. Moreover, these two thermodynamic quantities were clearly shown to be related for the case of hydrogen adsorption on cation-exchanged zeolites,[35] and very recent experimental results suggest that the same applies to localized hydrogen adsorption on MOFs.[34]

With the aim to gain further insight on the role of the correlation between standard adsorption enthalpy and entropy, we report herein on variable-temperature infrared (VTIR)[36,37] spectroscopic studies on hydrogen adsorption on MIL-100(Cr) and MIL-101(Cr), which are MOFs having open metal (Cr^{III}) cations. ΔH^0 and ΔS^0 values are reported for both cases, the results are discussed in the broader context of available literature data, and the implications for hydrogen storage and delivery by using MOFs are highlighted.

Results and Discussion

MIL-100(Cr) and MIL-101(Cr) are mesoporous MOFs that have the chemical composition $Cr^{III}OF_x(OH)_{1-x}(H_2O)_y\{C_6H_3(CO_2)_3\}zH_2O$ ($y + z \approx 28$) and $Cr_3F(H_2O)O\{(O_2C)C_6H_4(CO_2)\}_3nH_2O$ ($n \approx 25$), respectively. Both are Cr^{III} carboxylates built from trimers of chromium octahedra sharing a common oxygen atom and are linked to-

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gether by either trimesate (MIL-100) or terephthalate (MIL-101) rigid ligands. There is one excess positive electric charge per trimer, which is compensated by either a fluoride anion, in MIL-101, or by a variable ratio of (F^-, OH^-) in MIL-100. Note also that there is a terminal H_2O ligand that can be removed in both cases by appropriate thermal treatment to leave an open (coordinatively unsaturated) cationic site. After solvent removal, the framework structure (which is cubic in both cases) shows empty cages having a free diameter in the range 2.9 to 3.4 nm, which are accessible through a window of 0.55 and 0.86 nm (MIL-100) and 1.2 and 1.6 nm (MIL-101). Further details on these structures can be found elsewhere.[29,38,39] The internal surface area (Langmuir) was reported to be as large as 3100 and 5900 $m^2 g^{-1}$ for MIL-100(Cr) and MIL-101(Cr), respectively,[29,39] which, in principle, could render these materials good candidates for hydrogen storage.

For IR spectroscopy, thin, self-supported wafers of the MOF samples were prepared and thermally activated (degassed) inside a home-made cryogenic IR cell[40,41] that allowed us to carry out: (1) in situ sample activation, (2) hydrogen dosage and (3) VTIR spectroscopy of adsorbed hydrogen while simultaneously recording the temperature and equilibrium pressure inside the cell. Once dosed with hydrogen, the cell was closed, and a series of IR spectra was taken at fixed temperature values in the range 79–105 K.

Representative VTIR spectra (in the H–H stretching region) of hydrogen adsorbed on MIL-100(Cr) are shown in Figure 1. A single H–H stretching band is seen, centred at 4050 cm^{-1}, which is assigned to H_2 molecules interacting with the Cr^{III} cationic centres in the framework of MIL-100(Cr). Polarization of the H_2 molecule by the cationic centre renders the H–H stretching mode IR active and brings about a bathochromic shift from the gas phase value (4163 cm^{-1}) of the Raman-active H–H stretching mode of the free H_2 molecule, a fact that is widely documented for localized H_2 adsorption on both zeolites[42–44] and MOFs.[6,34] Note, however, that, in general terms, the magnitude of the bathochromic shift cannot be directly correlated with the polarization power of the cation, since it is known to depend critically on the actual structure of the hydrogen adsorption complex.[45–49] Representative VTIR spectra of dihydrogen adsorbed on MIL-101(Cr) are depicted in Figure 2. Again, a single IR absorption band appears, centred at 4066 cm^{-1}, which comes from the H–H stretching mode of H_2 interacting with the cationic adsorbing centres in the MIL-101(Cr) framework.

From the integrated absorbance of IR spectra recorded over a temperature range while simultaneously recording temperature (T) and equilibrium pressure (p) inside a closed IR cell, the standard adsorption enthalpy, ΔH^0, and entropy, ΔS^0, involved in the hydrogen adsorption process can be determined by following the VTIR method discussed in detail elsewhere.[36,50] In essence, at any given temperature, the integrated intensity, A, of the corresponding IR absorption band should be proportional to the surface coverage, θ, thus informing on the activity (in the thermodynamic sense) of both the adsorbed species and the empty adsorption sites, $1 - \theta$. Simultaneously, the equilibrium pressure provides similar information for the gas phase. Therefore, the corresponding equilibrium constant, K, can be determined, and the variation of K with temperature yields the corresponding values of ΔH^0 and ΔS^0. Assuming Langmuir-type adsorption, Equation (1) can be written:

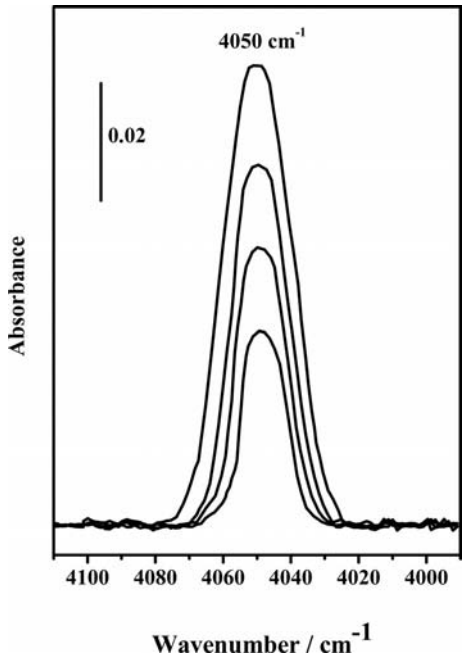

Figure 1. Representative VTIR spectra (MOF blank subtracted) of H_2 adsorbed on MIL-100(Cr). From top to bottom the temperature goes from 87 to 118 K and the equilibrium pressure from 0.51 to 0.97 mbar.

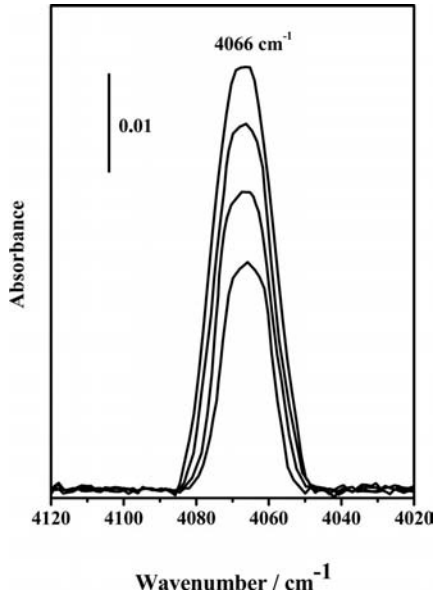

Figure 2. Representative VTIR spectra (MOF blank subtracted) of H_2 adsorbed on MIL-101(Cr). From top to bottom the temperature goes from 78 to 89 K and the equilibrium pressure from 3.42 to 3.83 mbar.

$$\theta = A/A_M = K(T)p/[1 + K(T)p] \quad (1)$$

where A_M is the integrated intensity corresponding to full coverage ($\theta = 1$). Combination of Equation (1) with the well-known van 't Hoff equation [Equation (2)] yields Equation (3).

$$K(T) = \exp(-\Delta H^0/RT)\exp(\Delta S^0/R) \quad (2)$$

$$\ln[A/(A_M - A)p] = (-\Delta H^0/RT) + (\Delta S^0/R) \quad (3)$$

from which ΔH^0 and ΔS^0 can be obtained.

Figure 3 depicts the plot of the left-hand side of Equation (3) against the reciprocal of the temperature obtained from the whole set of VTIR spectra recorded for hydrogen adsorbed on MIL-100(Cr) (Figure 3a) and on MIL-101(Cr) (Figure 3b). They correspond to a coverage range, θ, spanning (approximately) 0.3 to 0.9. From the straight lines obtained, the corresponding values of standard adsorption enthalpy and entropy were calculated to be ΔH^0 = –6.9 kJ mol^{-1} and ΔS^0 = –80 J mol^{-1} K^{-1} for MIL-100(Cr), and ΔH^0 = –9.5 kJ mol^{-1} and ΔS^0 = –112 J mol^{-1} K^{-1} for MIL-101(Cr). Estimated error limits are ± 1 kJ mol^{-1} for enthalpy and ± 10 J mol^{-1} K^{-1} for entropy. Within error limits, the ΔH^0 values reported herein coincide with those determined, by microcalorimetric measurement at a low coverage, by Latroche et al.,[51] who give a ΔH^0 value in the range –5.6 to –6.3 kJ mol^{-1} for dihydrogen on MIL-100(Cr), and –9.3 to –10 kJ mol^{-1} on MIL-101(Cr). No corresponding values of ΔS^0 were reported.

Our results show that, referring to absolute values, ΔS^0 increases in parallel with ΔH^0. This positive correlation should be analyzed in the broader context of previously reported data for hydrogen adsorption on cation-exchanged zeolites[52–55] and on MOFs having coordinatively unsaturated metal cations.[34] For this purpose, the relevant data are summarized in Table 1. Note that, while there is a wealth of reported data for zeolites, experimentally determined data of ΔS^0 were previously reported for only two MOFs: CPO-27-Mg and CPO-27-Co (also termed Mg-MOF-74 and Co-MOF-74).[34]

Data summarized in Table 1 show compelling evidence that hydrogen adsorption on MOFs having open cation sites follows (approximately) the same positive correlation between ΔH^0 and ΔS^0 previously found for zeolites.[35,56] Reasons for such a correlation, which were discussed in more detail elsewhere,[35] can be summarized in the argument that the stronger the interaction between H_2 molecules and the adsorbing centre is, the greater will be the corresponding decrease of motion freedom, which results in an increasing order of the system. Hence, referring to absolute values, a greater ΔH^0 will result in a correspondingly greater ΔS^0. In fact, a positive correlation between ΔH^0 and ΔS^0 (sometimes referred to as entropy–enthalpy compensation) was also reported several times in the literature for a range of chemical processes involving weak interaction forces; among them are formation of weakly associated molecular complexes,[57,58] weak hydrogen bonding[59,60] and Langmuir-type adsorption from solution.[59] Regarding localized hydrogen adsorption in zeolites and MOFs, further insight can be obtained by plotting ΔH^0 against ΔS^0, as

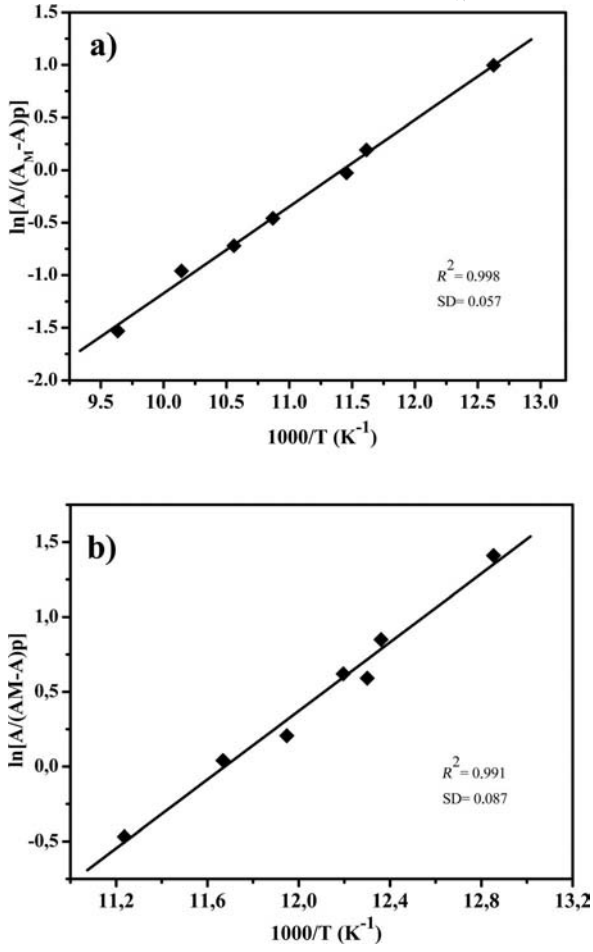

Figure 3. Plot of the left-hand side of Equation (3) against the reciprocal of the temperature for hydrogen adsorption on (a) MIL-100(Cr) and (b) MIL-101(Cr). R is the linear regression coefficient and SD is the standard deviation.

Table 1. Thermodynamic data for hydrogen adsorption on several zeolites and MOFs having coordinatively unsaturated metal cations. Error limits for ΔH^0 and ΔS^0 are ±1 kJ mol^{-1} and ±10 J mol^{-1} K^{-1}, respectively.

Adsorbent	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta S^{0[a]}$ (J mol^{-1} K^{-1})	Ref.
MIL-100(Cr)	6.9	80	this work
MIL-101(Cr)	9.5	112	this work
CPO-27-Mg	9.4	120	[34]
CPO-27-Co	11.2	130	[34]
(Mg,Na)-Y	18	136	[44]
(Ca,Na)-Y	15	127	[54]
Ca-X	12.5	118	[54]
Mg-X	13	114	[48]
Li-FER	4.1	57	[46]
Na-FER	6	78	[53]
K-FER	3.5	57	[53]
Li-ZSM-5	6.5	90	[55]
Na-ZSM-5	10.3	121	[52]

[a] Referred to a standard state at 1 Torr (1.32 mb). Within the perfect gas approximation, ΔS^0 changes by +55 J mol^{-1} K^{-1} when referred to a standard state at 1 bar.[35]

depicted in Figure 4. Although some experimentally determined points show small deviations (and data for some more MOFs would be desirable), Figure 4 clearly shows that enthalpy–entropy correlation does not follow a straight line, but a distinctively concave curve; showing that the rate of entropy change gradually decreases as ΔH^0 increases more and more. The reason for this trend is that, since the adsorbed dihydrogen molecules cannot lose more than all of their degrees of freedom of motion, ΔS^0 has an inherent limit, whereas (in principle) ΔH^0 has no definite limit. At this point, it should be noted that the ΔS^0 values quoted in Table 1 (and plotted in Figure 4) are referred to a standard state at 1 Torr (1.32 mbar) and 100 K, which are representative of the temperature and pressure at which IR spectra were obtained. Therefore, the limiting value of ΔS^0 applicable to data reported in Figure 4 is the entropy content of 1 mol of hydrogen at 1 Torr and 100 K, which amounts to (approximately)[56] 180 J mol^{-1} K^{-1}. However, that limit is not reached in the adsorption process, because some rotational and vibrational freedom (against the adsorption site) remains in the adsorbed state,[43,61,62] and that is why the concave curve in Figure 4 steeply rises in its upper part. Worthy of note is that a similar phenomenon was reported in the literature for several weak molecular association processes.[63,64]

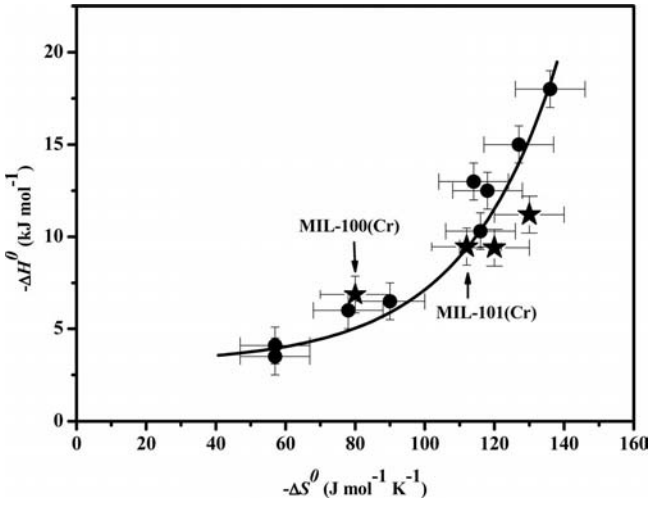

Figure 4. Standard adsorption enthalpy vs. entropy for hydrogen adsorption on cation-exchanged zeolites (circles) and on MOFs having open cation sites (stars). Data taken from Table 1.

Enthalpy–entropy correlation, as shown herein for hydrogen adsorption on MOFs, has an important consequence for hydrogen storage in these materials. With a focus on porous carbons, and following standard thermodynamics, Bhatia and Myers[65] derived Equation (4).

$$\Delta H^0_{opt} = T\Delta S^0 + [(RT/2)\ln(P_1P_2/P_0^2)] \quad (4)$$

This equation gives the optimum value of adsorption enthalpy (ΔH^0_{opt}) for maximum hydrogen storage and delivery as a function of temperature (T) and adsorption entropy (ΔS^0), P_0 being the standard pressure value to which ΔS^0 is referred (1 bar), P_1 the hydrogen loading pressure and P_2 the exhaust pressure; meaning that Equation (4) applies to hydrogen storage/delivery cycles between pressures P_1 and P_2 at a temperature T. Assuming P_1 = 30 bar and P_2 = 1.5 bar as reasonable values, and taking ΔS^0 = –66.5 J mol^{-1} K^{-1} as a representative value of entropy change, Equation (4) yields ΔH^0 = –15.1 kJ mol^{-1} for T = 298 K. Such a value of ΔH^0 is very often taken to be the target to pursue when seeking porous materials for hydrogen storage at ambient temperature. It should be noted, however, that, although the value ΔS^0 = –66.5 J mol^{-1} K^{-1} can represent a good approximation for the case of carbons and other adsorbents showing only weak (nonlocalized) hydrogen adsorption, the situation changes very significantly in the case of MOFs (and other adsorbents) showing stronger (localized) interaction with adsorbed hydrogen. Correct application of Equation (4) to the latter case implies the use of the actual value of ΔS^0 (instead of –66.5 J mol^{-1} K^{-1}); and that will raise ΔH^0_{opt} well over the frequently quoted target of –15.1 kJ mol^{-1}. Extrapolation of the curve in Figure 4 suggests that a ΔH^0_{opt} value in the range of about –22 to –25 kJ mol^{-1} would be needed for optimum hydrogen storage/delivery cycles between 30 and 1.5 bar at ambient temperature. Further evidence that this is so can be found in a recent report by Bae and Snurr, who studied hydrogen adsorption on several MOFs having open metal cations by the grand canonical Monte Carlo simulation.[66] Not only did they find a positive correlation between Q_{st} and ΔS^0, but also that the optimum value of Q_{st} is in the range 18.2–22 kJ mol^{-1} for hydrogen storage/delivery cycles between 120 and 1.5 bar at ambient temperature. When the different pressure range is taken into account, the Q_{st} range given by Bae and Snurr practically coincides with the foregoing optimum ΔH^0 range derived from our experimental measurements.

Finally, we wish to remark that the ΔH^0 values reported herein for hydrogen adsorption on MIL-100(Cr) and MIL-101(Cr), and likewise all of the others summarized in Table 1, correspond to a very low hydrogen uptake; $\theta < 1$, θ = 1 being the value of monolayer coverage of the sites showing localized H_2 adsorption. It is true that MOFs and other porous materials having large cavities can adsorb (under adequate pressure) large amounts of hydrogen; but most of that corresponds to molecules that, not being in contact with relatively strong adsorption sites, would show a small ΔH^0 value (about 4–6 kJ mol^{-1}), which is too small for hydrogen storage at (or near to) ambient temperature. As already suggested elsewhere,[1,67] what would work best is a large void volume made up of narrow pores. Ideally, all adsorbed molecules should interact directly with adsorbing centres located either in the pore wall or at the external surface of the (porous) crystal. Actually, these two strategies do not mutually exclude each other. Synthesis of MOFs, or other suitable (porous) materials, composed of nanosized crystals would result in a large increase of external surface area, which could create more coordinatively unsaturated cationic sites and also facilitate fast hydrogen diffusion into narrow pores.

Conclusions

Hydrogen adsorption (at low temperature) on the metal–organic frameworks MIL-100(Cr) and MIL-101(Cr) was studied by VTIR spectroscopy. The results show that, for localized H_2 adsorption giving rise to the corresponding IR absorption bands, the standard adsorption enthalpy (ΔH^0) has the value of –6.9 and –9.5 kJ mol^{-1} for MIL-100(Cr) and MIL-101(Cr), respectively. The corresponding values for the entropy change are –80 and –112 J mol^{-1} K^{-1}. These values of thermodynamic quantities show a positive correlation between ΔH^0 and ΔS^0, similar to that previously found for hydrogen adsorption on several cation exchanged zeolites, and also on the MOFs CPO-27-Mg and CPO-27-Co. The implications of such an enthalpy–entropy correlation for hydrogen storage and delivery by using MOFs are discussed. In particular, it is argued that the optimum value of ΔH^0 for storage/delivery cycles at ambient temperature (in the pressure range 30 to 1.5 bar) is likely to fall in the range –22 to –25 kJ mol^{-1}, which is significantly different from the often quoted value of ΔH^0_{opt} = –15.1 kJ mol^{-1}.

Experimental Section

The MIL-100(Cr) and MIL-101(Cr) samples used were synthesized at 493 K under hydrothermal conditions by following the procedure described by Férey et al.[29,39,68] and checked by powder X-ray diffraction. VTIR spectroscopy was carried out by using a home-made IR cell that was equipped with a platinum resistance thermometer (Tinsley) and a capacitance pressure gauge (MKS, Baratron). The accuracy of temperature and pressure measurements was ±2 K and ±10^{-4} Torr, respectively.[69] For IR measurements, a thin, self-supported wafer of the MOF sample was prepared and activated (degassed) inside the IR cell under a dynamic vacuum (residual pressure less than 10^{-4} Torr) at 400 K for 10 h, followed by degassing at 553 K for 5 h. The cell was then dosed with hydrogen and closed, and transmission FTIR spectra were recorded at several fixed temperature values (within the range 79–105 K) while simultaneously registering the hydrogen pressure inside the cell. A Bruker IFS66 spectrometer was used, working at 3 cm^{-1} resolution.

Acknowledgments

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