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Number of metallic clusters in Y zeolites obtained from ^{129}Xe NMR

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We present a simple model which permits to obtain the number of metallic clusters entrapped in Y zeolites from the curves of the chemical shifts of ^{129}Xe NMR against the pressure of Xe. From the metal loading the average number of atoms per cluster can also be calculated. We apply the model to Pt/NaY and the bimetallic Pt–Cu/NaY.

Keywords: ^{129}Xe NMR; Pt clusters in NaY; Pt–Cu bimetallic clusters in NaY

1. Introduction

The NMR chemical shift of ^{129}Xe adsorbed on zeolites is helpful to determine parameters such as the void volume, acidity, nature of cations, metal particles, effects of chemisorption on these, and coke deposits. The technique was originally introduced by Fraissard and co-workers [1,2].

Recent work on the subject [3,4] has lead to the conclusion that the Xe atoms sample many crystallites on the NMR timescale rather than merely a few supercages as was previously assumed [1,2].

Xe exchanges very rapidly between supported metal clusters in large cavities, the cage walls and adjacent zeolite crystals. As a result of this fast exchange only a single NMR line is obtained. Taking Pt/NaY as an example the chemical shift δ in ^{129}Xe NMR can approximately be written in terms of the chemical shifts of

Xe on the metal cluster, δ_{Pt}, and on the zeolite wall, δ_{NaY}, and the relative amounts of Xe in the different positions, $N_{\mathrm{Xe-Pt}}$ and $N_{\mathrm{Xe-NaY}}$ respectively [5,6],

$$\delta(\delta_{\mathrm{Pt}} N_{\mathrm{Xe-Pt}} + \delta_{\mathrm{NaY}} N_{\mathrm{Xe-NaY}})/N_{\mathrm{Xe}}. \tag{1}$$

In eq. (1) N_{Xe} represents the total amount of adsorbed Xe given by

$$N_{\mathrm{Xe}} = N_{\mathrm{Xe-Pt}} + N_{\mathrm{Xe-NaY}}. \tag{2}$$

(Note that in the case of Pt–Cu bimetallic particles δ_{Pt} and $N_{\mathrm{Xe-Pt}}$ are replaced by δ_{PtCu} and $N_{\mathrm{Xe-PtCu}}$, respectively.) Ryoo [5] suggested that the relative amounts $N_{\mathrm{Xe-Pt}}$ and $N_{\mathrm{Xe-NaY}}$ can be obtained from the Xe adsorption isotherms.

The aim of this letter is to present a simple model to calculate the number of metal clusters per supercage from the ^{129}Xe NMR chemical shift as a function of the Xe pressure. As we will see the model can explain in a very simple way the trend of these curves. Fraissard and co-workers have demonstrated that the Xe chemical shift is sensitive to the concentration and size of the clusters [2]. However, their analysis is based on the variation of the Xe chemical shift as a function of the amount of chemisorbed hydrogen on the metal particles. To apply our model we do not need to study the evolution of the Xe chemical shift as a function of chemisorbed hydrogen and therefore we think that our model is an improvement with respect to Fraissard's method. In the following discussion we consider literature data on Xe isotherms and ^{129}Xe NMR chemical shift at room temperature [1–6]. The systems considerated are NaY, Pt/NaY and Pt–Cu/NaY for which considerable information has previously been obtained with different chemical and physical probes [6–9].

2. Xe adsorption isotherms

Xe adsorption isotherms at room temperature on pure NaY were reported by Tway and Apple [3]. They also showed that the chemical shift of ^{129}Xe NMR and the Xe uptake versus pressure for NaY zeolites do not depend on the crystallite aggregate sizes.

Ryoo and co-workers [5,6] reported Xe adsorption isotherms at room temperature on different Pt_x/NaY and $\mathrm{Pt}_x\mathrm{Cu}_y$/NaY samples. Here x and y represent the metal loading as number of atoms per supercage. (Note that $8x$ and $8y$ represent the metal loading as number of Pt and Cu atoms per unit cell, respectively.) The samples investigated were: $\mathrm{Pt}_{0.89}$/NaY, $\mathrm{Pt}_{0.44}$/NaY, $\mathrm{Pt}_{0.18}$/NaY and $\mathrm{Pt}_{0.89}\mathrm{Cu}_{0.89}$/NaY. Xe isotherms on the sample $\mathrm{Pt}_{0.89}$/NaY were also measured after chemisorption of O_2 and H_2. The sample $\mathrm{Pt}_{0.89}\mathrm{Cu}_{0.89}$/NaY was also investigated after chemisorption of O_2.

Ryoo [5] suggested that the Xe isotherms can be rationalized as the sum of two Langmuir adsorption isotherms: one for weak adsorption on the zeolite and the other for strong adsorption on the metal clusters. According to Ryoo the number of Xe atoms adsorbed per supercage in the Pt/NaY catalysts can be written as

$$N_{Xe} = N_{Pt} wbp/(1+bp) + (1 - N_{Pt}) zap/(1+ap). \tag{3}$$

A similar expression can be written for the Pt_xCu_y/NaY catalysts. In the above equation N_{Pt} represents the fraction of supercages containing a metal cluster (number of clusters per supercage, a number between 0 and 1), $N_{NaY} = (1 - N_{Pt})$ represents the fraction of empty supercages, w represents the total number of Xe atom adsorbed on a metal cluster, and z represents the maximum number of Xe atoms that can fit an empty supercage at very high pressure. Note that w will be the maximum number of Xe atoms that can contact the surface of the metal cluster and therefore it will depend on the size and shape of the cluster. We consider $w = 4$ because the supercage has 4 windows and only one Xe atom of 4.3 Å size can be in contact with the cluster through a supercage aperture of 7.4 Å in diameter. As $bp \gg 1$ for $p_{Xe} \geqslant 50$ Torr [5,6], but $ap \ll 1$ for $p_{Xe} \leqslant 400$ Torr [3], we can write

$$N_{Xe} = N_{Pt} 4 + (1 - N_{Pt}) zap. \tag{4}$$

In the case of the pure NaY system ($N_{Pt} = 0$) we obtain

$$N_{Xe} = zap. \tag{5}$$

Eq. (5) is in accordance with the data obtained by Tway and Apple [3]. In table 1 the relevant data are compiled from published N_{Xe} versus p_{Xe} curves at room temperature [3,5,6]. From ref. [3] we obtain $za \approx 0.0033$ Torr^{-1} for pure NaY at room temperature independent of the crystallite aggregate sizes.

As first suggested by Ryoo [5] one can calculate N_{Pt} from the intercept of the linear part of the Xe adsorption isotherm at $p_{Xe} = 0$. It is then straightforward to get the average number of metal atoms per cluster m, i.e. the nuclearity of the cluster, considering that $N_{Pt} m = n_{Pt}$, where n_{Pt} is the metal loading in atoms per supercage ($n_{Pt} = x$). (Note that n_{Pt} can be calculated from the Pt loading in wt% according to the equation $n_{Pt} = 10.75$ [Pt wt%/(100 − Pt wt%)], where Pt wt% is on a wet basis.) The results of these calculations are reported in table 1.

It is interesting to note that if $bp \ll 1$, eq. (4) would be replaced by

$$N_{Xe} = [za + N_{Pt}(4b - za)] p. \tag{6}$$

As the heat of adsorption of Xe on metals covered with chemisorbed layers, i.e. of oxygen, will be much smaller than on clean metal, eq. (6) might be adequate for situations where the metal clusters surface has been exposed to chemisorptives such as oxygen. Eq. (6) can account for different values obtained experimentally for the slopes of N_{Xe} versus p after chemisorption on the metal clusters. As can be noted from the results of table 1 the slopes of N_{Xe} versus p (which depend on the b values according to eq. (6)) seem to depend on the nature of the clusters and on the chemisorbed atoms.

Table 1
Results of the Xe adsorption isotherms at room temperature for the NaY, Pt/NaY and Pt–Cu/NaY systems. The x and y values represent the number of Pt and Cu atoms per supercage, respectively ($x = n_{Pt}$ and $y = n_{Cu}$). N is the number of mono- or bi-metallic clusters per supercage ($N = N_{Pt}$ or $N = N_{PtCu}$), m is the average number of atoms per cluster obtained by the equation $m = n/N$, where $n = n_{Pt}$ and $m = m_{Pt}$, or $n = (n_{Pt} + n_{Cu})$ and $m = (m_{Pt} + m_{Cu})$, in the case of mono- or bi-metallic clusters, respectively. For the clusters after chemisorption the numbers N and m are reported in parentheses because they are assumed to be the same as for the bare clusters

System Pt_xCu_y/NaY	Intercept	Slope ($Torr^{-1}$)	N	m	Ref.
NaY		0.0033 [a]			[3]
	< 0.002				[5]
$Pt_{0.18}$	0.012	0.0024	0.0030	59	[5]
$Pt_{0.44}$	0.031	0.0023	0.0078	57	[5]
$Pt_{0.89}$	0.061	0.0035	0.015	59	[6]
		0.0025			[5]
$Pt_{0.89}$ with $H_{(ads)}$	< 0.002	0.0023	(0.015)	(59)	[5]
$Pt_{0.89}$ with $O_{(ads)}$	0.005	0.0034	(0.015)	(59)	[6]
$Cu_{0.89}Pt_{0.89}$	0.066	0.0031	0.017	108	[6]
$Cu_{0.89}Pt_{0.89}$ with $O_{(ads)}$	0.003	0.0030	(0.017)	(108)	[6]

[a] To calculate the slope za from N_{Xe} (moles Xe adsorbed per gram of zeolite) versus p for NaY (fig. 17 of ref. [3]) we have used the factor 2.87×10^{20} supercages per gram of zeolite (wet basis). The dry basis would lead to 3.78×10^{20} supercages per gram of zeolite with a slope of 0.0025 $Torr^{-1}$.

It is noteworthy that for all the Pt/NaY samples reported in table 1 the Pt dispersion was in the range 0.8–1.0; the lower dispersions were obtained with the samples with higher loading and after reduction in H_2 at 300–450°C [2,4,6–8]. Assuming for the Pt cluster a density of 21.4 g/cm^3 (massive Pt at room temperature), we can calculate that up to 50–60 Pt atoms can fit the Y supercage volume (about a sphere with a diameter of 12 Å). We believe, however, that such a number of Pt atoms per cluster is overestimated because in the same supercage both the Na^+ ions and the H^+ ions (introduced during the reduction process in H_2) limit the room available to the metal cluster. Considering a Pt crystallite with an icosahedral structure it is also possible to account for the high dispersion measured for the Pt clusters in Y zeolites. In fact the 13-atom icosahedron has a theoretical dispersion (fraction of Pt atoms exposed at the surface) of $12/13 = 0.915$.

It may be recalled that the question regarding the true size of the Pt clusters has been addressed by several authors using different techniques. The evidence from wide-angle X-ray scattering (WAXS) [10] and extended X-ray absorption fine structure spectroscopy (EXAFS) [10,11] favored Pt clusters with size of about 10 Å and containing about 20–40 Pt atoms. Indirect techniques such as exchange of $-OH$ protons with D_2 [12] and ^{129}Xe NMR [1,2] concluded there are 6–8 Pt atoms per cluster. By studying the same sample by WAXS, EXAFS, HRTEM (high resolution transmission electron microscopy), and ^{129}Xe NMR, it was concluded that the Pt clusters contain around 16–30 atoms and are in the size range of 7–11 Å [13].

As for the Cu–Pt/NaY system there have been reported dispersion values in the range 0.6–0.7 for the more dilute samples [6–8] and of 0.44 for the $Cu_{0.89}Pt_{0.89}$/NaY sample [6]. EXAFS results on the $Pt_{0.26}Cu_{0.26}$/NaY sample [9] have shown that the coordination number Pt–Pt is about 5 (about 6 for Pt/NaY with the same Pt load), and the coordination number Pt–Cu is about 2 (the coordination number Cu–Cu is almost zero). These results suggest that the CuPt bimetallic clusters have a cherry type structure with the Pt atom in the center and copper atoms prevailing on the surface of Pt particles. A similar result has been reported for $Pt_{0.89}Cu_{0.89}$/NaY sample [6].

From the above discussion and from the results reported in table 1 it appears that the Xe adsorption method leads to values of the mean number of atoms per cluster that are larger with respect to the values obtained by other physicochemical techniques.

We also note that according to eq. (4) the assumption of a greater number of Xe atoms in contact with the cluster ($w > 4$) would lead to lower values of the number of clusters per supercage, and therefore to larger values for their average nuclearity. Lower values of the cluster nuclearity could be calculated assuming lower values for w. This could be the case when two clusters are located in two adjacent supercages, presumably interconnected by Pt necks.

3. ^{129}Xe NMR chemical shift

In general a hyperbolic-shaped relationship for the chemical shift of ^{129}Xe NMR and the Xe pressure (or concentration of physisorbed Xe in moles of Xe per gram of zeolite) has been observed for Pt/NaY or other multivalent cation-exchanged Y type zeolites [1–4,6].

We develop our model starting from eq. (1). Considering the results of the Xe adsorption isotherms we can write

$$\delta(p) = \delta_{Pt} N_{Pt} 4 / \left[N_{Pt} 4 + (1 - N_{Pt}) zap \right] + \delta_{NaY}(p). \qquad (7)$$

In eq. (7) we assume that the number of Xe atoms in contact with the cluster is $w = 4$ and that the fraction of empty supercages to be filled by Xe atoms is very close to 1 ($N_{Pt} \ll 0.1$),

$$\begin{aligned} X_{Xe-NaY}/N_{Xe} &= (1 - N_{Pt}) zap / \left[N_{Pt} 4 + (1 - N_{Pt}) zap \right] \\ &= N_{NaY} zap / (4 - 4N_{NaY} + N_{NaY} zap) \approx 1. \end{aligned} \qquad (8)$$

(This would imply $N_{NaY} \gg 0.9$, and indeed the results reported in table 1 support this assumption. If this is not the case the term $\delta_{NaY}(p)$ in eq. (7) should be replaced by $\delta_{NaY}(p) N_{Xe-NaY}/N_{Xe}$.)

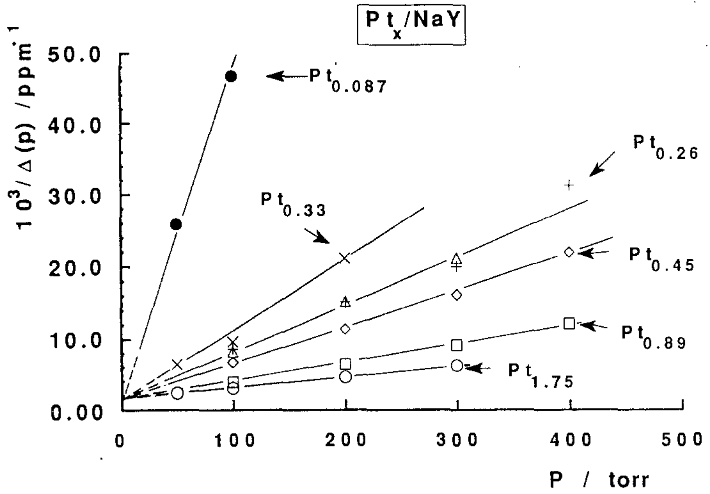

Fig. 1. Linearized ^{129}Xe NMR chemical shifts versus p (eq. (9)) for Pt$_x$/NaY samples (x represents the number of Pt atoms per supercage). Most of the experimental data δ_{Pt} versus p are taken from the literature (see table 2).

The chemical shifts $\delta_{NaY}(p)$ for pure NaY are easily measured and similar results were obtained in different laboratories [2,6]. We recall that δ_{NaY} is a function of the Xe pressure because it also takes into account the effect of collisions between Xe atoms. It is also of interest to note that in the case of formation of large metal agglomerates on the external surface of zeolites the chemical shift of Xe becomes almost the same as that of pure NaY [2,6]. Our method to obtain N_{Pt} from the chemical shift of adsorbed Xe is based on eq. (7). If we define $\Delta(p) = \delta(p) - \delta_{NaY}(p)$ it is possible to linearize eq. (7) in its useful form:

$$1/\Delta(p) = (1/\delta_{Pt}) + [(za/4\delta_{Pt})(1 - N_{Pt})/N_{Pt}]\, p,$$

$$1/\Delta(p) = I + Sp. \qquad (9)$$

From a plot of $1/\Delta(p)$ versus p we can obtain δ_{Pt} from the intercept (I) and N_{Pt} from the slope (S) and the intercept (I) of the straight line representing the ^{129}Xe NMR data. Examples of application of eq. (9) are reported in fig. 1 and in fig. 2 for the Pt$_x$/NaY and Pt$_x$Cu$_y$/NaY systems, respectively. Note that the factor za in eq. (9) is a constant and its value has been obtained previously from the Xe adsorption isotherm on NaY: $za \approx 0.0033$ Torr^{-1} at room temperature [3].

N_{Pt} can be calculated by means of the expression

$$N_{Pt} = 0.0033(I)/[4(S) + 0.0033(I)]. \qquad (10)$$

We note that the calculation of N_{Pt} from the slope and the intercept of a straight line is in principle more accurate than the intercept only. Moreover the accuracy of the ^{129}Xe NMR is very high (≈ 1 ppm). This is confirmed by the

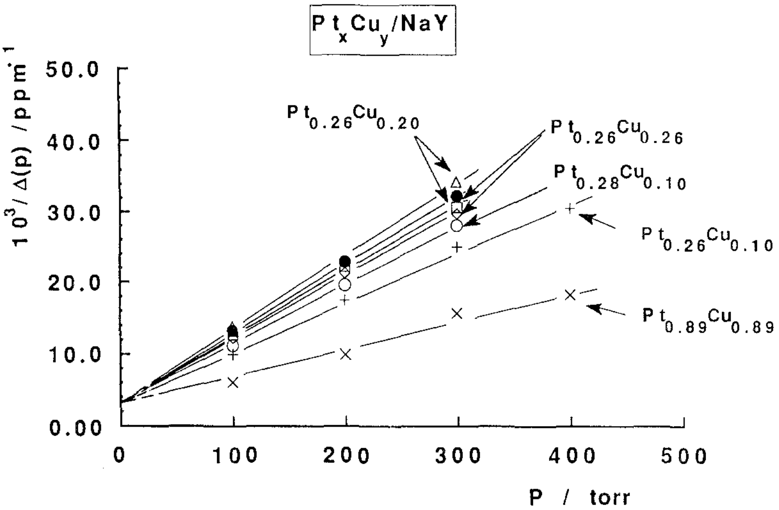

Fig. 2. Linearized ^{129}Xe NMR chemical shifts versus p (eq. (9)) for Pt_xCu_y/NaY samples (x and y represent the number of Pt and Cu atoms per supercage, respectively). Most of the experimental data δ_{PtCu} versus p are taken from the literature (see table 2).

data in table 2 from which it emerges that the mean number of atoms per cluster obtained from ^{129}Xe NMR is in very good agreement with the results of other physicochemical characterizations [9–13].

Table 2 shows that the intercept I, as expected, depends on the chemical nature of the cluster; from the intercepts we calculate $\delta_{Pt} \approx 625$ ppm and $\delta_{PtCu} \approx 333$ ppm. This result is related to the larger heat of absorption and polarization of adsorbed Xe on Pt than on Cu (see ref. [6] and references cited therein).

It should be noted that when eq. (8) is not a good approximation the value of N_{Pt} obtained by means of eqs. (7)–(10) can be used in successive iterations to calculate the true N_{Pt} value in a self-consistent manner. In fact the first approximate N_{Pt} value permits the calculation, as a function of p, of the quantities $\delta_{NaY}N_{Xe-NaY}/N_{Xe}$ and $\Delta(p) = \delta(p) - \delta_{NaY}(p)N_{Xe-NaY}/N_{Xe}$. Using this modified $\Delta(p)$ value in eqs. (9) and (10) we can then calculate a second N_{Pt} value and, if necessary, continue the iterations to get a self-consistent N_{Pt} value.

Tway and Apple [3] reported that the ^{129}Xe linewidth of the NMR resonance in pure NaY depends on the crystallite aggregate sizes. The data for the $Pt_{0.26-0.28}Cu_y$/NaY system reported in fig. 3 show that with constant crystallite size of the NaY support the ^{129}Xe linewidth depends also on the metal clusters distribution within the zeolite crystallites. We suggest that Xe experiences a more uniform environment when the copper loading increases from $y = 0$ to $y = 0.10$–0.26 at constant Pt loading. This is probably related to the increase of the number of clusters per supercages as show the data in table 2.

Table 2
Intercepts (I), slopes (S), number of mono- or bi-metallic clusters per supercages ($N = N_{\mathrm{Pt}}$ or $N = N_{\mathrm{PtCu}}$) and number of atoms per clusters ($m = m_{\mathrm{Pt}} = n_{\mathrm{Pt}}/N_{\mathrm{Pt}}$ or $m = (m_{\mathrm{Pt}} + m_{\mathrm{Cu}}) = (n_{\mathrm{Pt}} + n_{\mathrm{Cu}})/N_{\mathrm{PtCu}}$) obtained from the linearized equation of the ^{129}Xe NMR (eqs. (9) and (10)) applied to Pt_x/NaY and $\mathrm{Pt}_x\mathrm{Cu}_y$/NaY systems. The $\mathrm{Pt}_x\mathrm{Cu}_y$/NaY samples of ref. [6] were prepared by simultaneous ion exchange of Cu^{2+} and $[\mathrm{Pt(NH_3)_4}]^{2+}$ into NaY. The new results presented in this paper are relative to samples prepared by sequential ion exchange of Cu^{2+} into *non reduced* Pt/NaY (ref. [8]). The present results show that with our metal loading the two preparation methods lead to the same samples. (See ref. [6] for the experimental details of ^{129}Xe NMR measurements.)

Sample $\mathrm{Pt}_x\mathrm{Cu}_y$/NaY	$I \times 10^3$	$S \times 10^5$	N	m	Ref.
$\mathrm{Pt}_{1.75}$	1.6	1.55	0.078	22	[1]
$\mathrm{Pt}_{0.89}$	1.6	2.60	0.048	18	[6]
$\mathrm{Pt}_{0.45}$	1.6	5.10	0.025	18	[4]
$\mathrm{Pt}_{0.26}$	1.6	6.47	0.020	13	[6]
$\mathrm{Pt}_{0.26}$	1.6	6.47	0.020	13	this work
$\mathrm{Pt}_{0.33}$	1.6	9.70	0.013	25	[1]
$\mathrm{Pt}_{0.087}$	1.6	45.1	0.0029	30	[1]
$\mathrm{Pt}_{0.89}\mathrm{Cu}_{0.89}$	3.0	4.20	0.038	47	[6]
$\mathrm{Pt}_{0.26}\mathrm{Cu}_{0.10}$	3.0	7.00	0.034	11	[6]
$\mathrm{Pt}_{0.28}\mathrm{Cu}_{0.10}$	3.0	8.30	0.030	13	this work
$\mathrm{Pt}_{0.26}\mathrm{Cu}_{0.20}$	3.0	9.30	0.026	18	this work
$\mathrm{Pt}_{0.26}\mathrm{Cu}_{0.26}$	3.0	9.00	0.027	19	this work
$\mathrm{Pt}_{0.26}\mathrm{Cu}_{0.20}$	3.0	10.7	0.023	20	[6]
$\mathrm{Pt}_{0.26}\mathrm{Cu}_{0.26}$	3.0	9.80	0.025	21	[6]

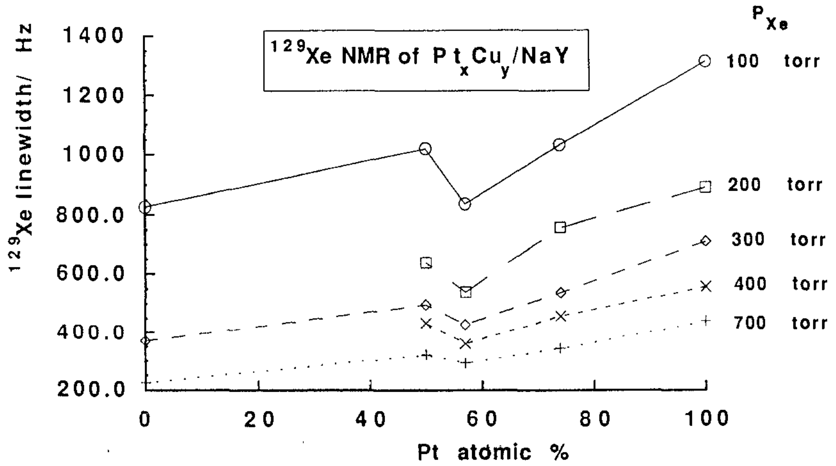

Fig. 3. ^{129}Xe NMR linewidth as a function of Pt at% and Xe pressure for the $\mathrm{Pt}_x\mathrm{Cu}_y$/NaY samples prepared according to ref. [8] (see table 2).

4. Conclusions

It appears possible to calculate the concentration of metal or alloy clusters entrapped in the supercages of Y zeolite from the ^{129}Xe NMR chemical shifts and their dependence on the Xe pressure.

Acknowledgement

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