

# AN APPLICATION OF $^{129}\text{Xe}$ NMR OF ADSORBED XENON TO THE STUDY OF SILICA-BASED CATALYSTS

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## 1. Introduction

$^{129}\text{Xe}$  NMR of adsorbed xenon was found to be a useful tool for the characterization of microporous solids (zeolites, clathrates, molecular sieves) which have pore sizes close to the xenon free diameter of 4.4 Å [1-3]. Much less attention has been paid to the study of porous solids with the pore sizes much larger than the diameter of the xenon atom.

Recently,  $^{129}\text{Xe}$  NMR spectroscopy of adsorbed xenon was used to characterize mesoporous silicas [4-6]. A correlation between the  $^{129}\text{Xe}$  NMR chemical shift  $\delta$  (ppm) and the pore diameter  $D$  (Å) in the range of 20-400 Å was obtained for silica samples with well-defined structure and narrow pore size distribution [6]:

$$\delta = 115/(1+D/131) \quad (1)$$

In the present communication,  $^{129}\text{Xe}$  NMR is extended to the study of mesoporous silica-based catalysts.

## 2. Experimental

The silica chosen as the support material was Cabosil EH5. A toluene solution of titanium (IV) isopropoxide, a 1-propanol solution of zirconium (IV) propoxide, a methanol solution of aluminium acetylacetonate and a  $\text{CH}_2\text{Cl}_2$  solution of tetrabutyl tin were used to prepare the corresponding samples by the incipient-wetness impregnation method. The preparations were performed inside a glove box to avoid preoxidation by atmospheric moisture. After impregnation, each catalyst was dried at room temperature with subsequent calcination at 500°C.

The pore structures of the samples were characterized by nitrogen adsorption and capillary condensation (77K) on a Micromeritics ASAP 2400. The mesopore size distributions (Fig. 1) were calculated from desorption branches of isotherms in the range of capillary-condensation hysteresis by the Broekhoff and de Boer method for cylindrical pores [7].

Xenon with a natural abundance of  $^{129}\text{Xe}$  isotope (26%) was used for the NMR experiments. The NMR spectra were recorded on a Bruker MSL-400 spectrometer at a frequency of 110.6 MHz. The pulse width was 10  $\mu\text{s}$  with a 2 s delay, the number of scans was from 5000 to 10000. The chemical shifts were measured relative to gaseous xenon at a low pressure with an accuracy of  $\pm 1$  ppm.

### 3. Results and discussion

The xenon adsorption isotherms for the parent silica and the supported metal oxide catalysts, measured up to 500 Torr of xenon pressure (293 K), were found to obey the Henry's law with nearly identical Henry constants of  $(1.9 \pm 0.3) \cdot 10^{17}$  atoms/Torr-g. Henry's type of isotherms is responsible for the independence of the  $^{129}\text{Xe}$  chemical shift upon xenon pressure for all the samples under study that is in agreement with [4, 6].

The  $^{129}\text{Xe}$  NMR spectra for the silica and the supported catalysts (293 K, 110-150  $\mu\text{mol/g}$  of adsorbed xenon) are presented in Fig. 2. It follows from these spectra that the supporting of the metal oxides affects the  $^{129}\text{Xe}$  NMR chemical shifts and line widths.

The  $^{129}\text{Xe}$  NMR spectrum of xenon adsorbed on  $\text{SiO}_2$  shows along with a line at 0 ppm from gaseous xenon between silica grains also a line at 71 ppm due to an adsorbed xenon (Fig. 2-a). According to Eq. (1), this value of shift corresponds to the mean pore diameter  $D_{\text{NMR}} = 81 \text{ \AA}$  (Table 1). Two other diameters: ( $D_{\text{BET}}$ ) - determined from the BET region of the nitrogen isotherm ( $D_{\text{BET}} = 4V_P/A_{\text{BET}}$ ), and ( $D_{\text{des}}$ ) - determined from the desorption branch of the hysteresis loop are also collected in Table 1.

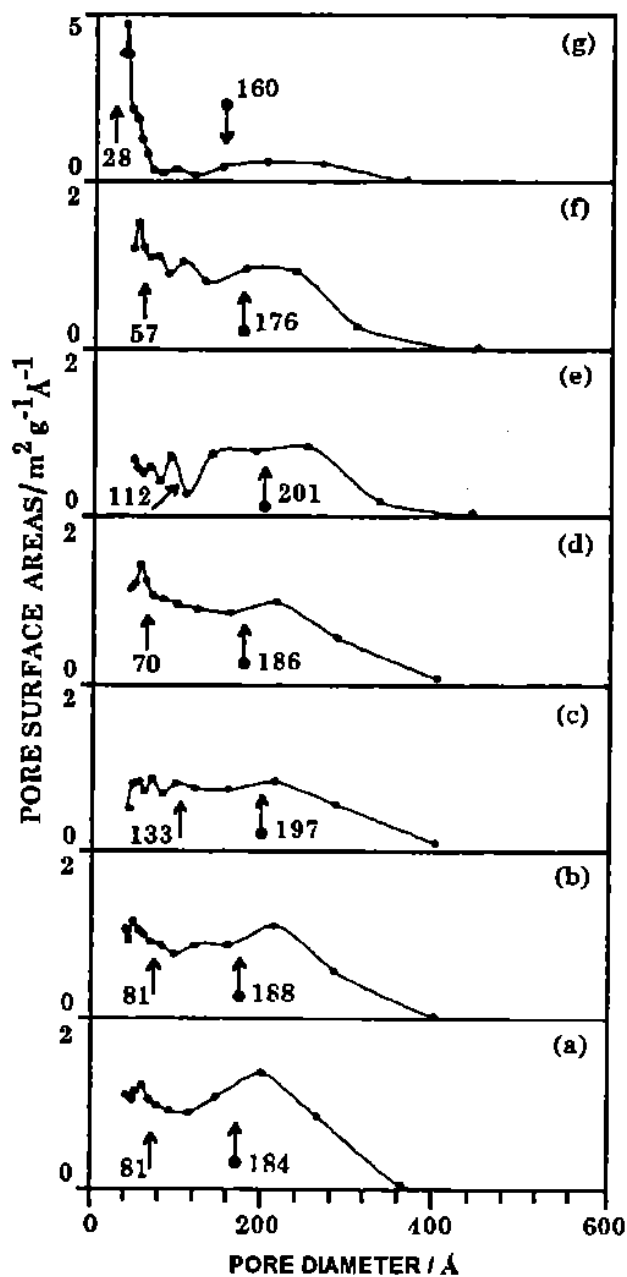
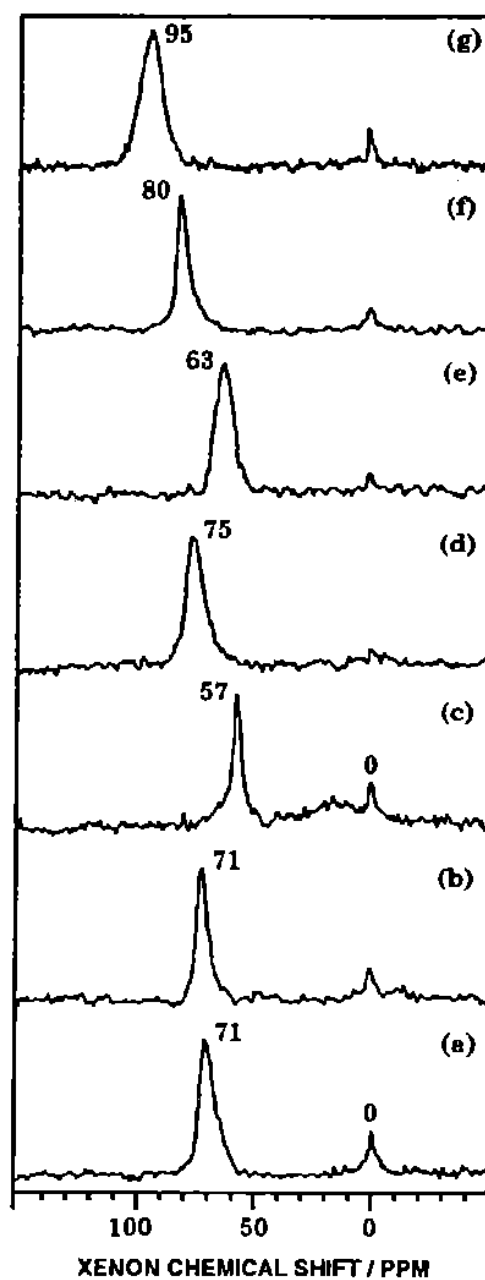
Supporting of 10%  $\text{TiO}_2$  has a small effect upon both the porosimetry and  $^{129}\text{Xe}$  NMR data (Figs. 1, 2-b). It can be concluded that the supported titanium oxide species essentially do not change the interior structure of silica, while the distribution of the high-dispersed titania over the silica surface is relatively uniform.

More pronounced changes are observed for the 10%  $\text{Al}_2\text{O}_3/\text{SiO}_2$  catalyst. In this case, the  $^{129}\text{Xe}$  chemical shift decreases compared with that of silica (Fig. 2-c). Porosimetry data indicate a decrease in the content of both type of pores with a simultaneous increase of both  $D_{\text{NMR}}$  and  $D_{\text{des}}$  (Table 1). This indicates the filling of the silica pores by large enough alumina species.  $^{27}\text{Al}$  MAS NMR spectrum of this sample also suggests the formation of large alumina particles with a regular structure that perturb the texture of the silica support.

For the 10%  $\text{SnO}_2/\text{SiO}_2$  sample, the  $^{129}\text{Xe}$  NMR line slightly moves to low field (Fig. 2-d). The surface area and the pore volume remain practically unchanged as compared with initial silica (Table 1). The slight growth of  $\delta$  could be attributed to a small decrease of the mean pore diameter due to an increase in the percentage of small pores. This is confirmed by porosimetry data which indeed indicate an increase of the relative amount of pores with  $D$  ca. 60  $\text{\AA}$  (Fig. 1-d). The  $^{119}\text{Sn}$  NMR spectrum of this catalyst shows that tin oxide forms disordered and probably two-dimensional surface species. However, supporting 25%  $\text{SnO}_2$  on  $\text{SiO}_2$  decreases, rather than increases, the

TABLE 1. Morphology of the  $\text{MeO}_x/\text{SiO}_2$  catalysts as determined by nitrogen porosimetry and  $^{129}\text{Xe}$  NMR

Sample	$A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )	$D_{\text{BET}}$ ( $\text{\AA}$ )	$D_{\text{des}}$ ( $\text{\AA}$ )	$D_{\text{NMR}}$ ( $\text{\AA}$ )
$\text{SiO}_2$	355	1.39	156	184	81
10% $\text{TiO}_2/\text{SiO}_2$	309	1.24	161	188	81
10% $\text{Al}_2\text{O}_3/\text{SiO}_2$	236	1.11	189	197	133
10% $\text{SnO}_2/\text{SiO}_2$	344	1.26	146	186	70
25% $\text{SnO}_2/\text{SiO}_2$	202	1.01	199	201	112
10% $\text{ZrO}_2/\text{SiO}_2$	332	1.15	139	176	57
30% $\text{ZrO}_2/\text{SiO}_2$	338	0.91	108	160	28

Figure 1. Desorption pore size distributions ( $\uparrow - D_{\text{NMR}}$ ,  $\downarrow - D_{\text{des}}$ )Figure 2.  $^{129}\text{Xe}$  NMR spectra of adsorbed xenon

(a) -  $\text{SiO}_2$ ; (b) - 10%  $\text{TiO}_2/\text{SiO}_2$ ; (c) - 10%  $\text{Al}_2\text{O}_3/\text{SiO}_2$ ; (d) - 10%  $\text{SnO}_2/\text{SiO}_2$ ; (e) - 25%  $\text{SnO}_2/\text{SiO}_2$ ; (f) - 10%  $\text{ZrO}_2/\text{SiO}_2$ ; (g) - 30%  $\text{ZrO}_2/\text{SiO}_2$ .

$^{129}\text{Xe}$  NMR chemical shift (Fig.2-e). This indicates a decrease of the amount of small pores and an increase of the mean pore diameter, which is also supported by porosimetry data (Fig.1-e, Table 1). It can be concluded, therefore, that in this sample the oxide species occupy significantly the pores of silica due to the formation of large tin oxide particles. This conclusion also follows from  $^{119}\text{Sn}$  NMR measurements which show that regular oxide particles with a structure close to bulk  $\text{SnO}_2$  are formed for the 25%  $\text{SnO}_2/\text{SiO}_2$  sample.

For the 10%  $\text{ZrO}_2/\text{SiO}_2$  catalyst, the  $^{129}\text{Xe}$  NMR measurements demonstrates an increased  $\delta$ -value compared with that of silica (Fig.2-f). At the same time, porosimetry data show a considerable increase in the content of pores in the 40-60 Å range (Fig.1-f). The enhancement of the  $\text{ZrO}_2$  content up to 30% makes this effect more pronounced (Fig.1-g). The growth of the chemical shift up to 95 ppm is in excellent qualitative agreement with the increase of the amount of narrow pores and with the decrease of the mean pore diameter  $D_{\text{des}}=160$  Å and  $D_{\text{BET}}=108$  Å (Fig.1-g, Table 1). Thus, both  $^{129}\text{Xe}$  NMR and nitrogen porosimetry measurements suggest that the zirconia oxide species create a highly developed pore structure within the silica pores that has a large impact on  $^{129}\text{Xe}$  NMR spectra.

The use of  $^{129}\text{Xe}$  as a probe-atom provides information on the porous structure of the catalysts which complements that obtained with the conventional nitrogen adsorption and capillary condensation methods. The discrepancy between  $D_{\text{NMR}}$  and both  $D_{\text{BET}}$  and  $D_{\text{des}}$  seems due to a broader and bimodal distribution of pores (Fig.1), in contrast with the silica samples studied earlier [6]. Despite the fact that Eq. (1) should be valid for samples with unimodal pore size distributions, the tendency in variation of the calculated pore diameter  $D_{\text{NMR}}$  qualitatively agrees with the tendency in variation of the pore diameters found from nitrogen adsorption/desorption data (Table 1).

Recently, the structure of heteropoly acid  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (HPA) supported on silica was studied by  $^{129}\text{Xe}$  NMR [8]. The NMR spectral parameters (number of lines, their widths and chemical shifts) were strongly dependent on the HPA loading and on the state of the surface HPA species. For these catalysts, the microporosity accessible for xenon penetration was found in accord with nitrogen porosimetry.

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