



# Acidity of sulfated tin oxide and sulfated zirconia: A view from solid-state NMR spectroscopy

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## ABSTRACT

Acidic properties of  $\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{SnO}_2$ , and  $\text{SO}_4^{2-}/\text{SnO}_2$  were studied by solid-state NMR spectroscopy.  $^1\text{H}$  MAS NMR indicated that  $\text{SO}_4^{2-}$  was able to react with the hydroxyl groups of  $\text{ZrO}_2$  and  $\text{SnO}_2$ , leading to the formation of new acid sites.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  MAS NMR spectra of adsorbed probe molecules indicated that both Brønsted and Lewis acid sites were present on  $\text{SO}_4^{2-}/\text{ZrO}_2$ , but only Brønsted acid site existed on  $\text{SO}_4^{2-}/\text{SnO}_2$ . Acid strength of  $\text{SO}_4^{2-}/\text{SnO}_2$  was stronger than that of  $\text{SO}_4^{2-}/\text{ZrO}_2$ . Both of them were slightly stronger than that of HZSM-5, but still weaker than that of 100%  $\text{H}_2\text{SO}_4$ .

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## 1. Introduction

New environmental legislation and the drive towards “Green Chemistry” have led to the development of environmentally friendly solid acid catalysts, leading to minimum pollution and wastes. Arata et al. reported a range of active sulfated metal oxides including  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ ,  $\text{SO}_4^{2-}/\text{SnO}_2$ ,  $\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/\text{SiO}_2$ ,  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ , and  $\text{SO}_4^{2-}/\text{HfO}_2$  [1–6]. Sulfated tin oxide ( $\text{SO}_4^{2-}/\text{SnO}_2$ ) is one of the candidates with the strongest acidity among the sulfated metal oxides.  $\text{SO}_4^{2-}/\text{SnO}_2$  showed activities much higher than those of  $\text{SO}_4^{2-}/\text{ZrO}_2$  for many reactions [2–6]. Nevertheless,  $\text{SO}_4^{2-}/\text{SnO}_2$  was scarcely investigated because of the difficulty in its preparation. The structure, type, number and strengths of the acid sites on  $\text{SO}_4^{2-}/\text{SnO}_2$  are still not well-understood. So, the acid properties of  $\text{SO}_4^{2-}/\text{SnO}_2$  are needed to be examined for better understanding its high catalytic activities. Solid-state NMR spectroscopy combined with probe molecule technique is a powerful tool for the measurement of the acidity of solid acid [7–12]. In this communication, we reported the use of pyridine-*d*<sub>5</sub>, 2-<sup>13</sup>C-acetone, trimethylphosphine, and trimethylphosphine oxide as probe molecules to study the differences of the acidic nature of  $\text{SO}_4^{2-}/\text{ZrO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$  catalysts by solid-state NMR spectroscopy.

## 2. Experimental

$\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{SnO}_2$ , and  $\text{SO}_4^{2-}/\text{SnO}_2$  were prepared by the reported method [3]. The samples were dehydrated before  $^1\text{H}$  MAS NMR experiments and the adsorption of the probe molecules. The adsorption of the probe molecules were conducted according to the literatures [7,11].

All NMR experiments were carried out on a Varian Infinityplus-400 spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  MAS NMR chemical shifts were externally referenced to tetramethylsilane, hexamethylbenzene and 85%  $\text{H}_3\text{PO}_4$  solution, respectively.

## 3. Results and discussion

The prepared samples were characterized and the textural properties of the samples were listed in Table 1.

### 3.1. $^1\text{H}$ MAS NMR spectra

$^1\text{H}$  MAS NMR can be used to identify different surface OH groups. Generally, the chemical shifts of hydroxyl groups increased with the acid strengths.  $^1\text{H}$  MAS NMR spectra of the dehydrated samples were shown in Fig. 1.  $^1\text{H}$  MAS NMR spectra of  $\text{ZrO}_2$  and  $\text{SO}_4^{2-}/\text{ZrO}_2$  consisted of an intense signal at 5.2 and 6.4 ppm, respectively (Fig. 1a and b). For  $^1\text{H}$  MAS NMR spectrum of  $\text{SnO}_2$ , the major peak at 5.1 ppm was observed (Fig. 1c). In  $^1\text{H}$  MAS NMR spectrum of  $\text{SO}_4^{2-}/\text{SnO}_2$ , additional two peaks at 8.1 and

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**Table 1**

Textural properties of various samples.

Samples	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	Average crystal size/nm	Sulfate content/wt.%	Color
ZrO <sub>2</sub>	112	15.6	–	White
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	134	12.2	2.30	White
SnO <sub>2</sub>	28	16.0	–	Yellow
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	93	4.8	3.31	Yellow

7.5 ppm were observed (Fig. 1d). We tentatively assigned the signals at 8.1, 7.5 and 6.4 ppm to strong acidic OH groups (Brønsted acid sites) formed by H<sub>2</sub>SO<sub>4</sub> treatment, while the peaks at ca. 5.1 ppm to weak acidic ZrOH or SnOH groups, and other peaks to nonacidic OH groups.

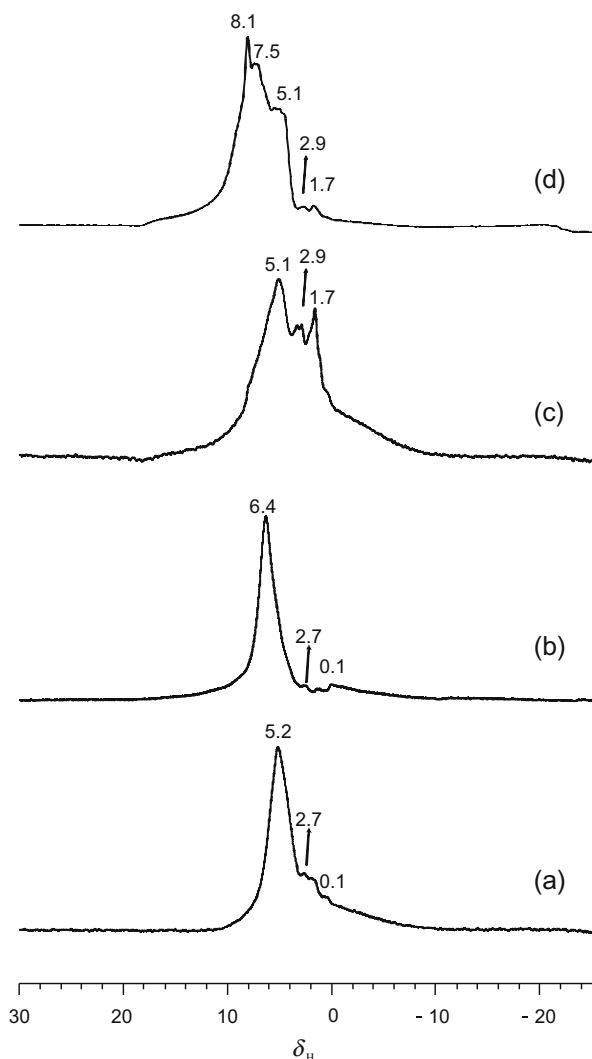
### 3.2. <sup>1</sup>H MAS NMR spectra of adsorbed pyridine-*d*<sub>5</sub>

The formation of the hydrogen bond between pyridine-*d*<sub>5</sub> and weak or nonacidic OH groups shifts <sup>1</sup>H MAS NMR signal position from 2 to 10 ppm [12]. In the case of acidic OH groups (Brønsted acid sites), the adsorption of pyridine-*d*<sub>5</sub> results in <sup>1</sup>H MAS NMR signals with chemical shifts in the range of 12–20 ppm [12]. The larger downfield signals resulted from a proton transfer to the probe molecule, forming pyridinium ions. Our recent work indi-

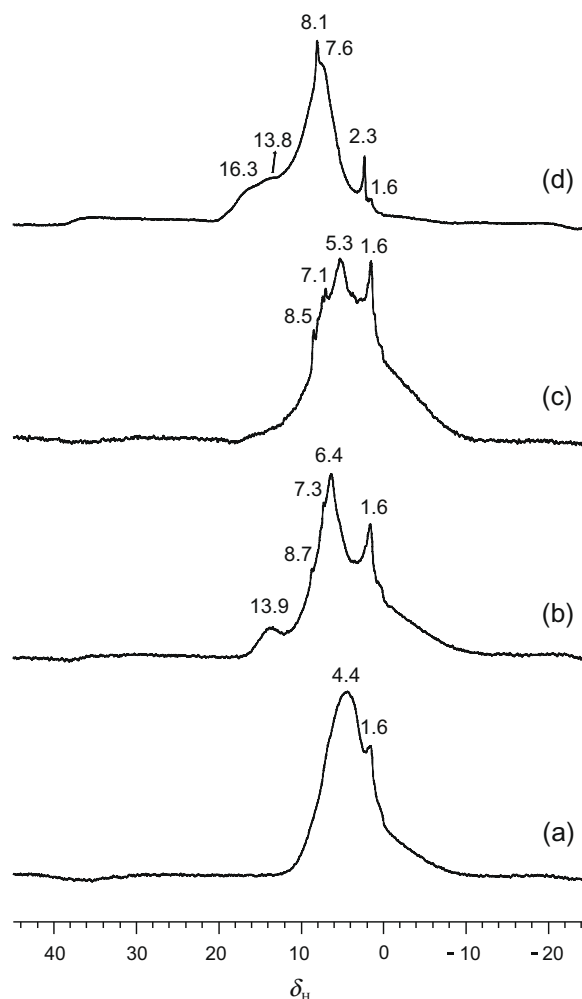
cated that the <sup>1</sup>H chemical shift of pyridinium ions could be used as a scale to measure the acid strength: a smaller chemical shift corresponded to a stronger acid strength [13]. The adsorption of pyridine-*d*<sub>5</sub> onto ZrO<sub>2</sub> resulted in a broad signal at 4.4 ppm (Fig. 2a). In contrast, after the adsorption of pyridine-*d*<sub>5</sub> onto SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (Fig. 2b), a signal appeared at 13.9 ppm. <sup>1</sup>H MAS NMR spectrum (Fig. 2c) of pyridine-*d*<sub>5</sub>-loaded SnO<sub>2</sub> resembled that of ZrO<sub>2</sub>, only hydrogen-bonded pyridine was detected. But in the spectrum of pyridine-*d*<sub>5</sub> loaded on SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> (Fig. 2d), there were two signals at 16.3 and 13.8 ppm, indicative of the formation of two types of pyridine ions. The chemical shifts of the signals suggested that the acid strengths of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> were stronger than that of H-ZSM-5 zeolite (having a <sup>1</sup>H chemical shift of 15.5 ppm). The signals at ca. 8.7 and 7.3 ppm in <sup>1</sup>H MAS spectrum of pyridine-*d*<sub>5</sub>-loaded SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> were probably due to the H/D exchange between the deuterium bound to the ring of pyridine-*d*<sub>5</sub> and the acidic protons [14].

### 3.3. <sup>13</sup>C MAS NMR spectra of adsorbed 2-<sup>13</sup>C-acetone

The formation of a hydrogen bond between the acidic proton and the carbonyl oxygen of adsorbed 2-<sup>13</sup>C-acetone will cause a downfield shift of the carbonyl carbon. Generally, the stronger the Brønsted acidity, the stronger the hydrogen bonding between the carbonyl carbon and the acidic proton, and consequently the larger the <sup>13</sup>C isotropic chemical shift [8,9]. Fig. 3 showed the <sup>13</sup>C



**Fig. 1.** <sup>1</sup>H MAS NMR spectra of ZrO<sub>2</sub> (a), SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (b), SnO<sub>2</sub> (c) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> (d).



**Fig. 2.** <sup>1</sup>H MAS NMR spectra of pyridine-*d*<sub>5</sub> loaded on ZrO<sub>2</sub> (a), SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (b), SnO<sub>2</sub> (c) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> (d).

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