

## Characterization of Precursors of VPO Catalysts by $^{31}\text{P}$ and $^{93}\text{Nb}$ Solid State NMR

**J. G. Eon, R. A. S. San Gil<sup>\*</sup>, E. R. Lachter, M. H. C. La Cruz**

Instituto de Química, Universidade Federal do Rio de Janeiro, Ed. do CT, bloco A, Ilha do Fundão 21941-972, Rio de Janeiro, Brazil

**A. D. Farias, P. G. P. Oliveira**

Divisão de Catálise, Instituto Nacional de Tecnologia, Rio de Janeiro, Brasil

**F. M. Reguera, W. A. Gonzalez**

Dep. Engenharia Química, Instituto Militar de Engenharia, Rio de Janeiro, Brazil

**S. Caldarelli, J. C. Volta**

Institute de Recherche sur la Catalyse, CNRS, France

**Keywords:**  $^{93}\text{Nb}$  NMR, niobium phosphate, VPO catalysts

**Abstract:** *In this communication we show that  $^{31}\text{P}$  and  $^{93}\text{Nb}$  solid state NMR provides a quick means of evaluating commercial and synthesized niobium phosphate samples.*

Niobium-based materials are commonly used in target catalysts, as supports or doping agents.<sup>1</sup> The literature has shown that vanadium phosphorus oxide (VPO) catalysts have widely been applied as promoters in reactions of selective oxidation of propane to acrylic acid and of butane to maleic anhydride in only one step.<sup>2,3</sup> Some authors report an increase in activity promoted by doping both catalysts with niobium. For VPO niobium-doped catalysts niobium was added by using niobium ethoxide<sup>3</sup> or niobium phosphate.<sup>4</sup> The knowledge of the catalytic species and of the true promoters of this reaction is of great importance for carrying out this process. So far, data reported in previous works are scarce and somewhat controversial. Concerning the characterization of niobium compounds and niobium-derived materials, some works report on the use of  $^{93}\text{Nb}$  solid state nuclear magnetic resonance (solid state NMR), but to our knowledge, there is no

report on the characterization of bulk or crystalline niobium phosphate samples using this technique. The characterization of niobium phosphate is usually carried out by Fourier transform infrared (FTIR) spectroscopy and ultraviolet-visible (UV/VIS) techniques. In the case of crystalline samples, X-ray diffraction (XRD) has been used.<sup>5</sup>

In this communication we present the preliminary results of the use of solid-state NMR to characterize bulk samples of  $\text{NbPO}_4$  from distinct sources, for which  $^{31}\text{P}$  and  $^{93}\text{Nb}$  were used as probes.

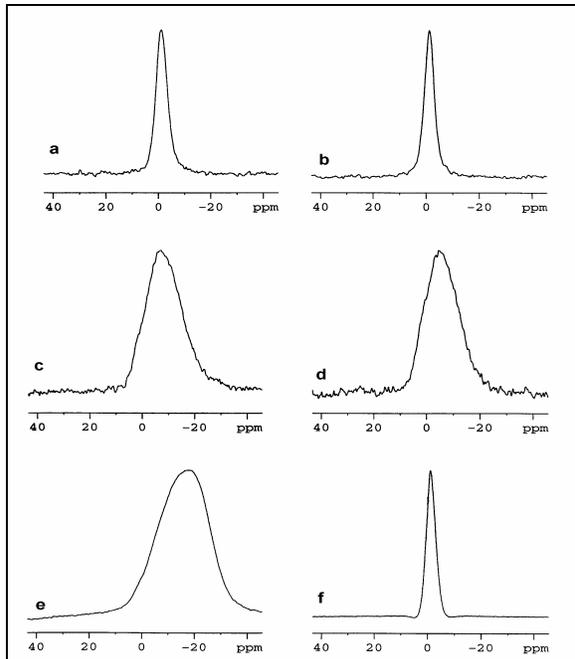
Niobium phosphate  $\text{NbOPO}_4 \cdot 3\text{H}_2\text{O}$  samples (a, b, d and f) were synthesized from  $\text{Nb}_2\text{O}_5$  as described in the literature.<sup>2</sup> Samples c, e, g and h are commercial products. The products were characterized by elemental analysis, XRD and FTIR.  $^{31}\text{P}$  and  $^{93}\text{Nb}$  NMR spectra in the solid state were recorded on a Bruker Avance DSX-400 (9.4 Tesla), operating at 161.98 MHz and

---

<sup>\*</sup> rsangil@iq.ufrj.br

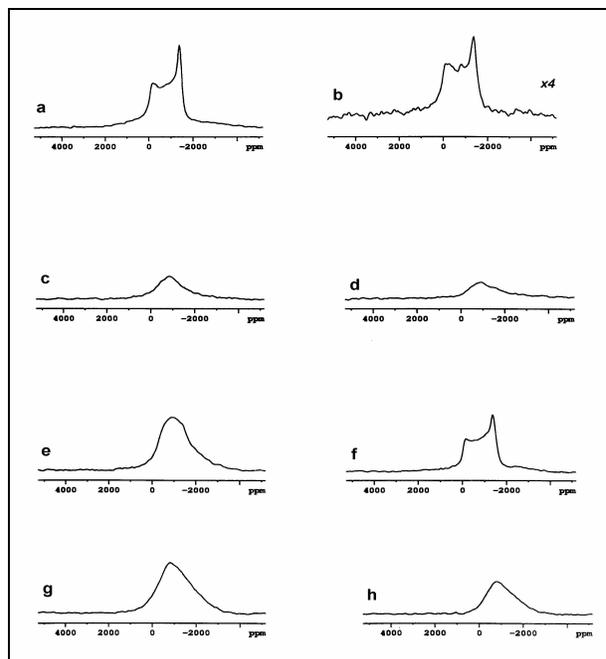
97.83 MHz, respectively, with Bruker CP/BUT probe and zirconium oxide rotors of 4 mm diameter. Acquisition conditions for  $^{31}\text{P}$  were as follows: Bloch decay pulse sequence with high power proton decoupling;  $\text{P1}(\pi/2)$ , 4.3  $\mu\text{s}$ ; AQ, 15.81ms; D1, 60 s; spectral window 50kHz; Number of spectra, 12. Acquisition conditions for  $^{93}\text{Nb}$  'wideline': Hahn spin-echo pulse sequence ( $90-\tau_1-180-\tau_2-\text{AQ}$ );  $\text{P1}(\pi/2)$ , 1.6  $\mu\text{s}$ ; AQ-0.357 ms; D1, 0.5s; D6, 0.02ms; D7, 0.014 ms; spectral window 3.33 MHz; number of scans, 0.5k. Samples of phosphoric acid (85%),  $\text{NbCl}_5 \cdot \text{CH}_3\text{CN}$  (0.0 ppm) and  $\text{LiNbO}_4$  (- 1025 ppm) were used as reference for P and Nb spectra.

Figure 1 displays  $^{31}\text{P}$  MAS NMR spectra obtained for different samples and Figure 2



**Figure 1.**  $^{31}\text{P}$  MAS NMR spectra of niobium phosphates from different sources (a) synthesized from  $\text{Nb}_2\text{O}_5$  PA; (b) synthesized from  $\text{Nb}_2\text{O}_5$  CBMM, route 1; (c) commercial, CBMM, lot 1; (d) synthesized from commercial  $\text{Nb}_2\text{O}_5$ ; (e) commercial, CBMM, lot 2; (f) synthesized from  $\text{Nb}_2\text{O}_5$  CBMM, route 2.

shows  $^{93}\text{Nb}$  wideline spectra. As can be seen, depending on the source of niobium phosphate, different chemical shifts and lineshapes can be found. The results of  $^{31}\text{P}$  chemical shifts and linewidths are listed in Table 1. The enlarged width observed for samples c – e in  $^{31}\text{P}$  MAS spectra suggest that maybe more than one type of phosphorous is present or that those samples are amorphous. This trend was also observed in the spectra of  $^{93}\text{Nb}$ , where samples a, b and f present the central transition lineshape typical of one type of high crystallinity Nb site, possessing high quadrupole coupling constant ( $C_Q \geq 2\text{MHz}$ ) and asymmetry parameter  $\eta_Q \sim 0$  (axial symmetry).<sup>6</sup>



**Figure 2.**  $^{93}\text{Nb}$  wideline spectra of niobium phosphates from different sources (a) synthesized from  $\text{Nb}_2\text{O}_5$  PA; (b) synthesized from  $\text{Nb}_2\text{O}_5$  CBMM, route 1; (c) commercial, CBMM, lot 1; (d) synthesized from commercial  $\text{Nb}_2\text{O}_5$ ; (e) commercial, CBMM, lot 2; (f) synthesized from  $\text{Nb}_2\text{O}_5$  CBMM, route 2; (g) and (h) two samples of  $\text{Nb}_2\text{O}_5$  from CBMM, included for comparison.

On the other hand, for samples c, d, e, g and h only a broad signal could be observed, indicating the presence of more than one type of Nb, with distinct isotropic chemical shifts and/or different linewidths.<sup>6</sup>

**Table 1.** Chemical shifts ( $\delta$ , ppm) and linewidths ( $\Delta\nu_{1/2}$ , Hz) of  $^{31}\text{P}$  MAS NMR spectra obtained for  $\text{NbPO}_4$  samples

Sample	$^{31}\text{P}$ chem. shift, ppm	$\Delta\nu_{1/2}$ , Hz
a	-1.5	762
b	-1.5	667
c	-7.4	2477
d	-4.4	2450
e	-17.9	3716
f	-1.4	660

We found that the samples with  $^{31}\text{P}$  signal in higher frequencies (around -1.5 ppm) were the same with crystalline pattern with  $\eta \sim 0$  (axial symmetry) in the  $^{93}\text{Nb}$  wideline spectra. These results suggest that  $^{93}\text{Nb}$  NMR spectroscopy could be used to evaluate oxidation catalysts precursors. Further measurements are underway to simulate  $^{93}\text{Nb}$  wideline spectra in order to determine nuclear quadrupole coupling

constants and isotropic chemical shifts for  $^{93}\text{Nb}$  in crystalline niobium phosphate samples.

### Acknowledgements

The authors thank CNPq-PICS (2002) and CAPES-COFECUB (2003, Proc. 436/03) programs for support.

### References

1. K. Tanabe, *Catal. Today* **78** (2003) 65.
2. S.A. Holmes, J.A. Saeedi, V.V. Gulians, P. Boolchand, D. Georgiev, U. Hackler, E. Sobkow, *Catal. Today* **67** (2001) 403.
3. A.M.D. Farias, W.A. Gonzalez, P.G.P. Oliveira, J.G. Eon, J.M. Herrmann, M. Aouine, S. Loidant, J.C. Volta, *J.Catal.* **208** (2002) 238.
4. P.G. P. Oliveira, J.G. Eon, M. Chavant, A.S. Riché, V. Martin, S. Caldarelli, J.C. Volta, *Catal. Today* **57** (2000) 177.
5. M. Ziolk, *Catal. Today* **78** (2003) 47.
6. M.E. Smith, E.R.H. van Eck, *Progress in Nuclear Magn. Reson. Spectrosc.* **34** (1999) 159.