

# Effective acidities of catalysts based on Niobium Phosphate in relation with their catalytic activity in reactions of biomass conversion

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**Abstract:** The scope of this note is to clarify the concepts of *intrinsic* and *effective* acidity for heterogeneous acid catalysts working in liquids (water, hydro-alcoholic solutions, etc.) and relevant current methods of acidity characterization. Original techniques (spectroscopic, volumetric, and thermal with/without probe adsorption) to characterize acidity of solids at liquid-phase interfaces have to be refined to permit studying the nature, site-density and strength of the sites. Examples will be presented on niobium oxophosphate (NbP), a recognized *water-tolerant* solid acid catalyst, and some derived materials and on Nb-P-Si ternary oxides, recently emerged as interesting acid catalytic materials in reactions of biomass conversion.

**Keywords:** Solid acid catalysts, intrinsic and effective acidity, niobium oxophosphate.

## 1. Introduction

Because solid acids are environmentally friendly with respect to corrosiveness, safety, ease of separation and recovery, and they give less-waste, the replacement of liquid acids still used in acid-catalyzed processes with suitable solid acids is highly desirable in various traditional and novel domains like chemical industry, environmental catalysis, and biomass (carbohydrate) valorization.

In particular, for acid catalytic reactions in which water participates as a reactant/product or solvent (as hydrolysis, hydration, esterification, etc.), only few solid acids are acceptable in terms of activity, stability and insolubility. Therefore, important advantages follow the development of solid acid catalysts and aqueous heterogeneous catalysis. It is then necessary that the techniques for acid catalyst characterization be adapted to liquid environment, to determine the *effective* nature (LAS or BAS), site density, strength, and distribution of the acid sites in the same (or similar) liquids where the solid acids work [1]. Last but not least, the knowledge of the *effective* acid characteristics makes possible to establish sound acidity-activity relations when the catalyst works in water or in other liquids.

Herein, the successful use of the well-known niobium oxophosphate acid catalyst (NbP) and of several other catalysts obtained by acid modification of NbP is presented in the reactions of hydrolysis of cellobiose to HMF (5-hydroxymethylfurfural) with relationships with *effective* acidity. Furthermore, the *effective* acidity and activity in the reaction of inulin hydrolysis of a series of new ternary oxide catalysts (Nb-P-Si) recently emerged as interesting solid acids are also presented [2, 3].

## 2. Experimental

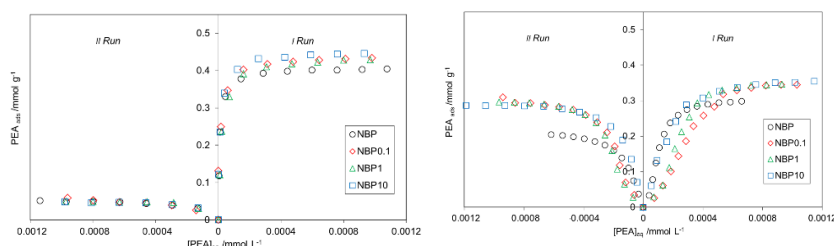
NbP was kindly supplied from CBMM, Brasil. Other samples obtained by acidic treatments of NbP with HCl (at 0.1 M, 1.0 M, and 10 M: NbP01, NbP1, and NbP10, respectively) have been studied. Another series of Nb-P-Si oxide samples constituted of Nb<sub>2</sub>O<sub>5</sub> and P<sub>2</sub>O<sub>5</sub> (1:1) in concentration from 2.5 to 10 mol% (and SiO<sub>2</sub> from 95 to 80 mol%) (2.5NbPS, 5NbPS, 7.5NbPS, and 10NbPS) has been studied. The *intrinsic* and *effective* nature of acid sites have been determined with FT-IR (Biorad, FTS-60A) experiments of pyridine desorption. The surface acid site strength has been measured with calorimetric experiments (Calvet Titrys calorimeter) in different liquids (cyclohexane, isopropanol, water, and their mixtures) by 2-phenylethylamine (PEA) as probe and volumetric experiments, by PEA adsorption isotherms, allowed the determination of the amount of acid sites in various liquids and liquid mixtures. The catalytic tests of hydrolysis of cellobiose (disaccharide of glucose, linked by  $\beta$ ,1-4 glycosidic bonds) and of inulin (polymer chain of fructose residues

linked by  $\beta$ -1,2 bonds and terminated with sucrose residue) have been realized under mild conditions (80-130°C) in liquid water with slurry reactor or with flow reactor working in continuous recirculation.

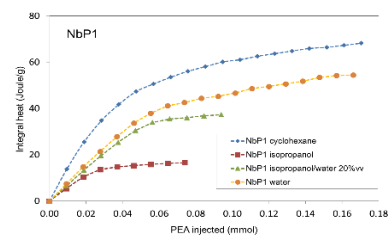
### 3. Results and discussion

The *intrinsic* and *effective* acid properties of NbP and of the derived samples (NbP01, NbP1, and NbP10) have been determined by titration in cyclohexane and water, respectively (Fig. 1) in an adsorption line comprising a HPLC [3]. A similar titration performed in a titration calorimeter in different liquids was realized (Fig. 2 shows the example of NbP1). *Effective* acid strength varied significantly in the different liquids, in water great part of the intrinsic acidity was maintained. The Brønsted or Lewis nature of the acid sites was determined with pyridine thermo-desorption experiments by FT-IR in vapor phase and in in solution. The results show that the surface of NbP possesses both water-tolerant LAS and BAS, without any significant modification of the LAS/BAS ratio determined in vapor and in water, while all the other samples have higher LAS/BAS ratio in water than in vapor (Fig. 3). The results of the catalytic tests of conversion of cellobiose to HMF and of hydrolysis of inulin in liquid water, confirmed the good acidity of all the studied acid catalysts. In cellobiose hydrolysis reaction, carried out at 130°C, towards glucose and low amount of fructose, HMF (5-hydroxymethylfurfural) was observed among the products. Low-temperature hydrolysis of inulin (50-90°C) gave fructose with very high selectivity. In this reaction, the higher activity of NbP than the other NbP-samples (Fig. 4) was justified the presence in the former of a higher amount of water-tolerant BAS..

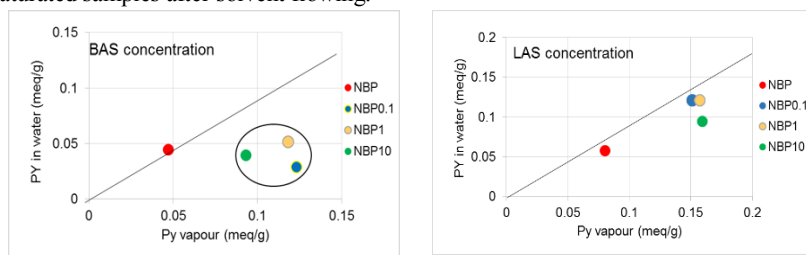
The series of Nb-P-Si oxides have different acid properties, in water they show much more BAS than LAS, this surface composition governed the catalytic activity of this catalyst series [2, 3].



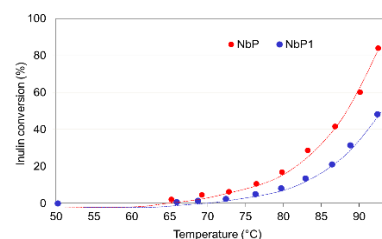
**Figure 1.** Acid-base volumetric titration of NbP and derived samples with PEA probe in cyclohexane (left) and in water (right). I run on fresh samples and II run on PEA-saturated samples after solvent flowing.



**Figure 2.** Acid-base calorimetric titration of NbP1 in different liquids.



**Figure 3.** Comparison between amount of Bronsted (left) and Lewis (right) acid sites of NbP and derived samples in vapor phase and in water, as determined by FT-IR with pyridine thermodesorption experiments.



**Figure 4.** Activity of NbP and NbP1 in inulin hydrolysis in water.

### 4. Conclusions

Acidity determination of catalysts under the environment in which they work (*effective* acidity) represents a challenge activity which will provide useful information for the catalyst optimization in given reactions.

### References

1. A. Gervasini, A. Auroux, *Thermochim. Acta*, 567 (2013) 8.
2. A. Aronne, A. Gervasini, et al. *J. Phys. Chem C*, 121(2017) 17378.
3. A. Aronne, A. Gervasini, et al. *Mol. Catal.* In press.