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Niobic acid and niobium phosphate as highly acidic viable catalysts in aqueous medium: Fructose dehydration reaction

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Abstract

The catalytic properties of niobic acid ($Nb_2O_5{\cdot}nH_2O$) and niobium phosphate ($NbOPO_4$) surfaces were studied in the reaction of fructose dehydration carried out in water. The reaction was performed in a continuous reactor at different temperatures 90–110 °C and pressures (from 2 to 6 bar). Superior activity and selectivity to 5-hydroxymethyl-2-furaldehyde (HMF) of niobium phosphate compared to niobic acid was observed. The initial higher catalytic performance of niobium phosphate than niobic acid could be related to the higher effective acidity of its surface, as was evidenced by acid–base titrations realized in different polar liquids. Deactivation studies showed a deeper decay for niobium phosphate than niobic acid at short time on stream, while, for higher time, light losses of activity were observed for both the catalysts.

Keywords: Niobic acid; Niobium phosphate; Solid acids; Heterogeneous catalysis; Fructose conversion; 5-Hydroxymethyl-2-furaldehyde (HMF)

1. Introduction

At present, a significant number of acid-catalyzed reactions (esterifications, hydrolyses, Friedel-Crafts reactions, and so forth) are still carried out with conventional homogeneous acids. Several problems, such as toxicity, corrosion, difficulty of separation and recover of products and catalyst, accompany the processes involving such conventional acids. Therefore, their replacement with solid acids is highly desirable in the chemical industry. Solid acids are environmentally friendly with respect to corrosiveness and safety, and their separation and recovery is very easy [1].

A peculiar problem is represented by the reactions involving water as reactant, solvent, or product. In water, or very highly protic medium, very few solid acids can maintain the desirable characteristics of activity and stability without deactivation of their acid sites. The development of insoluble water-tolerant solid acids are expected to give great benefits in industrial applications. In fact, the use of aqueous solutions of reactants includes various advantages: low cost, no inflammability, nontoxicity, safety. Although water requires more energy in the final separation steps, its recycling is less desirable than that of organic liquids.

Among the catalytic materials, zeolites, heteropoly compounds, oxides, phosphates, and resins can be envisaged [1–3]. For organic reactions in water, hydrophobic high-silica zeolites are the most active. The high acidity, low surface area, and water solubility properties of heteropolyacids can change by substitution of their protons by alkaline cations. Heteropolyanions-salts with large monovalent ions (e.g., Cs^+) have high surfaces, are insoluble in water, and showed high activity for acid-catalyzed reactions. Oxides and phosphates (e.g., silica-alumina, zirconium molibdate, zirconium phosphate, etc.) represent a wide class of acid solids which have been used in a variety of reactions (hydrolysis, esterifications, dehydrations). In this class of materials, niobium containing catalysts have found applications in several catalytic processes requiring strong acid properties even in aqueous phase. In particular, niobic acid ($Nb_2O_5{\cdot}nH_2O$, hereafter called NBO) and niobium phosphate ($NbOPO_4$, hereafter called NBP) materials have attracted great interest as catalysts, due to their strong acid properties which can be preserved in polar liquids [4,5]. The Brønsted acidity of niobic acid is very high ($H_0 \leq -5.6$), niobium phosphate has also

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acid properties ($H_0 \leq -8.2$) with a higher ratio of Lewis/Brønsted acid sites. The textural, acidic, and catalytic properties of NBP are superior to those of NBO, with the advantage that these properties are preserved at higher temperatures [6–10].

In a recent work [11], the intrinsic and effective acidity of NBO and NBP surfaces was studied by a multitechnique approach using different basic molecular probes and methodologies. The ''intrinsic'' surface acidities of the two solids, determined under vacuum or inert atmospheres, were compared with the ''effective'' acidities measured in liquids of different polarities and proticities. In the present work, the catalytic performances of the two surfaces are compared in the dehydration of fructose to 5-hydroxymethyl-2-furaldehyde (HMF) in aqueous phase. The catalytic activities measured in the reaction have been related with the effective acidities of the two surfaces. In the last decade, reactions of this type have attracted much attention because of the demand of renewable resources, such as biomass, as substitutes for mineral raw materials for production of various chemicals. HMF is a furanic monomer suitable for the preparation of polymers starting from nonpetroleum renewable resources [12,13]. Several studies have been reported in the literature on the performances of NBO and NBP as catalysts of dehydration of fructose, evaluated in batch conditions [14,15]. In these conditions, NBP catalysts showed good activity (around 30%) coupled with extremely high selectivity to HMF (around 90%) for short time of reaction (up to 30 min) with very low amounts of parallel by-products (levulinic and formic acids). For longer reaction times (1–2 h), the selectivity to HMF lowered. This behaviour could be attributed to the formation of polymeric by-products from HMF evolution. In the present investigation, the reaction of fructose dehydration to HMF, as main product, on the NBO and NBP surfaces was studied in aqueous medium in a continuous fixed bed tubular reactor. The development of valid catalysts able to work in a continuous process can be of relevant interest for a future industrial application of this reaction.

2. Experimental

2.1. Materials

D(−)-fructose (RPE C.Erba) was used as substrate.

The catalysts employed were $Nb_2O_5 \cdot nH_2O$ (NBO) and $NbOPO_4$ (NBP), supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM) in powder form. Their composition and main characteristics are reported in Table 1. The surface acidities reported in Table 1 were determined by using different physico-chemical techniques [11]: calorimerty–volumetry (gas–solid titration by ammonia adsorption), thermal desorption (TPD) (solid–gas desorption of different basic probes adsorbed on the catalyst surface, performed with a thermogravimetric (TGA) apparatus), and pulse liquid-chromatographic technique (liquid–solid dynamic titration by 2-phenyl-ethylamine (PEA) in different solvents, performed with a HPLC apparatus).

Before use, NBP and NBO samples were humidified during one night, pressed for 30 s at 2.9 t cm^{-2}, crushed in a mortar and sieved separating 20–45 and 45–100 mesh fractions. The samples were then dried in a rotative oven (Büchi GKR-50) at 150 °C and 20 mbar for ca. 90 h, to allow an exact mass evaluation of the amount of catalyst employed for each test.

2.2. Kinetic measurements

The kinetic tests of fructose catalytic dehydration to HMF were performed in a continuous reaction line (Fig. 1) equipped with: dosing pump (HPLC pump, Waters 501), stainless steel (AISI 316) pre-heater and fixed-bed tubular flow reactor (25 cm long, 0.6 cm internal diameter) with axial thermowell. Both the pre-heater and the reactor were assembled in an oven with forced circulation of hot air, kept at constant temperature.

The catalyst sample (3–4 g) was held in the middle of the reactor, between two sand beds. The aqueous fructose solution (ca. 0.3 M) was continuously fed into the catalytic reactor.

For each kinetic run, performed at fixed temperature, fresh catalyst was employed. The feed flow rate was randomly varied

Table 1
Surface properties of the NBO and NBP samples [11]

Catalyst	Composition [wt.%]		B.E.T. surface [$m^2 g^{-1}$]	Intrinsic acidity [μequiv g^{-1}]				Effective acidity [μequiv g^{-1}]	
				Ammonia adsorption		Thermal desorption		Pulse titration	
				n_{tot}[a]	n_{irr}[b]	PEA[c]	AN[d]	Cy[e]	Met[f]
NBO	Nb_2O_5 H_2O	80 20	108	222	131	251	76	207	71
NBP	Nb_2O_5 P_2O_5 K_2O	66.7 15.9 2.1	142	283	160	335	160	400	151

[a] Total amount of ammonia retained, determined at 0.26 mbar of equilibrium pressure.

[b] ''Irreversible'' amount of ammonia retained, determined from the difference between the amounts adsorbed in the first and second adsorptions at 0.26 mbar.

[c] Determined by 2-phenylethylamine (PEA) desorption.

[d] Determined by aniline desorption.

[e] Determined by 2-phenylethylamine (PEA) titration in cyclohexane.

[f] Determined by 2-phenylethylamine (PEA) titration in methanol.

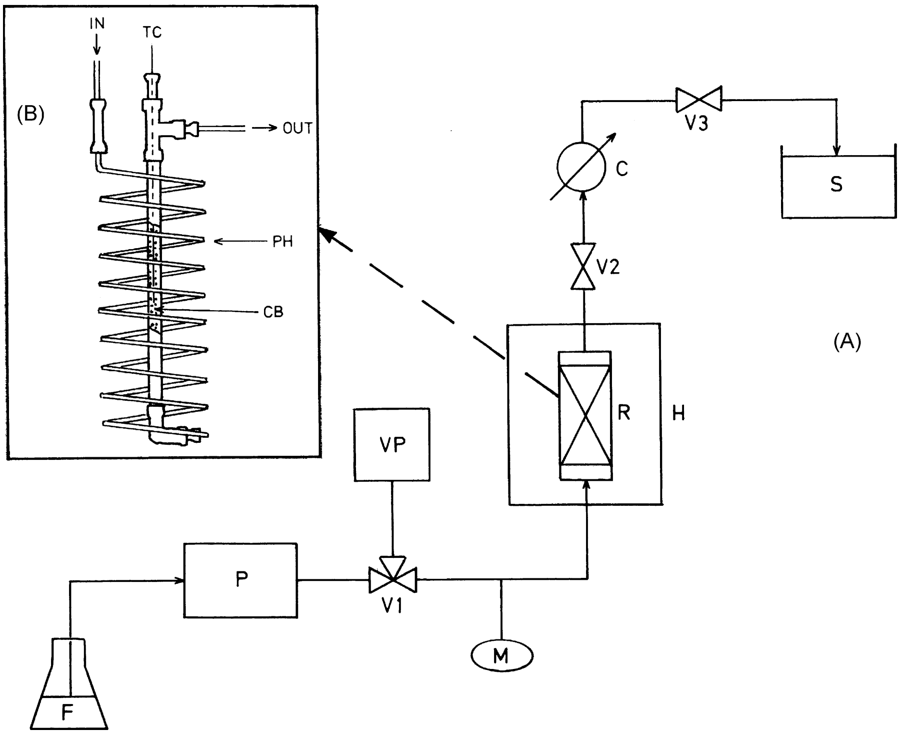

Fig. 1. Part A, scheme of the continuous reaction line used for the catalytic experiments: feed reservoir (F); dosing pump (P); vacuum pump (VP); manual three ways-valve (V1); manometer (M); catalytic reactor (R); oven (H); manual two ways-valve (V2); cooler (C); manual precision valve (V3); auto-sampler collector (S). Part B, scheme of the catalytic reactor with pre-heater (PH), thermocouple (TC), and catalytic bed (CB).

to obtain different contact times (from 5 to 55 min g ml^{-1}). After each change of flow rate, at least 60 ml of solution was left to flow before collecting samples for the analysis, so ensuring the stationary conditions to be obtained. At least three analyses were performed at each stationary point, averaging the results.

The reaction temperature was varied in the range 90–110 °C. The pressure in the reactor was kept between 2 and 6 bar by means of a micrometric valve at the end of the reaction line, to avoid the evaporation of water and the formation of gas bubbles in the catalytic bed.

The products were analysed in a liquid-chromatography apparatus (HPLC), consisting of injector (Waters U6K), pump (Waters 510), heater (Waters CHM) for the column, and refractive index detector (Waters 410). A Sugar-Pack I column operating at 90 °C and eluted with an aqueous solution of Ca–EDTA (10^{-4} M) was used.

2.3. Catalyst stability tests

The stability of both catalysts was tested at 100 °C with constant flow rate of fructose solution (0.09 ml min^{-1}) up to 200–230 h of time on stream, with the same procedure described above for the kinetic tests.

3. Results and discussion

3.1. Catalysts and characteristics

In Table 1, a summary of the main characteristics of the NBO and NBP catalysts studied is reported. It is known that the acid properties are the characteristic surface feature of both of the catalysts [4,16,17]. As it has been detailed in a recent paper [11], each surface possesses an intrinsic acidity (number of acid sites and their relevant acid strength) and can possess different effective acidities. The distinction between the intrinsic acidity of the solid and that effective becomes a topic of prominent importance when one aims to identify sound relationships between the catalytic activity and surface acidity for reactions carried out in liquid phase. In liquid phase, some of the acidic groups at the surface can interact with the solvent molecules in a manner which hinders their catalytic action.

In this perspective, the intrinsic and effective acidities of the NBO and NBP surfaces were examined by a multitechnique approach employing different basic probes [11]. In Table 1, a summary of the main results obtained is presented, focused on the number of total and strong acid sites titrated in different conditions. The intrinsic acidity was measured by adsorption (with ammonia probe) and thermal desorption (with aniline, AN, and 2-phenylethylamine, PEA, probes) methods, carried out under vacuum and inert atmosphere, respectively. By gas–solid ammonia adsorption, the total number of sites (n_{tot}) was determined from the first isotherm collected (assuming a 1:1 stoichiometry for the ammonia adsorption on the acid site). After evacuation, a second adsorption was performed and the difference between the amounts adsorbed in the first and second runs was used to estimate the irreversibly adsorbed amount (n_{irr}) corresponding to strong acid sites. Comparing the n_{tot} and n_{irr} values of NBP and NBO, a higher intrinsic acidity of NBP clearly emerged. By a different approach that studied the solid–gas desorption of base probes, the number of total and strong acid sites could be discriminated by using two differently basic probes that, after adsorption on the surfaces, were thermally desorbed. PEA (pK_a = 9.84) was able to titrate the totality of the acid sites and AN (pK_a = 4.58) titrated only the strongest acid sites. In this case too, NBP surface emerged as more acidic than NBO. The effective acidities were measured, by a liquid–solid dynamic titration, with PEA probe in liquids of different polarity and proticity (cyclohexane, 0.3 Debye, and methanol, 1.7 Debye). In cyclohexane, PEA titrated the total number of acid sites while in methanol only the strongest sites could be titrated by such basic probe. In conclusion, the higher intrinsic and effective acidity in high polar and protic solvent (methanol) of NBP surface than that of NBO clearly emerged. On NBP, a roughly double number of strong acid sites than NBO was titrated. In particular, the strongest acid sites of the NBO and NBP surfaces are essentially those able to strongly retain ammonia (n_{irr}) and they are similar in number to those titrated by AN in the thermal desorption experiments and to those titrated by PEA in methanol. The strong acid sites correspond roughly to 45 and 40% of the total acid sites for NBP and NBO, respectively.

3.2. Catalytic activity

The reaction of dehydration of fructose over solid acidic catalysts in water is known to be a complex reaction with parallel, consecutive and equilibrium steps [13–15,18–22]. The analytical method above reported (i.e., HPLC with a Sugar-Pack I column) is an easy and useful method for a quantitative analysis of fructose and HMF. However, it is not easy to recognize and quantitatively determine the presence of all the other reaction products, such as levulinic and formic acids as well as condensation products of fructose, as di-D-fructose dianhydrides, because of the overlapping of chromatographic signals. A more detailed analysis, of the collected samples, carried out by the use of other analytical methods (GC–MS, TLC, etc.) evidences that, among the possible di-D-fructose dianhydrides, the most abundant intermediate compound is β-D-fructofuranose β-D-fructopyranose 2,1′:3,2′-dianydride [23]. A deeper analysis as well as the kinetic interpretation of the reaction mechanism are in progress. In the present paper, the discussion of the catalytic results is focused on global conversion of fructose and selectivity to HMF.

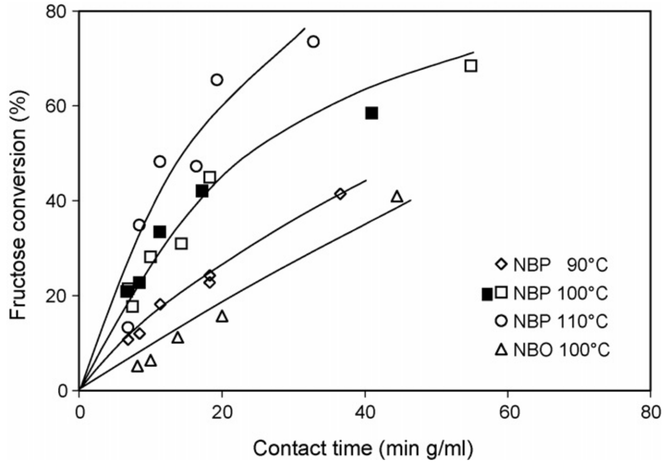

Fig. 2. Fructose conversion vs. contact time for the NBO and NBP catalysts at different reaction temperatures (particle size: 20–45 mesh, open symbols; 45–100 mesh, filled symbol).

Fig. 2 shows the trend of fructose conversion as a function of contact time, for the two catalysts under different experimental conditions. NBP was tested at three temperatures (90, 100, and 110 °C). As expected, the fructose conversion regularly increased with contact time as well as with temperature, attaining 70–80% at the more severe conditions, 100 and 110 °C. At 100 °C for NBP, runs with two different catalyst particle sizes, 20–45 and 45–100 mesh, were carried out. The obtained results were very similar indicating absence of diffusion phenomena on the reaction course in the used conditions. NBO showed a lower catalytic activity, being the conversion at 100 °C clearly lower than that of NBP at 90 °C.

However, the kinetic trend followed by the reaction seems to be the same with both the catalysts. Despite the complex reaction mechanism usually invoked for dehydration of fructose [13,18–20], a simplified interpretation can be done considering, as a first approximation, the fructose dehydration globally as a first-order reaction, as already done for analogous reactions [24]. The acceptable linear trend (linear correlation coefficient averaging around 0.95) obtained in every case when reporting $-\ln(1-y)$ versus contact time (where y indicates fractional conversion) supports the above approximation on the reaction order. The apparent rate coefficients obtained by linear regression are reported in Table 2. Apparent kinetic parameters (ln A and E_a) were also obtained for NBP with a good linear correlation coefficient (Table 2).

In Fig. 3, the selectivity to HMF as a function of fructose conversion is reported. A general increasing trend can be

Table 2
Apparent rate coefficients and kinetic parameters for the global reaction of dehydration of fructose

Catalyst	Size (mesh)	Rate coefficients (ml g^{-1} min^{-1})			Kinetic parameters
		90 °C	100 °C	110 °C	
NBP	20–45	0.0149	0.0229	0.0442	E_a (kJ mol^{-1}) = 65.8 ± 8.0, ln A[a] = 15.7 ± 1.9, r[b] = 0.986
	45–100		0.0251		
NBO	20–45		0.0108		

[a] A (ml g^{-1} min^{-1}).

[b] r, linear correlation coefficient.

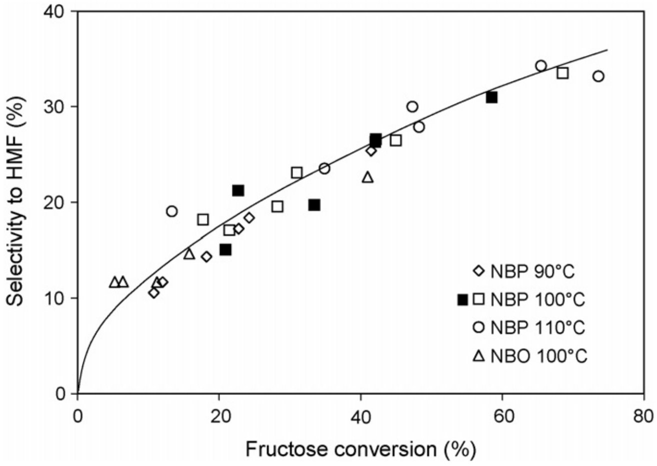

Fig. 3. Selectivity to 5-hydroxymethyl-2-furaldehyde (HMF) vs. fructose conversion for NBO and NBP catalysts at different reaction temperatures (particle size: 20–45 mesh, open symbols; 45–100 mesh, filled symbol).

observed; selectivity to HMF up to 30% was attained at about 80% fructose conversion. Such a trend suggests a reaction mechanism with formation of intermediate products, leading to HMF trough a consecutive reaction, or with a pre-equilibrium step involving fructose. Moreover, the trend shown in Fig. 3 is roughly identical for both the catalysts at the various temperatures studied. This indicates that the same mechanism might hold for both the catalysts.

Besides the evaluation of activity and selectivity, catalyst stability was also explored following the reaction for long time on stream, up to 200–220 h. A clear decreasing exponential trend of fructose conversion against reaction time was observed on NBP while a lighter decreasing trend was observed for NBO (Fig. 4). So, even if fructose conversion was markedly higher on NBP than NBO for short time on stream (up to ca. 50 h), the differences of activity between the two catalysts quite vanished for longer times (up to 200–220 h), where conversion values in the interval 15–20% were observed for both NBO and NBP. The reported behaviour is likely indicative of a fast deactivation of a part of the active acid sites of the NBP surface, in particular of the sites which are the most active and work with very high turnover. The remainder part of active sites on the NBO and NBP surfaces should be less sensitive to the deactivation effect. The loss of activity should be likely due to deposition of insoluble humines or coke on the catalyst surface The formation of humines is known to occur in this kind of reaction and it becomes significant after long reaction time [14,15,19]. Coke deposition on the surface of solid-acid catalysts utilized in analogous reactions of glucose in aqueous solutions was observed to be significant at temperature over 120 °C after a 24 h reaction time [24]. In our case temperature is lower, but time on stream is up to 250 h and also coke formation could occur. Humine and coke deposition on the catalyst surface is likely favoured on fixed bed of catalyst.

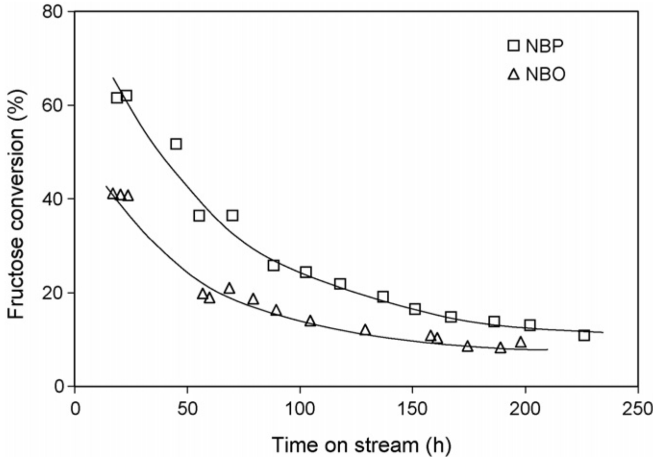

Fig. 4. Deactivation of NBO and NBP as a function of time on stream at 100 °C for the dehydration of fructose in water.

4. Conclusion

The superior catalytic performances of NBP surface, than those of NBO, in the dehydration reaction of fructose to HMF in water were already known and have been confirmed in this work. We can relate the positive catalytic activity of NBP to its higher intrinsic effective acidity, in terms of number of acid sites, that is maintained in highly polar and protic media.

Performing the reaction in continuous flow conditions, an interesting and unusual increasing trend of HMF selectivity with fructose conversion was observed. This behaviour was not observed in batch conditions where an opposite trend appeared, selectivity to HMF decreased as fructose conversion increased. The observed different behaviour of the dehydration reaction in flow and batch *operandi* method could be ascribed to secondary products that can more easily deposit on the catalytic surface in flow conditions and, on the contrary, could be continuously formed and removed from stirring in batch conditions.

In conclusion, the satisfactory activity, that remains satisfactory even if diminished at long time on NBP and on NBO too, together with the still active acid character in highly protic medium, indicate that these materials can be considered as interesting viable catalysts for reactions involving water or conducted in protic and polar media.

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