

Effect of protonation and deprotonation on surface charge density of Nb₂O₅

A thermodynamic approach

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Abstract The protonation and deprotonation of the Nb₂O₅ surface has been followed in order to understand the reactions of surface of this catalyst. The simultaneous potentiometric and conductometric titrations had been carried by using 50 mL of water suspension of Nb₂O₅ 40 g L⁻¹. The oxide was entirely deprotonated when adding 0.4 mL NaOH 1 mol L⁻¹, and later titrated with 0.1 mol L⁻¹. The titration had supplied K_1 and K_2 and the obtained values were 3.24×10^{-3} and 4.17×10^{-8} , respectively. The zero point charge was $\text{pH}_{\text{pzc}} = 4.94$. The thermodynamic studies were carried out by using 50 mL of a 40 g/L Nb₂O₅ aqueous suspension with the pH adjusted to pH_{PZC} value. The suspension was titrated with 0.5 mol/L of HNO₃ or NaOH for protonation or deprotonation studies, respectively, in an isoperibol calorimeter CSC ISC-4300. Thus, the obtained thermodynamic values of the protonation and deprotonation of Nb₂O₅ were $\Delta_{\text{dp}}G = -37.60$ kJ/mol, $\Delta_{\text{dp}}H = -23.72$ kJ/mol and $\Delta_{\text{dp}}S = 47$ J/(mol K).

Keywords Nb₂O₅ · pzc · Enthalpy of protonation and deprotonation

Introduction

The chemistry of niobium is not widely known. Over the years, many studies about its materials have been

increasing the interest in heterogeneous catalysis, where they are pure used, like promoters and supports. The characterization of these compounds has a great importance for discussing their catalytic activity and predicting their activity and selectivity in various reactions. Besides, Brazil produces around 210 ton/year, around 60% of the world production (2003) [1, 2].

The catalytic behaviors of Nb compounds are very distinct between their neighbors (V, Mo, and Zr), in spite of the small differences in electronegativity and ionic radius [3, 4]. Niobium compounds present phenomenological aspects of catalytic performance and surface structures when added in catalysts enhance the activity and selectivity, prolong catalyst life and exhibit a pronounced effect as supports of a known metal or metal oxide catalyst [3, 5]. In acid-catalyzed reactions, niobium presents high activity, selectivity, and stability in which water molecules participate, and the introduction of Nb₂O₅ of mixed oxides can increase its activity and selectivity, since its potential redox prolong properties of some metallic species as V, Cr, Mo, etc [2–7]. Because of its band gap energy (3.4 eV) near semiconductors sensibilized of UV radiation like as TiO₂, ZnO, Nb₂O₅ can be applied in photodegradation of organic wastewaters (pesticides, industrial effluents, and others) [8, 9].

As photocatalysis is a process that pH needs to be monitored, techniques like potentiometric and conductometric titrations contribute for understanding the reactions in oxide/electrolyte [10–12]. In this way, the aim of this article is to study the behavior of Nb₂O₅ because of its protonation and deprotonation in order to understand the surface reactions of this catalyst and observe its thermodynamic properties.

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Experimental

Surface area of Nb₂O₅

The metal oxide was dried in a vacuum line and its surface area characterization was analyzed in a BET Micrometrics ASAP 2020. According to Fig. 1, the surface area of Nb₂O₅ obtained was 145 m² g⁻¹.

Potentiometric and conductometric titrations

These experiments were carried out using 50 mL of a 40 g/L Nb₂O₅ aqueous suspension. The oxide was fully deprotonated by the addition of 0.4 mL of NaOH 1 mol/L. The solutions were titrated with a 0.1 mol/L HNO₃ solution. Surface charge density of Nb₂O₅ at any pH value was determined from *K* values by using the Eq. 4.

Thermodynamic titration

The thermodynamic studies were carried out by using 50 mL of aqueous suspension of Nb₂O₅ 40 g/L with the pH adjusted to pH_{PZC} value. The suspension was titrated with 0.5 mol/L of HNO₃ or NaOH for protonation or deprotonation studies, respectively, in an isoperibol calorimeter CSC ISC-4300. The heat corresponding to the difference in enthalpies of deprotonation and protonation ($\Delta_{dp}H$) was obtained by subtracting the heat obtained by base addition from heat obtained for the addition of acid. In the last step, this difference in heats was divided by the corresponding change in the extent of reaction [13].

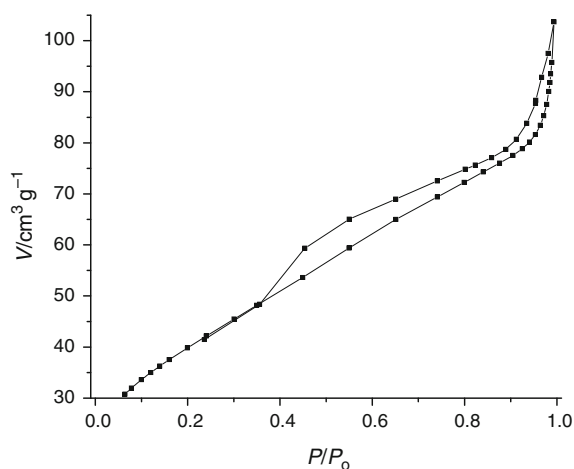
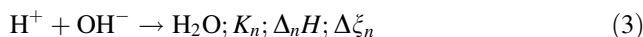
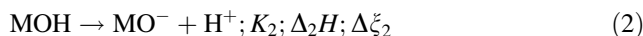


Fig. 1 Surface area analysis of Nb₂O₅

Results and discussion

Potentiometric and conductometric titrations

The electrostatic charge at a metal oxide aqueous interface is due to interactions of surface sites with potential for determining ions and is partially compensated by counterion association. Each surface reaction is accompanied by enthalpy changes, which are valuable information for characterizing the interfacial chemical and physical processes. According to the surface complexation model, the mechanism of surface charging will be interpreted by the 2-pK model which a metal oxide immersed in water is represented as an array of amphoteric sites which are treated as a diprotic acid. According to the following reactions will be considered [10–13]:



where *M* denotes metal at the solid surface, *K* the equilibrium constant for each reaction, ΔH the enthalpy for each reaction, $\Delta\xi$ the extent of reaction for each one. There are three kinds of superficial sites that most of them are MOH₂⁺ in strong acid medium, MO⁻ in strong basic medium and MOH, the intermediate amphoteric site, in pH_{pzc} region [14, 15]. According to this model, the surface charge density positive is characterized for pH < pH_{pzc} and negative for pH > pH_{pzc}. Using the relation between the hydronium concentration and the pH, the surface charge density of Nb₂O₅ can be written as [16]:

$$\sigma_0 = \frac{F}{A} \left(\frac{10^{-2\text{pH}} - K_1K_2}{10^{-2\text{pH}} + K_1 \cdot 10^{-\text{pH}} + K_1K_2} \right) N_T \quad (4)$$

where σ_0 is the surface charge density, *F* the Faraday constant, *A* the specific surface area, and *N_T* is the total number of moles of superficial sites. Equilibrium constants had been obtained by simultaneous potentiometric and conductometric titrations by using Henderson–Hasselbach equation. In this way, when $\sigma_0 = 0$, it means that it is the region of pH_{pzc} [16, 17]

According to Fig. 2, in the beginning the titration, the conductivity strongly decreased until the first equivalent point. Simultaneously, the potentiometric curve had a significant decrease because of the titration with strong acid due to the region of the sites MO⁻ which started to be protonated. The conductometric and potentiometric curves remained constant until the second equivalent point, due to the complete neutralization of the basic sites of MOH. After this point, the conductivity strongly increased, and the potentiometric curve decreased slowly, due to the excess of H₃O⁺ in solution. The simultaneous curve of

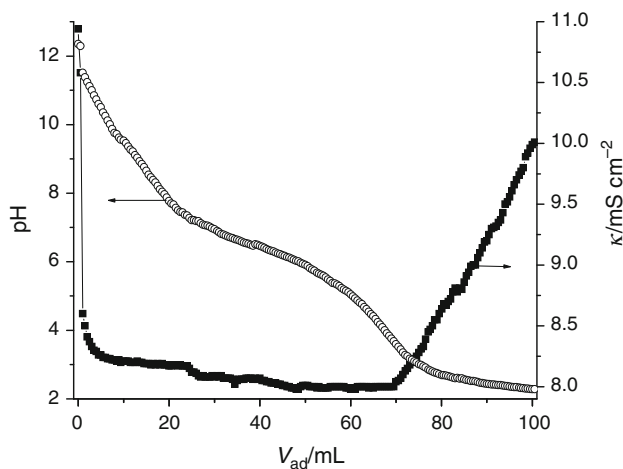


Fig. 2 Potentiometric and conductometric titration of Nb_2O_5

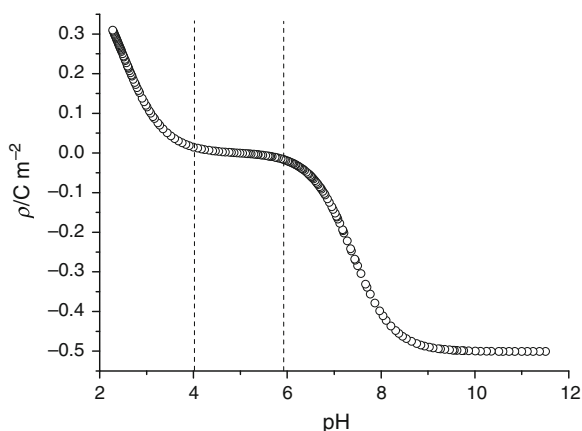


Fig. 3 Variation of surface charge density of Nb_2O_5 in function of pH values

potentiometric and conductometric titrations showed that K_1 and K_2 values were 3.24×10^{-3} and 4.17×10^{-8} , respectively. The zero charge condition at the surface occurred at point of zero charge (PZC), which is defined by $\sigma_0 = 0$. The point of zero charge (PZC) at 25°C was $\text{pH}_{\text{PZC}} = 4.94$ which was determined from $\text{p}K_1$ and $\text{p}K_2$ values (Fig. 3).

Calorimetry acid–base titrations

The enthalpy of any chemical reaction could be directly obtained by measuring the heat transferred from the reaction system to the surrounding at constant temperature and pressure. Reaction enthalpy could be also obtained from temperature dependency of an equilibrium constant of given reaction. The measurement of temperature dependency of the point of zero charge provides standard

reaction enthalpy and entropy, which values depend on the way how the reaction stoichiometry is expressed. Calorimetry data for surface reactions associated with charging of the interface cannot be simply interpreted since several reactions take place simultaneously and they are influenced by the electrostatic potentials [13].

The necessary correction for the neutralization heat reduces the accuracy of the results. Accordingly, it is suitable to minimize the extent of neutralization by using an acid to titrate the slightly acidic or neutral suspension. Analogously, a base can be used for titrating the basic region. Thus, it should also avoid the isoelectric region, i.e., the coagulation effects. In the case of titrations with concentrated acid or base, the dilution heat should also be taken into account. Evaluation of the (molar) enthalpies of surface reactions and electrostatic effects depends on the assumed mechanism of surface charging. At low ionic strength and also under conditions not far from zero surface charge, the heat effects, due to association of counterions, may be neglected.

The heat measured in calorimeter corresponds to the sum of the standard enthalpies of surface protonation and deprotonation reaction and neutralization [9]

$$Q_s = Q_m - Q_n = \Delta_p H \Delta \xi_p + \Delta_d H \Delta \xi_d \quad (5)$$

where Q_m , Q_n , and Q_s are the measured heat, heat of neutralization (calculated in a separated experiment), and heat associated with surface reactions, respectively. Reducing Eq. 5 [13]:

$$Q_s = (\Delta_d H^0 - \Delta_p H^0) \Delta \xi_d = \Delta_{dp} H^0 \Delta \xi_d \quad (6)$$

The compensation of the electrostatic effect will be more accurate if the initial and final pH values are closer to pH_{PZC} . According to Eq. 6, the difference between standard enthalpies of protonation and deprotonation reactions can be calculated by [13]:

$$\Delta_{dp} H^0 = \frac{Q_m - \Delta_n H \Delta \xi_n}{\Delta \xi_d} \quad (7)$$

Figure 4 clearly shows that while the pH increases until the pH_{PZC} , the reaction is characterized by an endothermic process. After this value, the curve decreases, showing an exothermic process. The difference from Gibbs energies of deprotonation and protonation were determined by using the equation $\Delta_{dp} G = RT \ln(K_p/K_d)$ and the corresponding entropy was obtained by using the equation $\Delta_{dp} S = (\Delta_{dp} H - \Delta_{dp} G)/T$ [13]. Thus, the obtained thermodynamic values of the protonation and deprotonation of Nb_2O_5 were $\Delta_{dp} G = -37.60$ kJ/mol, $\Delta_{dp} H = -23.72$ kJ/mol, and $\Delta_{dp} S = 47$ J/(mol K). The calorimetry analysis presented high thermal values in neutralization region (close pH_{PZC}) of Nb_2O_5 .

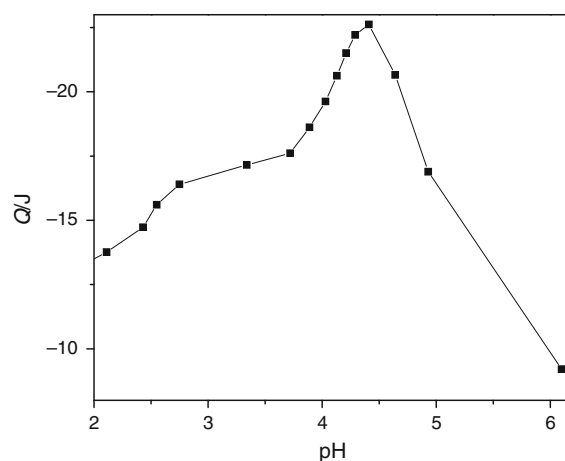


Fig. 4 Enthalpy of protonation and deprotonation of Nb_2O_5 in function of pH values

Conclusions

The thermodynamics data showed that between pH 4 and 5, it was observed the highest exothermic values of protonation and deprotonation of Nb_2O_5 surface. This fact is corroborated with the surface charge density and catalytic activity of Nb_2O_5 , which presented more effective catalytic results at pH around 5.

The obtained results showed the effect of pH on the electrostatic contributions to protonation enthalpy, entropy, and free Gibbs energy. All thermodynamic parameters were affected by electrostatic potential on the surface. On the other hand, the calorimetric experiments were based on the temperature dependency of an equilibrium parameter. Thus, the temperature dependency of pH of concentrated suspension provides interesting data about the electrostatic effect on interfacial thermodynamic parameters.

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