

Preparation and evaluation of zirconia microspheres as inorganic exchanger in adsorption of copper and nickel ions and as catalyst in hydrogen production from bioethanol

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Abstract

In this work, the preparation and performance of a zirconia microspheres inorganic exchanger in uptake of nickel and copper ammoniacal solution is showed. The yield of retention of the metallic ions was determined by inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES). Microspheres were characterized by X-ray diffraction (XRD), gas adsorption (BET). The catalyst of 6%Ni/3%Cu/ZrO₂ exhibits high activity for ethanol steam reforming with conversion of ethanol of 100% and selectivity of hydrogen of 60% at 550 °C. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The development of fuel cell technologies involves the storage of a liquid fuel, which would be easily transformed into hydrogen without polluting emissions. The production of H₂ from the steam reforming of alcohols could favor the use of hydrogen fuel, removing the difficulty of storage and distribution.

Alcohols exhibit high qualities as H₂ generations, since they are relative easily decomposed in the presence of water in a steam reforming reactor and generate a H₂-rich mixture suitable for feeding fuel cells. Many studies have been carried out on methanol steam reforming in last years [1–3], but little studies about ethanol steam reforming were published. Some considerations point to ethanol as an attractive alternative to methanol, although methanol presents a easily reform. The use of ethanol as fuel has received attention due to its lower toxicity [4], and it can be considered as a renewable raw material easily obtained from biomass [5]. Moreover, ethanol has a relatively high hydrogen content, and its reaction with

water under steam reforming conditions is able to produce 6 mol of H₂ per mole of ethanol reacted [6].

The production of hydrogen from steam reforming of ethanol can be attractive for countries with extensive plantation of sugar cane to produce important amounts of ethyl alcohol, like Brazil. Ethanol can be used, without any preliminary treatment, for hydrogen production if steam is reformed on appropriate catalysts.

The yield of hydrogen depends on the process variables such as temperature, reactants ratio and catalytic composition.

Much effort has been made to develop new catalysts for steam reforming of ethanol. Different catalysts have been studied for the steam reforming of ethanol.

Luengo et al. [7] have studied a nickel/copper/chromium catalysts supported on porous alumina from steam reforming of ethanol. The data obtained reveal high activity and good selectivity in H₂ and CO.

Mariño et al. [8] have studied the effect of different copper loading on catalytic behavior of Cu/Ni/K/Al₂O₃ catalyst from steam reforming of ethanol. They have found an acceptable performance to hydrogen at low temperature.

In a recent work, Klouz et al. [9] have studied the effect of the reaction temperature and water/ethanol ratio in the

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reforming process over Ni/Cu catalyst. The study allowed optimizing the experimental conditions in order to maximize hydrogen yield, to limit CO formation and carbon deposition and to propose a kinetic scheme.

Certain oxides and hydrous oxides (such as Zr, Mn, Al, Ti, Cr) have been utilized for many years principally due to their ability to act as substrate in adsorption or partition chromatography, and have proved to be excellent materials for a wide variety of analytical, preparative and industrial applications [10–13]. Inorganic ion exchangers have shown good thermal and radiation stability, and for this reason there is considerable interest in these materials in the atomic energy field [14,15]. They also show good resistance to oxidant agents, low solubility and anionic or cationic exchanger properties that depend on the solution acidity. They are easier and cheaper to prepare than the organic resins. As inorganic exchangers, they can be used in effluent treatments of nuclear fuel fabrication processes [16,17], in separation and purification of ^{99}Mo and recovery of valuables in industrial effluents [18]. Therefore, they have become of great interest in environmental projects. Moreover, inorganic oxides microspheres can be used as catalyst or catalyst supports [19].

Zirconia has been attracting attention as catalyst as well as catalyst support in recent years. Acid–base properties are one of the most important types of surface chemical properties of metal catalysts [20]. Zirconia has both acid and basic properties. This amphoteric character, in addition to its high thermal stability, makes ZrO_2 a promising catalytic material [21]. Are known to be chemically more stable than titania and γ -alumina [22]. The potential applications of zirconia are numerous in the ultrafiltration process and in the catalytic reaction systems for gas separations [23,24].

Zirconia shows ion exchange selectivities and exhibits both anionic and cationic characteristics. The anion capacity increases as the pH of the medium decreases while cationic exchange capacity increases as the pH increases. Then, the adsorption of cationic complexes of copper and nickel onto zirconia is affected by pH. Zirconia, like others hydrous oxides, has a very complex surface, which is dependent on pretreatment and chemical environment [25].

Unfortunately, zirconia is usually supplied as a powder. Although it can be used as small columns, for preparative operation or work with greater volumes, powder zirconia is not reliable, and does not perform well. In this work, a chromatographic zirconia was specially prepared as microspheres. These materials fitted well as bed for chromatographic columns. The zirconia microspheres have been prepared by hydrolysis process. This process is based on a homogeneous hydrolysis.

As an inorganic ion exchanger, the capacity of the zirconia microspheres is assayed using ammoniacal solutions of copper and nickel. The zirconia microspheres exhibit an excellent performance as chromatographic material.

The aim of this work is to study the retention of copper and nickel in ammoniacal solutions on zirconia microspheres

and use it in hydrogen production from steam reforming of ethanol.

2. Experimental

2.1. Microspheres preparation

Catalyst of ZrO_2 microspheres was prepared from the hydrolysis process in equipment showed in Fig. 1. A colloidal solution prepared with aqueous solutions of zirconium nitrates, urea and hexamethylenetetramine as gelation agent was sprayed as droplets directly into a column with warmed oil (95°C), and spherical ZrO_2 gel particles are formed directly by internal gelation. The solids spheres were washed with a ammonium hydroxide solution, dried and calcined at different temperatures (80 , 160 , 320 and 440°C). At end of this preparation procedure, the catalysts have been characterized through sphericity, size classification and crystalline phases identification. The effect of using different pretreatment conditions was examined in retention of ions nickel and copper, using zirconia microspheres.

2.2. Retention of copper and nickel

All reagents used in the process were analytical grade, nickel and copper nitrate salts used for analytes were

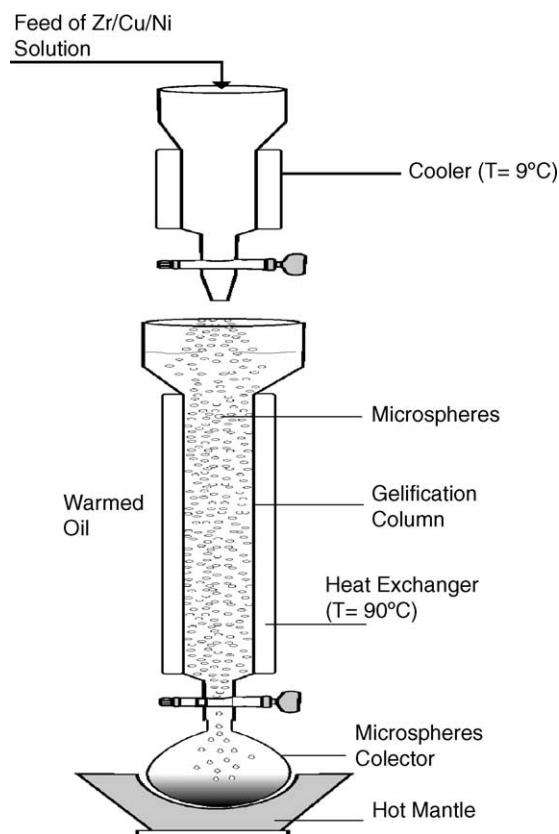


Fig. 1. Scheme of the equipment to microspheres preparation.

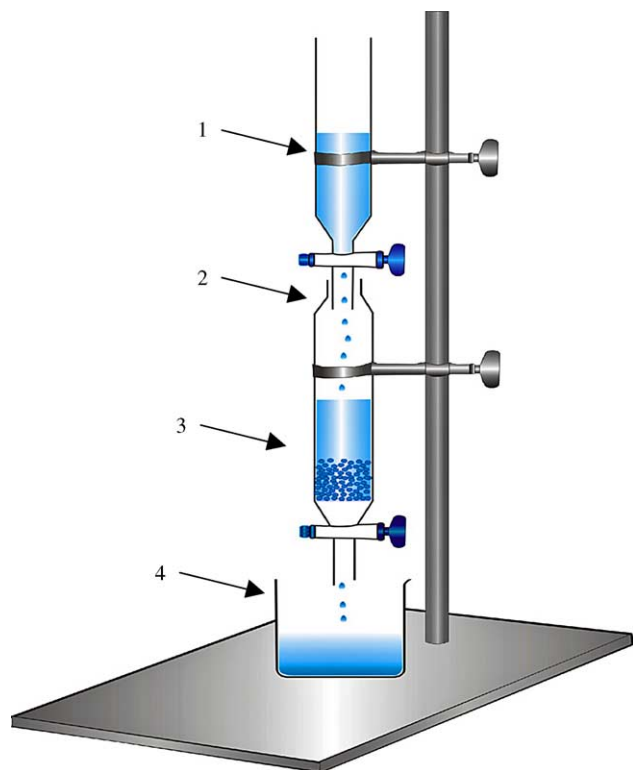


Fig. 2. Scheme of the chromatographic column: 1, metallic ions in solution; 2, chromatographic column; 3, zirconia microspheres and ions metallic adsorb; 4, metallic ions not adsorbed.

analytical reagent grade. For ion exchange experiments, the chromatographic column technique was employed. Glass columns (8 mm in diameter) were prepared and 10 g of zirconia microspheres was employed in each bed column shown in Fig. 2. Ammoniacal solutions of copper and nickel in pH 12 were used for retention of these elements in a support. The concentration of this solution $0.6 \text{ g L}^{-1} \text{ Cu}$ and $1.2 \text{ g L}^{-1} \text{ Ni}$ was selected to obtain 3.0 and 6.0% of the copper and nickel, respectively, onto the support.

Determination of adsorption characteristics of this substrate for copper and nickel was carried out under dynamic conditions.

These columns were conditioned with 500 mL of ammonium hydroxide 1 mol L^{-1} . The rate of addition of solution was $1 \text{ mL min}^{-1} \text{ cm}^{-2}$.

It has been studied the retention of copper and nickel solution and simultaneous retention of both elements. Zirconia microspheres after adsorption with Ni and Cu were calcined at $450 \text{ }^\circ\text{C}$ for 4 h.

2.3. Apparatus and test conditions for hydrogen production

A distilled water/ethanol reactant solution (with molar ratio of 3:1) was prepared and introduced into a reservoir. An electrically heated quartz tube served to vaporize and preheat the stream. The reactor pressure was maintained at 1 atm. The reagents inlet flow was controlled by a peristaltic pump, in order to operate at 1 mL min^{-1} . All reaction temperatures were regulated by means of chromo-alumel thermocouples and electrical resistances. The reaction mixture was vaporized and introduced into a fixed linear quartz microreactor (10 mm diameter) and passed over the catalyst bed contained about 8.0 g of each catalyst (ZrO_2 , Cu/ZrO_2 , Ni/ZrO_2 and Ni/Cu/ZrO_2), centrally positioned within the reactor. Fig. 3 shows a simplified scheme of the experimental procedure.

2.4. Analytical procedures

The chemical composition of solution contained ions Cu and Ni was determined by inductively coupled plasma atomic emission spectroscopy analysis (Spectro Flame M 120E – Spectro Analytical).

The X-ray powder diffraction (XRD) was applied to identify the crystal phases using a Rigaku X-ray diffraction

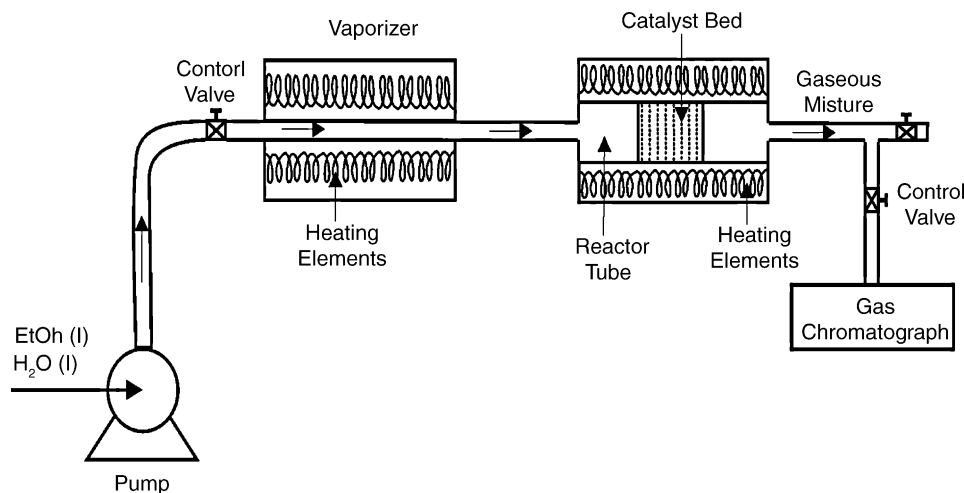


Fig. 3. Scheme of ethanol steam reforming process.

equipment. Phase identification was done using the reference database JCPDS-files.

The surface area of each catalyst was determined according to the Brunauer–Emmett–Teller method (BET) by nitrogen adsorption using a micrometrics ASAP 2010 instrument.

The composition of the output stream was analyzed by gas chromatography. A Shimadzu GC-14B equipped with a TCD detector and Porapack Q column were used to analyze the conversion of the ethanol. Molecular sieve 5A column was used to determine CO, CO₂, CH₄ and H₂ compositions.

3. Results and discussion

3.1. Chemical composition

In the present work, zirconia microspheres were obtained by hydrolysis process and the catalyst was prepared by the chromatographic technique. Glass column (8 mm in diameter) were prepared and 10 g of zirconia microspheres according to the burn temperature 80, 160, 320 and 440 °C was employed in each bed column.

Table 1 shows the chemical composition of the effluent of copper and nickel (not retained in zirconia microspheres) determined by inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES).

It is observed in the Table 1 that the capacity of retention of the metallic ions decreases with the increase of the temperature. The zirconia microspheres submitted to the temperature of 80 °C have been shown with larger capacity of retention of the metallic ions in compared to the microspheres submitted in the other temperatures, indicating that in low temperatures, the support of zirconia possesses a porous structure with great retention capacity.

Adsorption velocities have a decisive effect on retention of the elements. Greater velocities than 1 mL min⁻¹ produces a lost of significant amount of copper and nickel, due to tendency of the inorganic exchanger in absorbing the metallic ions slowly, thus larger velocities cause losses of the elements and generate larger amount of effluents.

3.2. Structural characteristics of catalysts

3.2.1. BET surface area measurements

Table 2 shows the effect of the surface area, of the different catalysts after calcinations at 450 °C for 4 h and the selectivity

Table 1
Chemical composition of the effluent Ni and Cu determined by ICP-AES

Temperature (°C)	Elements (ppm)	
	Ni	Cu
80	179.9	6.9
160	308.3	31.4
320	312.8	55.4
440	361.2	78.5

Table 2

Pore structure data of zirconia based catalysts after calcining at 450 °C for 4 h and selectivity of hydrogen

Catalyst	S-BET (m ² g ⁻¹)	EtOH conversion (%)	S (H ₂)
Pure ZrO ₂	42.8	100	28
6%Ni/ZrO ₂	45.5	100	33
3%Cu/ZrO ₂	47.8	100	38
6%Ni/3%Cu/ZrO ₂	87.43	100	60

of hydrogen at temperature 550 °C and H₂O/EtOH molar ratio 3:1.

It is interesting to note that the heat treatment under the same conditions shows different results. The surface area and pore volume in the catalysts system Ni/Cu/ZrO₂ are larger than that of pure ZrO₂ calcined at the same temperature. These results suggest that Ni and Cu increase the surface area and pore volume, improves the thermal stability of support ZrO₂. From the results, it was observed that ethanol is completely converted over temperature 550 °C and the selectivity of hydrogen for the systems catalytic pure ZrO₂, 6%Ni/ZrO₂, 3%Cu/ZrO₂ were 28, 33 and 38%, respectively, while the selectivity for system 6%Ni/3%Cu/ZrO₂ was 60.0%. This system catalyst (6%Ni/3%Cu/ZrO₂) was chosen for the next experiments.

3.2.2. X-ray diffraction analysis

Fig. 4 shows the X-ray diffraction patterns of the catalysts prepared by simultaneous retention of nickel and copper and calcined at temperature 900 °C for 4 h. It was observed that the catalysts had a crystalline structure.

It can be seen that for copper loading to 2.0 wt%, no peak corresponding to CuO is detected; however, the existence of Cu/ZrO₂ can be not discarded. Metal oxide phase can be determined with certainty only with the catalysts containing more than 3.0 wt% of the transition metals. The peak 28.3 refers zirconia and exhibit monoclinic phase structure, after heat treatment at 900 °C. The peak of nickel showed as possible present phase NiO ($2\theta = 45.5$) and NiZrO₂ ($2\theta = 35.4$ and 65.68).

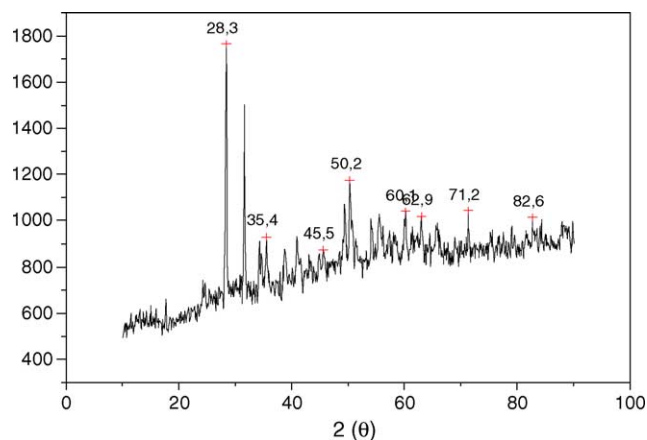


Fig. 4. X-ray diffraction patterns of 6%Ni/3%Cu/ZrO₂ catalysts.

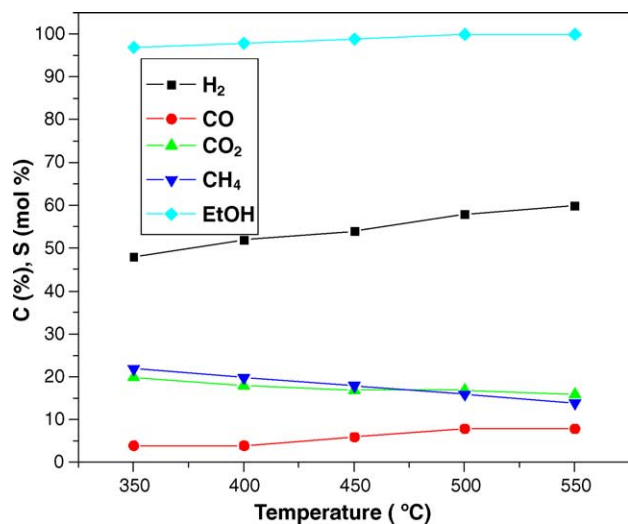


Fig. 5. Effect of reaction temperature on conversion ethanol and on selectivity of H₂, CO, CO₂ and CH₄, obtained over the 6%Ni/3%Cu/ZrO₂ catalyst. Experimental conditions: H₂O/EtOH mol ratio 3:1.

3.3. Catalytic tests

The steam reforming of ethanol was conducted with 6%Ni/3%Cu/ZrO catalysts prepared by method of inorganic exchange.

3.3.1. Effect of temperature on selectivity of hydrogen

The molar ratio water/ethanol is initially fixed to 3/1 according to work with an excess of water than stoichiometry of steam reforming reaction.

The results obtained are presented in Fig. 5, for 6%Ni/3%Cu/ZrO₂ catalyst, in which the selectivity of each product and the conversion of ethanol are shown as a function of reaction temperature in the range 350–550 °C. With increase of the temperature, the conversion of ethanol increased. The conversion of ethanol reached 100% when the temperature was 550 °C.

At temperature 350 °C, the selectivity of hydrogen, methane, carbon dioxide and carbon oxide are 48, 22, 20 and 4%, respectively. When the temperature increase from 350 to 550 °C, the selectivity of hydrogen increased from 48 to 60%, while the selectivity of carbon dioxide and methane kept decreasing from 20 to 16% and from 22 to 14%, respectively. The selectivity of carbon monoxide increased from 4 to 8%.

3.3.2. Effect of the molar ratio of H₂O/EtOH on hydrogen selectivity

Fig. 6 shows the effect of the water and ethanol (H₂O/EtOH) molar ratio on reforming performances at 550 °C, using the system catalysts 6%Ni/3%Cu/ZrO₂.

The H₂O/EtOH molar ratio plays an important role in products selectivity. It can be observed that ethanol was totally converted at temperature values (550 °C) independent of the H₂O/EtOH molar ratio.

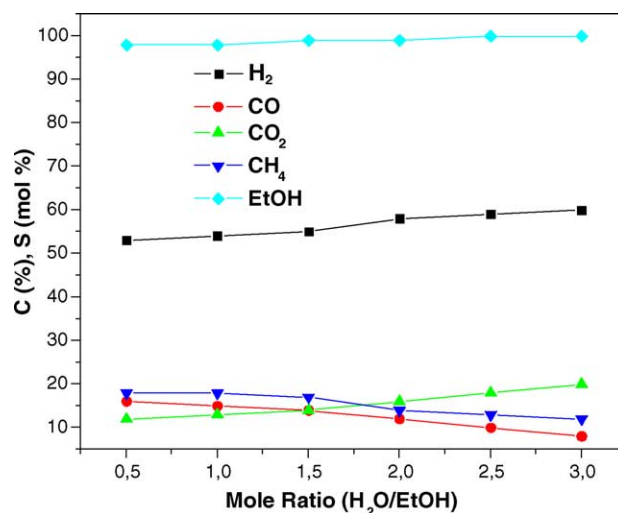


Fig. 6. Effect of mol ratios of H₂O/EtOH on the selectivity of H₂, CO, CO₂, CH₄ over the 6%Ni/3%Cu/ZrO₂ catalysts. Experimental conditions: temperature = 550 °C.

The results obtained indicate that by decreasing the H₂O/EtOH molar ratio, the selectivity to hydrogen and to carbon dioxide increases and the selectivity to methane remain almost constant. Moreover, the most significant effect upon increasing water content is increase of the H₂ and decrease of the CO production. This was rather expected from the water gas shift equilibrium displacement, as it strongly moves towards the CO₂ formation with the consequent increase of H₂ and the decrease of the CO concentration.

4. Conclusions

The aim of this process was the preparation of a catalyst by copper and nickel retention on zirconia microsphere and the hydrogen production by steam reforming of ethanol using the proposed catalyst.

Zirconia microspheres prepared by hydrolytic process and dried at 80 °C showed a good performance for use as inorganic exchanger in the adsorption of ammonium complexes of copper and nickel.

Steam reforming of ethanol was carried out in 550 °C and H₂O/EtOH molar ratio 3:1. Water/ethanol mixtures are perfectly suited for hydrogen production and may showed an advantage over pure ethanol because of the lower cost. Further on, water is a co-reactant in the reforming process.

In these experiments, a ZrO₂, 6%Ni/ZrO₂, 3%Cu/ZrO₂ or 6%Ni/3%Cu/ZrO₂ microspheres, were used as catalysts. It can be observed that the surface area increases in presence of the 6%Ni/3%Cu/ZrO₂ and this composition increased the hydrogen yield in a ethanol steam reforming. 6%Ni/ZrO₂ and 3%Cu/ZrO₂ microspheres showed practically the same behavior. ZrO₂ microspheres showed a lower catalytic activity.

This result can be optimized with a study of better simultaneous retention of nickel and copper on the zirconia microspheres.

Finally, it can be concluded that high temperature (550 °C), higher water ethanol molar ratio (3:1) promote, on 6% Ni/3% Cu/ZrO₂ catalyst, high hydrogen yield (60%). This catalyst is a good choice to be used in ethanol steam reforming processors for fuel cell applications.

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References

- [1] B. Lindström, L.J. Petterson, *J. Power Sources* 106 (2002) 264.
- [2] Y.-W. Suh, S.-H. Moon, H.-K. Rhee, *Catal. Today* 63 (2000) 447.
- [3] B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, *Appl. Catal. A: Gen.* 179 (1999) 21.
- [4] G. Maggio, S. Freni, S. Cavallaro, *J. Power Sources* 74 (1998) 17.
- [5] S. Freni, S. Cavallaro, N. Mondello, L. Spadaro, F. Frusteri, *Catálisis Commun.* 4 (2003) 259–268.
- [6] T. Ioannides, *J. Power Sources* 92 (2001) 17–25.
- [7] C.A. Luengo, G. Ciampi, M.O. Cencig, C. Steckelberg, M.A. Labore, *Int. J. Hydrogen Energy* 17 (9) (1992) 677–681.
- [8] F.J. Mariño, E.G. Cerrella, S. Duhalde, M. Jobbagy, M.A. Laborde, *Int. J. Hydrogen Energy* 23 (12) (1998) 1095–1101.
- [9] V. Klouz, V. Fierro, P. Denton, H. Katz, J.P. Lisse, S. Bouvot-Mauduit, C. Mirodatos, *J. Power Sources* 105 (2002) 26.
- [10] M.J. Fuller, *Chromatogr. Rev.* 14 (1971) 45.
- [11] J.L. Collins, B.Z. Egan, Development and testing of spheroidal inorganic sorbents, ORNL, TTP no. OR16C342, 1998.
- [12] J.A. Anderson, C.A. Fergunsson, *J. Non Crystalline Solids* 246 (1999) 177.
- [13] J.A.J. Rodrigues, M.A. Zacharias, A.R. Aquino, S.M.R. Rocha, *Eclética Química* 15 (1990) 41.
- [14] S. Yamagishi, *J. Nucl. Mater.* 254 (1998) 14.
- [15] G. Ledergerber, F. Ingold, *Nucl. Technol.* 114 (1996) 194.
- [16] H. Mimura, *J. Nucl. Sci. Technol.* 34 (5) (1997) 484.
- [17] W.R. Santos, “Preparação de Microesferas de Alumina por Processo Hidrolítico, Aplicação como Trocador Inorgânico em Cromatografia de Coluna”, Dissertação de Mestrado, Instituto de Química da Universidade de São Paulo, 1981.
- [18] F.M.S. Carvalho, “Três Novas Reações Seletivas para a precipitação de Mo(VI)—Processo Alternativo para a Separação e Purificação de Molibdênio”, Tese de Doutorado, Instituto de Química da Universidade de São Paulo, 1995.
- [19] Mel Cat. Doc.1010, Zirconium Compounds for Catalysis, Product Information.
- [20] K. Tanabe, M. Misano, Y. Ono, H. Hattori, *New Solid Acids and Bases*, Kodansha, Tokio, 1989.
- [21] T. Yamaguchi, *Catal. Today* 20 (1994) 199.
- [22] R. Bhave, *Inorganic Membranes, Synthesis, Characterization and Properties*, Van Nostrand Reinhold, New York, 1991.
- [23] A. Labort, J.P. Fabre, C. Guizard, L. Cot, J. Gillot, *New inorganic ultrafiltration membranes: titania and zirconia membranes*, *J. Am. Ceram. Soc.* 72 (2) (1989) 257–261.
- [24] C.H. Chang, R. Gopalan, Y.S. Lin, A comparative study on thermal and hydrothermal stability of alumina, titania and zirconia membranes, *J. Membr. Sci.* 91 (1994) 27–45.
- [25] L. Lindwist, *Acta Chim. Scand.* 5 (1951) 568.