

Performance of catalysts with Nb₂O₅ for hydrogen production from ethanol steam reforming

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ABSTRACT. Cu/Nb₂O₅ and Cu/Nb₂O₅/Al₂O₃ were studied as catalysts in ethanol steam-reforming for hydrogen production. They were prepared through impregnation, with different copper and Nb₂O₅ concentrations. Cu/ZnO/Al₂O₃ (G66), a commercial catalyst for methanol reforming was used for comparison. Temperature-programmed reduction data showed incomplete reduction of the copper, resulting in two reduction peaks, in opposition to CuO bulk, whose reduction occurred in one step (only one peak), it evidences a copper modification through Nb₂O₅. Results of diffuse reflectance spectra also evidenced the interaction. The catalytic tests showed that the niobium oxide dispersion on alumina improved the catalyst action; the ternary catalysts are the ones that show higher hydrogen production. They also produce ethyl ether as side product. The binary catalysts don't present parallel reaction, probably because when Cu/Nb₂O₅ is dispersed on alumina there is another type of catalytic site production, which produces ethyl ether.

Key words: ethanol steam reforming; hydrogen production; Cu/ Nb₂O₅ catalysts.

RESUMO. Desempenho de catalisadores com Nb₂O₅ para produção de hidrogênio a partir da reforma de etanol com vapor d'água. Reforma de etanol com vapor d'água, para produção de hidrogênio, foi estudada sobre catalisadores Cu/Nb₂O₅ e Cu/Nb₂O₅/Al₂O₃. Eles foram preparados por impregnação, com diferentes concentrações de cobre e Nb₂O₅. Um catalisador comercial, Cu/ZnO/Al₂O₃ (G66), de reforma do metanol, foi usado para comparação. Dados de redução à temperatura programada mostraram incompleta redução do cobre, com formação de dois picos de redução diferentemente do CuO mássico, cuja redução ocorre em uma única etapa (somente um pico), evidenciando que o cobre é modificado ao ser suportado sobre Nb₂O₅. Resultados de espectroscopia de reflectância difusa também evidenciam a interação. Testes catalíticos mostraram que a dispersão do pentóxido de nióbio sobre alumina melhorou a ação do catalisador, uma vez que os catalisadores ternários são os que apresentam maior produção de hidrogênio, apesar de também produzirem éter etílico como subproduto. Os catalisadores binários não catalisam reações paralelas, provavelmente, porque, quando Cu/Nb₂O₅ está disperso sobre alumina, há formação de um novo sítio ativo o qual produz éter etílico.

Palavras-chave: reforma de etanol com vapor d'água, produção de hidrogênio, catalisadores Cu/Nb₂O₅.

Introduction

Nowadays, the main difficulty on hydrogen utilization is its production cost. In this context, a cheaper production alternative could make viable the hydrogen utilization in fuel cells. The interest on fuel cells has increased. Nowadays, they use methane as hydrogen source, through reforming. Their problems are: high reaction temperature and the necessity of another reaction system to convert CO on CO₂; moreover, methane is a fossil fuel. The hydrogen production through methanol steam reform is a cheap and easy process, which is already

being tested (Ma *et al.*, 1996). This process has advantages like: low reaction temperature; no CO on the products; the supply is done with liquid fuel. In countries like Brazil, where ethanol is very cheap and made by biomass, it is interesting to study an alternative for methanol substitution by ethanol.

Due to the growing world energy demand, a diversification on energy sources is foreseen. With the fuels diversification, a renewable source, such as ethanol, becomes particularly attractive. Compared with methane or methanol, which are capable to produce hydrogen from steam-reform, its advantages are clear: ethanol is liquid, has low toxicity and its production is simple and cheap,

specially in countries like Brazil. In spite of that, the literature supplies little information regarding this reaction. However, publications are growing in the last years. Thermodynamic analysis has been done by some authors (Garcia and Laborde, 1991; Vasudeva *et al.*, 1996; Freni *et al.*, 1996) who have contributed to a better understanding of ethanol steam reforming. So, Vasudeva *et al.* (1996), who make a complementary work of Garcia and Laborde (1991), shows that hydrogen production is improved by water - ethanol mole ratio high (higher than stoichiometric) and temperature of 900K. Equilibrium hydrogen yields as high as 5.5 mole per mole of ethanol in the feed are obtainable against the stoichiometric value of 6.0. It was also concluded that the reaction happens in two stages: first, the decomposition of ethanol on CO and H₂ and later, the reaction of CO with steam (shift reaction), similar to methanol steam-reform.

The methanol reform reaction for H₂ industrial production uses Cu/ZnO/Al₂O₃ as catalyst; its active phase is formed through Cu-ZnO interaction. Authors like Pan *et al.* (1988), and Sengupta *et al.* (1989), believe that Cu⁰ is the active site, while zinc oxide has only the function of reverting copper sinterization. Other authors, however, accept that Cu⁺¹ dispersed on zinc oxide is the active phase (Herman *et al.*, 1979; Mehta *et al.*, 1979; Machado and Schmal, 1995).

Machado, 1995, showed the importance of the copper-semiconductor interaction in the active site generation for methanol steam reforming. Nb₂O₅ and TiO₂ were used to investigate the metal-semiconductor interaction of catalysts in methanol reforming, compared to ZnO, which is found in the commercial catalyst. Both Nb₂O₅ and TiO₂ present a semiconductivity generating property similar to ZnO. The results showed that the interaction between copper and semiconductor is responsible for the active site generation, which was checked through accomplished characterizations, as well as catalytic tests. Analyses of DRS (Diffuse Reflectance Spectra), TPR (Temperature Programmed Reduction) and XPS (X-Ray Photoelectron Spectroscopy) showed that the interaction begins form in the stage of the precursor calcinations, and it is completed in the reduction stage. In another work, Machado *et al.* (1996), analysed Cu/Nb₂O₅ catalysts with copper concentration varying between 5 and 22%, evidencing that the interaction between Cu and Nb₂O₅ produces the active site for the reaction. It was observed a correlation between copper contents and catalytic activity. Catalyst with lower copper content showed higher activity,

probably because of the smaller size of copper crystals, or because of the more exposed interaction copper-semiconductor. The use of those catalysts by Machado, in the ethanol reform, showed a similar action when compared with the methanol reform. However, the activity was lower, because by-products have been found when ethanol is the reagent.

Although there are some reports on ethanol reforming, the authors have not tried to compare the results with methanol reform, for they have not used semiconductors oxides among the studied supports. Like the work of Haga *et al.* (1997), which studied the role of the support in cobalt catalysts, finding better H₂ selectivity when alumina was the support, but they do not produce CO₂ as the other products. Mariño *et al.* (1998), also produce H₂ on ethanol reforming, but using Cu-Ni catalysts with different supports there is also CH₄, CO₂, CO, C₂H₄O and (C₂H₅)₂O production.

This present paper is part of a study aiming to develop catalysts for ethanol reforming. The choice of Cu-Nb₂O₅ catalysts was based on a methanol reforming catalyst, Cu/ZnO/Al₂O₃. In this work, ZnO was substituted for Nb₂O₅, which has similar semiconductor properties.

Material and methods

With a previous knowledge (Machado and Schmal, 1995) that Nb₂O₅ is a substitute for ZnO in catalysts for methanol steam reforming, several catalysts were prepared through impregnation and tested in ethanol steam reforming, for hydrogen production. So Cu/Nb₂O₅ and Cu/Nb₂O₅/Al₂O₃ were prepared, always through wet impregnation.

The binary catalysts were prepared from Cu(NO₃)₂·3H₂O P.A., VETEC (98%) solution and Nb₂O₅ (Nb₂O₅·nH₂O from CBMM, treated at 873K/4h on oxides atmosphere), in three different copper concentrations (3, 5 and 10%). The ternary catalysts were prepared through successive impregnation. At first Nb₂O₅ was impregnated in commercial aluminium oxide (Al₂O₃, 90, Merck) through an ammonium oxaloniobate solution (from CBMM). Water was evaporated on a shaker at 353K, after the precursor was dried for 24h/373K and calcined at 873K/4h on oxides atmosphere. Being impregnated later with a Cu(NO₃)₂ solution, as the binary ones, but with different copper concentrations (10% and 15%). After copper impregnation, all the catalysts were calcined at 648K/5h. A commercial catalyst, Cu/ZnO/Al₂O₃ (G66), was used for comparison.

A study to establish a kinetic control previously was carried out using a commercial catalyst. A space velocity that guaranteed no mass transfer on process was established. For the catalytic tests, a micro-unit was used, with an U-shaped glass reactor. A mixture containing 100 mg of catalyst and 400 mg of silica was introduced in the reactor. The silica functioned as inert to avoid aggregation and the simple packing of the catalyst during the activation. The catalysts were activated in flow of H₂-N₂ mixture (40% H₂), VHSV = 6X10⁴ cm³/h/g_{cat} at 573K/4h. After 4 hours on activation, the reaction began, in the same temperature, 573K, by introducing a mixture of ethanol and water with molar ratio H₂O/C₂H₅OH=1 and VHSV = 480 cm³/h/g_{cat}. After a steady state was set up, a liquid product sample was collected on 15min intervals, and the mass flow rate was determined. Gas flow was followed by a gas flowmeter and collected, too. The products were analysed on gas chromatography (Porapak Q column, VARIAN 3300).

The analyses of atomic absorption were accomplished in Varian spectrometer, AA PLUS. For the analyses of TPR, equipment built in DEQ/UEM (Chemical Engineering Department/ Universidade Estadual de Maringá) was used, with a heating rate of 10K/min up to 1220K, always using catalyst mass equivalent to 5 mg of copper. The analyses of DRS were accomplished in equipment Varian-Cary 5 (scan on NIR, VIS and UV), with accessory of diffuse reflectance geometry HARRICK Praying-Mantis. The samples were diluted at 10% on BaSO₄ powder. Calcined precursor was used. The analysis began at 200 nm and stopped at 1500 nm.

Results and discussion

Table 1 presents concentration data determined through atomic absorption, as well as the codes for the several prepared catalysts. We can observe that the results are different from nominal contents on ternary catalysts, due to problems inherent to ammonium oxaloniobate and copper nitrate preparation and purity.

Table 1. Catalysts Chemical Analysis (% W/W)

Code	Catalyst	Cu	Nb ₂ O ₅	Al ₂ O ₃
CNIT15.25	Cu/Nb ₂ O ₅ /Al ₂ O ₃	14.0%	25.9%	60.1%
CNIT10.25	Cu/Nb ₂ O ₅ /Al ₂ O ₃	10.0%	27.0%	63.0%
CNIT15.15	Cu/Nb ₂ O ₅ /Al ₂ O ₃	15.5%	12.7%	71.8%
CNIT10.15	Cu/Nb ₂ O ₅ /Al ₂ O ₃	7.6%	13.9%	78.5%
CNIB3	Cu/Nb ₂ O ₅	3.9%	96.1%	-
CNIB5	Cu/Nb ₂ O ₅	5.5%	94.5%	-
CNIB10	Cu/Nb ₂ O ₅	11.6%	88.4%	-
CZC30	Cu/ZnO/Al ₂ O ₃	30.0%	35.0%*	35.0%

*ZnO

Analysis of TPR showed variations in the reduction profile based on copper oxide mass (Machado, 1995), as we can see on Table 2 and Figures 1, 2 and 3. This variations may be connected with copper-niobium interaction. As it was determined in a previous work (Machado, 1995), the CuO reduction has one single soft curve, with a maximum (650K) and without shoulders. About 100% of the copper was reduced. In this work, in all the prepared catalysts the reduction temperature has occurred in lower values, and in two stages, showing a partial reduction and/or a different copper reduction difficulty. Fierro *et al.* (1994), studied anomalous temperature-programmed reduction of CuO, Cu₂O and CuO-ZnO catalysts and concluded that a double step of reduction on Cu⁺² is an evidence of a copper-support interaction that may cause only a difficult reduction or a reduction on two steps (from Cu⁺² to Cu⁺¹ and from Cu⁺¹ to Cu⁰). The presence of Cu⁺¹ in Cu/ZnO reduced catalyst was found by Herman *et al.* (1979) where, using XPS analyses (X-Ray Photoelectron Spectroscopy), the authors have found Cu⁺¹ in the vacancies of ZnO crystals. A stepped and incomplete reduction for commercial catalyst was found, too (see Figure 3 and Table 2), like Herman *et al.* (1979), and Fierro (1994). Due to the likeness of ZnO and Nb₂O₅ semiconductivity properties (Machado, 1995), we can infer that a partial and superficial reduction of the niobium pentoxide provides vacancies that allow to accommodate Cu⁺¹ ions. As the reduction is incomplete, Cu⁺¹ presence in the reduced catalysts is possible.

Table 2. Temperature-Programmed Reduction (TPR)

Symbol	(%) Reduction of CuO → Cu ⁰	(%) Reduction of Nb ₂ O ₅ → NbO ₂
CNIT15.25	76.74	3.77
CNIT10.25	52.88	4.17
CNIT15.15	67.67	-
CNIT10.15	72.50	-
CNIB3	92.10	5.24
CNIB5	93.76	5.29
CNIB10	79.34	4.02
CZC30	88.40	-

We can observe in Table 2 the niobium pentoxide reduction occurring in all the catalysts, although in low percentages, showing that the reduction occurs in the first crystal layers. In the catalysts CNIT15.15 and CNIT10.15 the niobium pentoxide reduction could not be measured, due to the small niobium contents on these catalysts. The commercial catalyst also presents a partial and one-step copper reduction and ZnO reduction, probably occurred during CuO reduction, because of its reduction at 627K (Machado, 1995).

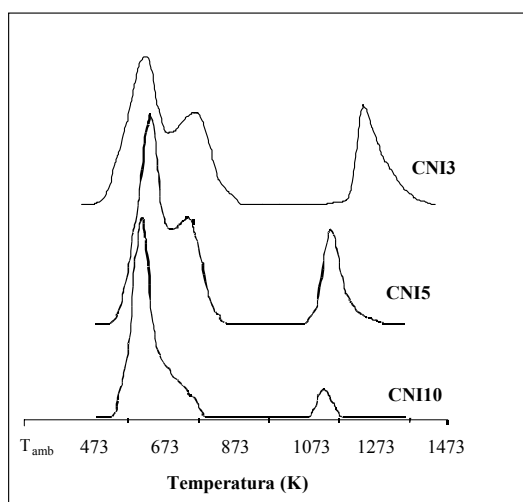


Figure 1. TPR curve of Cu/Nb₂O₅ binary catalyst

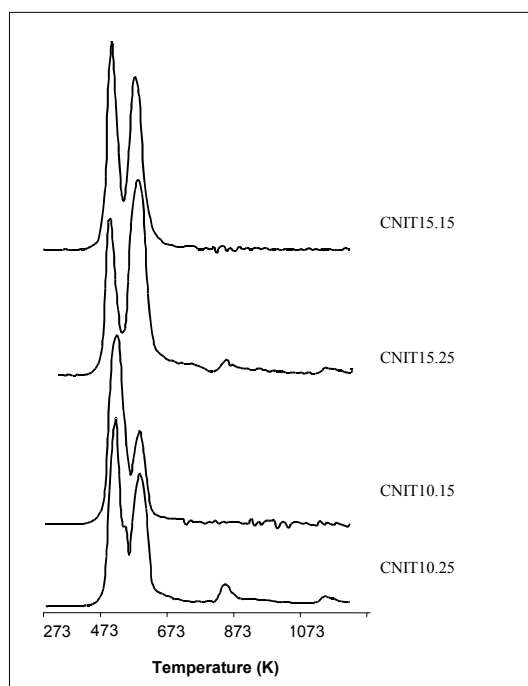


Figure 2. TPR curve of Cu/Nb₂O₅/Al₂O₃ ternary catalyst

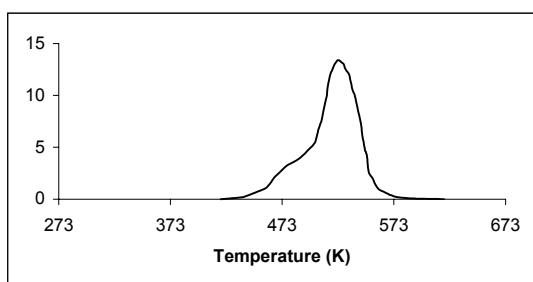


Figure 3. TPR curve of Cu/ZnO/Al₂O₃ commercial catalyst

The DRS analysis has shown that the content of copper or niobium pentoxide has influence on species absorbance. Tanaka *et al.* (1993), showed, through UV/VIS spectra, that while decreasing the loaded amount of Nb₂O₅, the peak position shifts to lower wavelength and the absorption band becomes narrower, concluding that the band energy gap position shifts to higher energy region with a decrease in the particle size of a semiconductor material. It happens on ternary catalysts in this work, showed on Table 3.

Table 3. Position of Maximum Absorption on Diffuse Reflectance Spectroscopy (DRS, UV-VIS)

Symbol	First Maximum, nm	Second Maximum, nm	Shoulder
CNIT15.25	194	771	488
CNIT10.25	215	773	489
CNIT15.15	194	769	466
CNIT10.15	209	767	456
CNIB3	322	778	-
CNIB5	313	774	-
CNIB10	340	846	-
CZC30	486		
CuO	-	737	-

The Figure 4 shows diffuse reflectance spectra for CZC30 and CuO catalysts. We can notice that it was one absorption maximum formation for CZC30 between ZnO (365 nm, Machado, 1995) and CuO (Table 3), showing structural alterations as Herman, 1979, has found. Chiorino *et al.* (1987), believes that such alterations happen in an over-saturated metastable Cu(II) in ZnO solid solution. On Nb₂O₅ catalysts, different results were observed for binary and ternary. On binaries, there is the presence of characteristic Nb₂O₅ absorption turned way for higher energy region (Nb₂O₅ pure has absorption maximum on 324nm, Machado 1995) and, for CuO, turned way for lower energy (Figure 4 and Table 3). But they do have an absorption arm with value near to CZC30 (see Figure 6), showing similar interaction among the two oxides. The binary catalysts, Figure 5, show a double maximum on spectra, with absorption characteristics of CuO and Nb₂O₅ without alteration from pure oxides. Chiorino *et al.* (1987), says about a minimal relation between CuO/ZnO and the solid solution is evident. Because ZnO and Nb₂O₅ show a similar energy gap between conduction and valency band, an over-saturated metastable Cu(II) in Nb₂O₅ solid solution may be supposed, which is evident only on ternary catalysts where the Cu - Nb₂O₅ is higher.

The results of the catalytic tests showed that there is a parallel reaction that only happens with the ternary catalysts, including the commercial one. The resulting reactions may be written as follows:

Wanted reaction $\rightarrow \text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 6 \text{H}_2$
 Parallel Reaction $\rightarrow 2 \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O}$

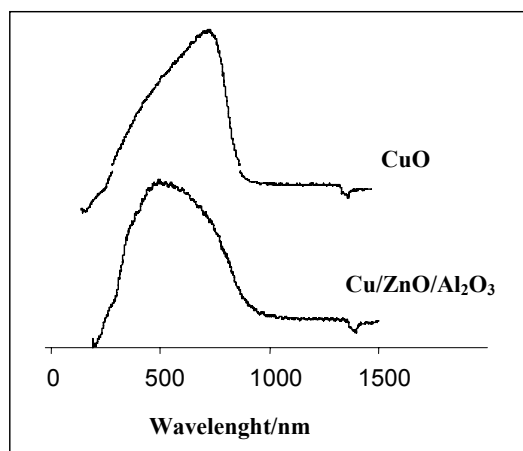


Figure 4. UV/VIS diffuse reflectance spectra of CuO and commercial catalyst

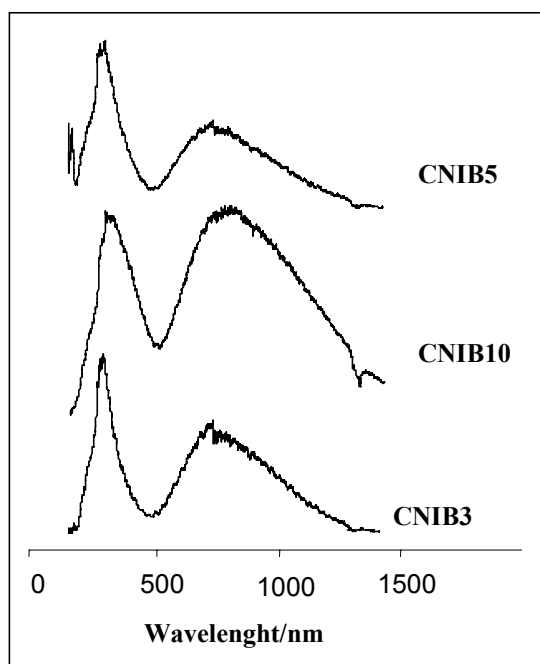


Figure 5. UV/VIS diffuse reflectance spectra of binary catalyst

The results showed that there is a difference of behaviour between binary and ternary catalysts. Table 4 shows that binary catalysts don't produce the ethyl ether sub product, while the others do. The commercial catalyst showed more conversion, with yield and selectivity similar to CNIT15.15 catalyst, which has less conversion. We can see similar features among ternary catalysts with Nb₂O₅ or ZnO as a semiconductor.

They are more active to convert ethanol but not selective to hydrogen.

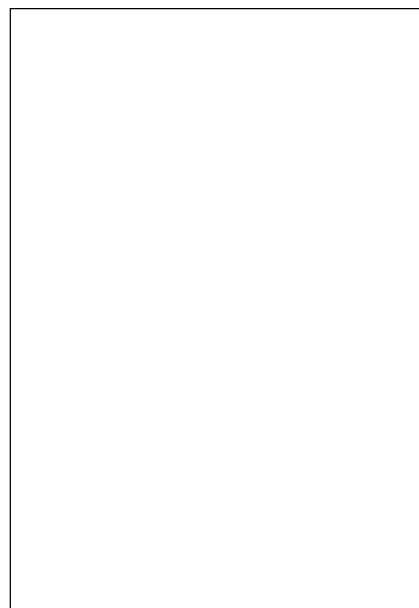


Figure 6. UV/VIS diffuse reflectance spectra of ternary catalyst

Table 4. Catalysts tests results

Symbol	Total Conv.(%) ^a	H ₂ Conv. (%) ^b	Yield (%) ^c	Selectivity ^d	mmol ethanol/ min.gCu ^e	mmol H ₂ / min.gCu ^f
CNIT15.25	12.03	6.25	51.5	12.75	103.00	318.0
CNIT10.25	11.39	9.71	85.2	69.6	151.00	771.0
CNIT15.15	6.97	4.76	60.0	18.00	53.66	193.2
CNIT10.15	10.80	2.04	19.8	2.97	127.00	150.0
CNIB3	3.90	3.90	100	∞	107.70	646.0
CNIB5	6.50	6.50	100	∞	140.60	844.0
CNIB10	6.69	6.69	100	∞	76.00	456.0
CZC30	15.45	9.53	62.0	19.6	50.50	188.0

^a – conversion based on all ethanol consumed; ^b – conversion based on ethanol which produces H₂; ^c – Yield, $Y = [F_{H_2}/(F_{ethanol0} - F_{ethanol})] \cdot 100$, F in mmol/min, subscript 0 means feed, Fogler 1999; ^d – Selectivity, $S = F_{H_2}/F_{ether}$, as in ^c, Fogler 1999; ^e – consume, ethanol consumed / mass of copper. Time; ^f – activity, H₂ produced / mass of copper. time

CNIT10.25 and CNIB5 catalysts were more efficient towards H₂ production. But, as CNIT10.15 produces ethyl ether, CNIB5 is the most active. Studies of temperature-programmed reduction, TPR, showed that in all catalysts copper reduction was under 100%, resulting in amounts of partially reduced or unreduced copper. For the ternary catalysts, the more active catalyst in H₂ production had lower copper reduction, 53%, and with partial reduction of Nb₂O₅, but for the binary catalysts it is not true. In this case, there is no direct relation: CNIB5 has near 94% reduction. There is a evidence that we

have differences created through niobia dispersion on alumina. This difference appears on DRS analysis by arm on 456-488 nm that does not appear on binary catalysts, and on ethyl ether formation. It is evident the formation Cu - semiconductor n oxide interaction in the active site formation, but there is an undesirable interaction created by ternary catalysts.

On binary catalysts, there is a good content of copper, 5%, showing that there is an ideal relation between copper and niobia.

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