

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Experimental and Theoretical Studies of Ni/Ni-based Catalysts for H₂ Generation

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ABSTRACT

Cu and Ni were supported on ZrO₂ by the impregnation method, and tested in the oxidative steam reforming of methanol (OSRM) reaction for H₂ production as a function of temperature. Surface area of the catalysts showed differences as a function of the order in which the metals were added to zirconia. Among them, the Cu/ZrO₂ catalyst had the lowest surface area. XRD patterns of the bimetallic catalysts did not show diffraction peaks of the Cu, Ni or bimetallic Cu-Ni alloys, because the metallic active phase was highly dispersed. In addition, TPR profiles of the bimetallic catalysts had the lowest reduction temperature compared with the monometallic samples. The reactivity of the catalysts in the range of 250-375 °C showed that the bimetallic samples prepared by successive impregnation had highest catalytic activity among all the catalysts studied. These results were also confirmed by theoretical calculations. The reactivity of the monometallic and bimetallic structures obtained by molecular simulation followed the next order: Ni_{shell}Cu_{core}/ZrO₂ \approx Cu_{shell}Ni_{core}/ZrO₂ > Ni/Cu/ZrO₂ > Cu/Ni/ZrO₂ > Cu-Ni/ZrO₂ > Cu/ZrO₂ > Ni/ZrO₂. These findings agree with the experimental results, indicating that the bimetallic catalysts prepared by successive impregnation show a higher reactivity than the Cu-Ni system obtained by co-impregnation. In addition, the selectivity for H₂ production was higher on these catalysts. This result could be associated also to the presence of the bimetallic Cu-Ni and core-shell Ni/Cu nanoparticles on the catalysts, as was evidenced by TEM-EDX analysis, suggesting that the OSRM reaction may be a structure-sensitive reaction.

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1. Introduction

The use of fossil fuels for energy supply in the world has caused various global environmental problems. For this reason it is becoming progressively more important to find ways of providing environmentally friendly energy. One promising alternative to fossil fuels is hydrogen, due to the importance as a clean source of energy, as well as, the increased demand in chemical industry. Hydrogen is a promising fuel for fuel cells and can be produced by steam reforming of natural gas, methanol and gasoline. At present, most of the world's hydrogen is produced from natural gas (~97 % CH_4) by a process called steam reforming. However, steam reforming of methane does not reduce the use of fossil fuels and it still releases carbon to the environment in the form of CO_2 . Thus, to achieve the benefits of the hydrogen economy, it is necessary produce hydrogen from non-fossil resources, such as water, methanol or ethanol using a renewable energy source. Among the different feedstocks available, alcohols are very promising candidates because these are easily decomposed in the presence of water and generate hydrogen-rich mixture at a relatively lower temperature. Steam Reforming (SR) and Oxidative Steam Reforming (OSR) of methanol has been extensively studied in recent years by our group [1-7]. However, comparing results between studies is challenging since the reaction evidently is very sensitive to the catalysts used .

2. Experimental

ZrO_2 was prepared by the sol-gel method and calcined a 400 °C. The prepared support were impregnated with an aqueous solution of $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ or $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ at an appropriate concentration to yield 3 wt % of copper and nickel respectively in the monometallic catalysts. Three bimetallic samples were prepared at 80%Cu and 20%Ni respectively to obtain 3 wt. % of total metallic phase. For the first sample, ZrO_2 was successively impregnated with an aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2$. Then, the excess of water was removed at 80 °C under constant stirring and the catalysts were dried at 110 °C and calcined at 400 °C for 2 h followed by cooling down to r.t. Then, an aqueous solution of $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ was added and the resulting solid was calcined at the same temperature and time. The as prepared catalysts will be referred as Ni/Cu/ ZrO_2 . For the second catalyst, the synthesis procedure was changed to the above sample mentioned. The labeling of this catalyst will be referred as Cu/Ni/ ZrO_2 . The third sample (Cu-Ni/ ZrO_2) was prepared by using a simultaneous impregnation (also called co-impregnation): an aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ were added to ZrO_2 and calcined at 400 °C for 2 h. All the samples were reduced at 450 °C using a mixture of H_2 (5%)/Ar (50 mL/min) stream for 1.5 h before characterization.

3. Results and discussion

ZrO_2 Xerogel was studied by means of TGA in order to select an appropriate calcination temperature leading to total decomposition of carbonaceous products from the synthesis towards the corresponding oxide. The obtained TGA-DSC curves for the xerogel (Figure not included) showed 22 % of the weight loss and it was attributed to the elimination of the physically adsorbed water, physical and chemical adsorbed alcohol and residual organic material

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coming from the synthesis. The observed exothermic peak at 433 °C on the zirconia xerogel can be ascribed to a change of phase from an amorphous material to crystalline tetragonal zirconia [6]. The specific surface area of bare ZrO₂ was 42 m²/g. After metallic phase impregnation and thermal treatments (calcination and reduction), the surface area of the catalysts diminished and was lower than bare support. Among them, the Cu/ZrO₂ and Cu-Ni/ZrO₂ catalysts had the lowest surface area, as well as, the total pore volume (Table 1).

Table 1. TPR peaks positions, °C and concentrations (%) of the reducible species in the Cu/Ni-base catalysts

Catalyst	Surface area	Total pore volume	Reduction temperature (°C)		H ₂ /MO	
	m ² /g	cm ³ /g	Before	after	before	After
ZrO ₂	42	0.0736	-	-	-	-
Cu/ZrO ₂	12	0.0271	217, 248, 290, 340	174	0.77	0.11
Cu/Ni/ZrO ₂	28	0.0512	192, 222	171	0.93	0.26
Cu-Ni/ZrO ₂	11	0.0262	203, 259	183	0.76	0.09
Ni/Cu/ZrO ₂	37	0.0582	185, 220	174	0.83	0.21
Ni/ZrO ₂	21	0.0333	349, 443	326, 447	0.76	0.63

Figure 1a showed a representative zone of the SEM image of the Ni/Cu/ZrO₂ catalyst. It is important to mention that the bare ZrO₂ and the other catalysts had the same morphology, so, particles with spherical tendency. This is understandable because we used the ZrO₂ previously stabilized at 450 °C to obtain the catalysts. Fig. 1b shows the XRD patterns of the catalysts before and after catalytic reaction in the range of 20 to 90 degrees 2θ. An expanded scale was used in order to illustrate the peaks of pure Cu and Ni phases or Cu/Ni alloys present on the ZrO₂. XRD patterns of the samples before the catalytic test evidenced diffraction peaks of the tetragonal and monoclinic phases of the ZrO₂. In addition, diffraction peaks of the metallic Cu and Ni phases were identified on the Cu/ZrO₂ and Ni/ZrO₂ catalysts respectively. The bimetallic catalysts did not exhibit diffraction peaks related to metallic Cu, Ni or bimetallic Cu-Ni alloys. This suggests that all metal particles were highly dispersed. After catalytic test, some changes were observed in the XRD patterns of the Ni/ZrO₂ and the bimetallic Cu-Ni/ZrO₂ catalysts (the later prepared by simultaneous impregnation). On the former catalyst, NiO phase was identified and on the bimetallic sample, a peak of the metallic copper appears. This finding evidences that the active phase is not stable on these catalysts and it was modified by the stream of the reaction.

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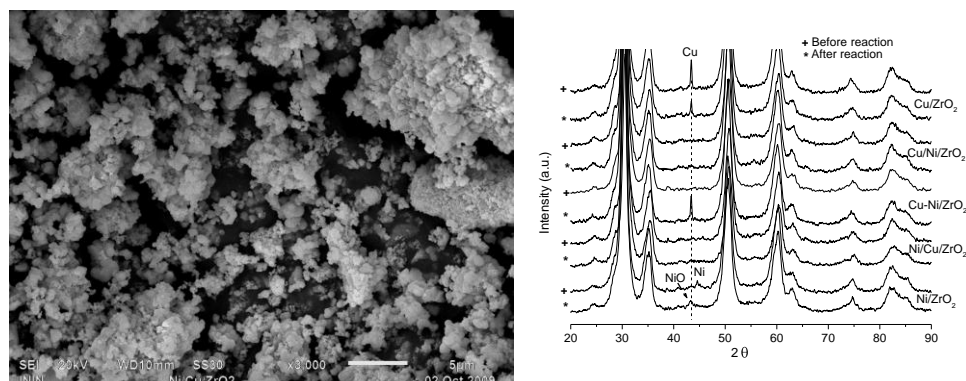


Figure 1. a) Typical SEM images of the fresh Ni/Cu/ZrO₂ catalyst. b) XRD patterns of the Cu-Ni base catalysts supported on ZrO₂ (before and after catalytic reaction).

Fig. 2 shows the theoretical calculations of the monometallic and bimetallic models over ZrO₂. After the geometry optimization of the theoretical models, the total energy and the energy of the gap had the next values: Ni_(shell)/Cu_(core)/ZrO₂ (-3193.49, 0.0027) eV, Cu_(shell)/Ni_(core)/ZrO₂ (-3429.43, 0.0159) eV, Ni/Cu/ZrO₂ (-3419.37, 0.0185) eV, Cu/Ni/ZrO₂ (-3488.39, 0.021) eV, Cu-Ni/ZrO₂ (-3655.28, 0.108) eV, Cu/ZrO₂ (-3810.23, 0.385) eV and Ni/ZrO₂ (-3832.18, 0.565) eV respectively. It is shown that the bimetallic models simulating the successive impregnation were less stable, because, the energy of the system is high, while, the energy of the bimetallic model prepared by simultaneous impregnation was low, as well as, on the monometallic models. An opposite behavior is observed in the energy of the gap. So, in the former models the energy of the gap is low, while in the later models the energy is high. The gap between HOMO and LUMO of the systems along with the total energy calculated, allows to evaluate the reactivity behavior of the system. So, a large gap of the system combined with a low total energy on the systems, low reactivity is expected. While, if the gap of the system is low and the total energy is large, high reactivity is expected [8]. The results of the theoretical calculations showed that reactivity of these systems followed the next order: Ni_(shell)/Cu_(core)/ZrO₂ ≈ Cu_{shell}Ni_{core}/ZrO₂ > Ni/Cu/ZrO₂ > Cu/Ni/ZrO₂ > Cu-Ni/ZrO₂, > Cu/ZrO₂ > Ni/ZrO₂. These theoretical results obtained after the simulation of the successive impregnation process and based on core-shell structures, show higher reactivity than in the simultaneous co-impregnation (Cu-Ni/ZrO₂) simulated process. Mainly in the literature, the theoretical studies reported are on unsupported core-shell particles and their alloys like Cu-Au particles, on this systems the studies have concentrated on the structural behavior of the clusters [9, 10], but no correlation with the catalytic activity was associated.

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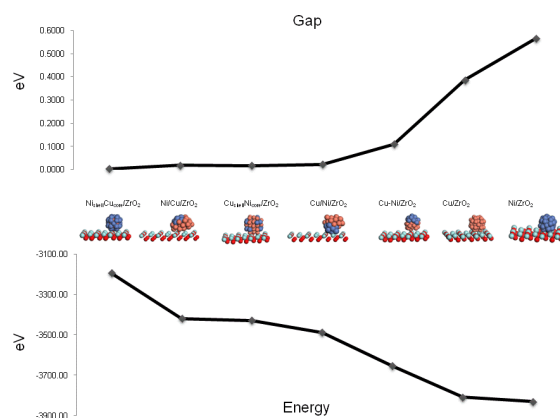


Figure 2. Molecular models of the bimetallic clusters: Top graph corresponds to gap-energy, in bottom graph showed the total energy of the systems. It showed that as the energy gap increases, the total energy of the system decreases, this indicates that the $\text{Ni}_{\text{(shell)}}\text{Cu}_{\text{(core)}}/\text{ZrO}_2$ and $\text{Cu}_{\text{(shell)}}\text{Ni}_{\text{(core)}}/\text{ZrO}_2$ are the most reactive, while the $\text{Cu-Ni}/\text{ZrO}_2$ is less reactive on the bimetallic models.

Oxidative steam reforming (OSR) of methanol reaction was carried out in order to investigate the effect of the active phase addition to the support. Fig. 3a shows the catalytic activity of the copper-nickel-base catalysts supported on ZrO_2 as a function of the reaction temperature. It was possible to observe that the Cu/ZrO_2 catalyst was better than Ni/ZrO_2 sample in the temperatures range studied in this work. This indicates that methanol conversion occurs preferentially on copper than on nickel. It is important to mention that the H_2 chemisorption process did not occur in these samples, for this reason the metal dispersion was not estimated and as a consequence the TOF could not be determined for each catalyst obtain/having a real comparison in the methanol conversion. When Ni was supported on ZrO_2 -monoclinic [1], the catalytic activity was similar to the obtained in this work up to 300 °C. On the other hand, it is clear that the preparation method of the catalyst has a significant influence on the OSRM reaction. The addition of 0.2 wt % of Ni to Cu/ZrO_2 catalyst leads to a considerable improvement in the methanol conversion, compared with the Ni/ZrO_2 sample. Among bimetallic samples, those prepared by the successive impregnation method showed high reactivity than the sample synthesized by simultaneous co-impregnation. The molecular properties HOMO and LUMO calculated by DFT of the bimetallic system prepared by successive impregnation, in special with core-shell particles, evidence that, these kinds of systems had more reactivity than bimetallic structure model obtained by simultaneous co-impregnation. Although experimentally the catalyst surface is different in the samples prepared by successive impregnation method, the theoretical reactivity predictions determined from the energy gap is similar in both bimetallic models, as seen in the in Figure 2. This may explain the catalytic behavior between the two catalytic species. In recently paper Strasser et al. [11] concluded that the platinum-rich shell on Pt-Cu nanoparticles, exhibits compressive strain, which results in a shift of the electronic band structure of platinum and weakening chemisorption

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of oxygenated species. These activity-strain relationships were consistent with computational predictions that compressive strain enhances oxygen-reduction reaction. In our case we observed that the catalytic activity is strongly related with the crystallinity and morphology of the active phase, the above mention was corroborated by means of XRD and TEM. The TEM analysis of the bimetallic particle with core-shell morphology; showed that there is no crystalline arrangement point to point or even line to line, which can be observable in the shell of the particle (Figure 3b). The crystalline anisotropy plays an important role in the methanol conversion in this research, because in the case of the core-shell Cu/Ni and Ni/Cu structures, the catalytic property increases in both cases, so the activity is not restricted by any preferred crystallographic direction. In the case of the Cu/ZrO₂ system having a crystalline arrangement in the (111) crystal direction, as seen in the XRD pattern of Figure 2, indicates that there are more particles with this type of crystalline plane which favors the catalytic activity but not as in the case of bimetallic core-shell particles; while in the case of Ni-base catalyst was observed that it has a poor crystallinity as observed in the XRD pattern (Fig. 2) with the (111) crystalline direction. This showed that there are few planes in the (111) crystalline direction influencing the catalytic anisotropic response. This means that even if there is a poorly crystalline monometallic active phase, the response in the catalytic activity does not resemble bimetallic systems with core-shell morphology, as well as when the active phase is a metallic alloy (Cu-Ni). This finding suggests that the OSRM reaction may be structure-sensitive. Yu-Hua et al. [12] studied the methanol decomposition on Ni(1 1 1) and Ni(1 0 0) surfaces using DFT-GGA (density functional theory-generalized gradient approximation). According to their results, the observed different behavior in the methanol interaction with Ni(1 1 1) or Ni(1 0 0), suggests that the methanol decomposition might be a structure-sensitive reaction, as it has been observed in our samples. The Cu-Ni/ZrO₂ sample had a similar behavior to the Cu/ZrO₂ catalyst until 300 °C. After this temperature the Cu-Ni/ZrO₂ sample exhibited the same catalytic activity than the other bimetallic samples. In addition, was observed that the active phase of the Cu-Ni/ZrO₂ catalyst was not stable, because, it was sinterized after catalytic reaction (Fig. 2). This effect could be explained the lower catalytic activity observed on this sample than on the other bimetallic samples prepared by successive impregnation. Mariño et al. [13, 14] found that the conversion of ethanol on the SRE reaction was improved when nickel content increased on the bimetallic Cu-Ni system. This behavior was attributed to the addition of Ni, which favors the segregation of Cu²⁺ ions in the catalytic surface that causes an increase in the catalytic activity. Thus the enhancement on the catalytic activity could be attributed to the bimetallic Cu-Ni species as was previously reported [1,5] and core-shell nanoparticles identified with TEM technique on the Ni/Cu/ZrO₂ catalyst. It is worth notice, that the BET surface area of the Cu/ZrO₂ sample is two times lower than Cu/Ni/ZrO₂ and Ni/Cu/ZrO₂ samples. Thus, the catalytic activity observed on the Cu/ZrO₂ could be attributed to the presence of highly dispersed Cu species rather than Cu bulk as reported for Cu/CeO₂ catalysts [2].

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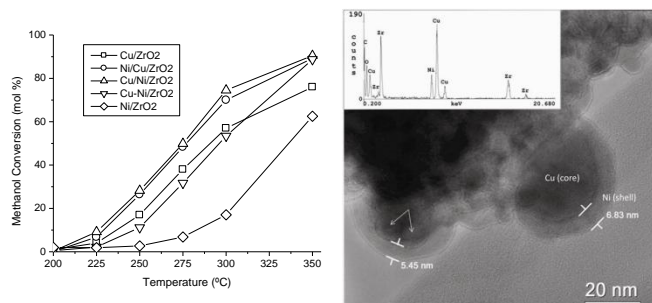


Figure 3. a) Steam reforming of methanol over copper-nickel-base catalysts supported on ZrO_2 ($\text{GHVS} = 24,000 \text{ h}^{-1}$). b) TEM image of Ni/Cu/ZrO_2 catalyst, core-shell nanoparticles were identified, the left side area shown two particles building the core. Inset image, EDX of the Ni/Cu core-shell nanoparticle. EDX analyses were performed in-situ with a spot of 10 nm and the electron beam was located at the Ni shell area.

During the OSRM reaction with copper-nickel base catalysts supported on ZrO_2 , the main products observed were H_2 , CO , CO_2 and H_2O . However, a small quantity of methyl formate was also present at temperatures below 275°C in almost all samples. Above this temperature, the methyl formate was unstable and was not detected. On copper- ZrO_2 systems [1], the production of $(\text{CH}_3)_2\text{O}$ and CH_2O during the OSRM was observed and it was suggested that they were produced on the support. Fig. 4a shows the hydrogen yield as a function of reaction temperature during the catalytic tests of the copper-nickel-base catalysts on the OSRM reaction. Hydrogen production was negligible up to 225°C and increase when the temperature was raised. Cu/Ni/ZrO_2 and Ni/Cu/ZrO_2 catalysts prepared by successive impregnation had the same H_2 yield after 250°C and it was higher than all samples. At the maximum reaction temperature, the H_2 yield is about $2.0 \mu\text{mol}$ for the Cu/Ni/ZrO_2 and Ni/Cu/ZrO_2 catalysts, this is close to the theoretical value (2.5) if a total reagents conversion is assumed. At this temperature the methanol conversion was nearly 100 %. On the other three samples the H_2 production was close to $1.5 \mu\text{mol}$. The CO_2 selectivity (Fig. 4b) is important at the beginning of the reaction and diminished as temperature was increased. This drop in the CO_2 selectivity was pronounced on the samples where the catalytic activity was nearly 100 %. In the case of the CO selectivity, this was produce after 275°C . The CO production at 350°C was 10 % for the monometallic samples and close to 40 % for the bimetallic catalysts. The decrease in the CO_2 selectivity and the formation of CO is probably due to the reverse water-gas shift (WGS) reaction that occurred on the bimetallic samples. Taking in account the results from methanol conversion and selectivity, it is considered that CH_3OH form CH_3OCHO and H_2 on the surface of the catalysts as the first step of the OSRM reaction. Then, CH_3OH is oxygenated to CH_3OCHO , and then decomposed to H_2 and CO . CH_3OH was hydrated in order to form CO_2 , H_2O and H_2 respectively as reported previously [1].

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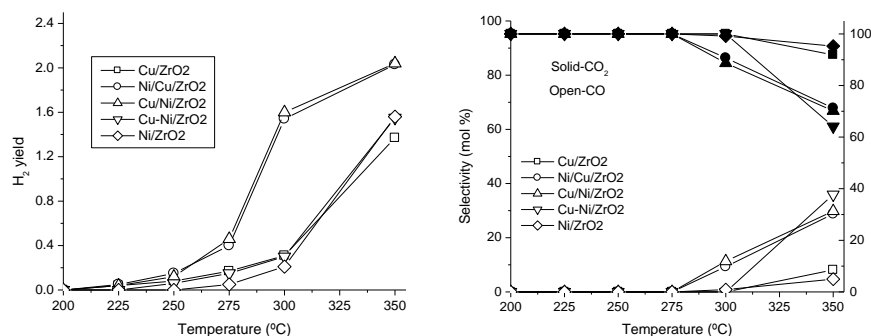


Fig. 4. a) H₂ yield as a function of the metal addition and temperature. (GHVS = 24,000 h⁻¹). b) Evolution on the selectivity of CO₂ and CO as a function of the metal addition and temperature. (GHVS = 24,000 h⁻¹).

4. Conclusions

In the present study, Cu/ZrO₂, Ni/ZrO₂ and three bimetallic copper-nickel catalysts supported on ZrO₂ were prepared by the impregnation method. The bimetallic Cu/Ni/ZrO₂ and Ni/Cu/ZrO₂ catalysts showed higher catalytic activity than bimetallic sample prepared by simultaneous impregnation and the monometallic catalysts on the OSRM reaction. Molecular simulation HOMO and LUMO properties of the bimetallic system prepared by successive impregnation with core-shell particles, confirm that these systems had more reactivity than bimetallic system obtained by simultaneous impregnation. In addition, the H₂ selectivity was higher on these bimetallic Cu/Ni/ZrO₂ and Ni/Cu/ZrO₂ catalysts. The former catalyst exhibited excellent stability in OSRM reaction and has great potential in fuel cell applications. These results could be associated to the presence of the bimetallic Cu-Ni and core-shell Ni/Cu nanoparticles present on the catalysts, as was evidenced by HREM-TEM-EDX and to the crystalline anisotropy of the active phase that plays an important role in the methanol conversion and selectivity. This finding suggests that the OSRM reaction may be a structure-sensitive reaction

5. Acknowledgements

Thanks to I.Q. Albina Gutiérrez Martínez, Carlos Salinas Molina and Jorge Pérez for technical support and to the project ININ-CA-711, ININ-CA-009, CONACYT CB-2008-01-104540 and CONACYT J-48924 for financial support. Authors would like to acknowledge Dra. Reyna Natividad Rangel and Dr. Carlos Ángeles for its valuable comments and suggestions on the manuscript.

6. References

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