PREPARATION OF Ni-Ga BIMETALLIC CATALYSTS BY WATER-IN-OIL MICROEMULSIONS FOR METHANOL SYNTHESIS VIA CO2 HYDROGENATION

Anibal Encina, Paulina Melo, Karen Aravena, Romel Jimenez, Alejandro Karelovic

Laboratorio de Carbono y Catálisis (CarboCat), Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad de Concepción, Concepción, Chile

Introduction

Methanol synthesis from syngas is a well-established process. It is generally operated at 230-280°C, 50-100 bar and with syngas feeds ($CO/CO_2/H_2$). Methanol can be synthesized from CO_2/H_2 as a way to help decreasing the concentration of CO_2 in the atmosphere. The hydrogen needed could be obtained from renewable sources whereas CO_2 sources could include direct capture of atmospheric CO_2 or flue gases from combustion units. In either case, the CO_2/H_2 reaction to produce methanol has different challenges compared to the commercial syngas to methanol process: The selectivity is important to avoid the formation of CO through the reverse water gas shift reaction (RWGS)[1]. High activity is required at low temperature where the selectivity is favored. NiGa catalysts have been recently reported to be as active as CuZnAl and more selective to methanol[2]. The catalysts of that study were prepared by impregnation of the Ni and Ga nitrates followed by reduction at 700°C to form NiGa alloys. Here, we study the preparation NiGa catalysts by water in oil microemulsions in order to i) control the size of the nanoalloys and ii) enhance the contact between the components to favor the alloy formation at lower temperatures.

Experimental

Microemulsions were prepared by mixing the appropriate amounts of surfactant (polyethylene glycol dodecyl ether, Brij-L4® from Sigma Aldrich), n-hexane and an aqueous solution containing Ni and Ga nitrates (0.65 M), under continuous agitation. The microemulsion was rapidly formed, as evidenced by the homogeneity of the solution and nonexistence of phase separation upon stopping the stirring. The n-hexane to surfactant molar ratio was 20. A similar microemulsion was prepared but instead of metal precursors, we used hydrazine ($N_2H_4*H_2O$, 80%, Sigma Aldrich) or NH_3 (NH_4OH, 25%, Merck) for the reduction and formation of precipitates inside the micelles. The molar ratio precipitating agent/metals was 10. Upon mixing the two microemulsions, a rapid change of color evidenced the reaction and formation of precipitates. After ca. 30 min, the support (SiO_2, Saint Gobain Norpro, 261 m^2/g) was added gently with continuous stirring. The amount added was the necessary to achieve a 15 wt% of metals on the catalyst. After 30 min the microemulsion was broken by the addition of ca. 500 mL acetone (Technical grade) and the suspension was filtered. This was followed by drying overnight in a stove at 110°C. The formation of the bimetallic phases was achieved via reduction in a flow of H_2 (50 mL/min) at 600 (2 or 12h) or 700°C (2h). The heating rate was 2°C/min. Catalysts were characterized by XRD, TEM and ICP. The evaluation of the materials in catalysis was carried out using a stainless steel fixed bed reactor. Catalysts were reduced in situ under a flow of H_2 (50 mL/min) at 650°C for 2h with a heating rate of 2°C/min. Afterwards, the temperature was reduced to 220°C and the feed was changed to H_2 (15 mL/min) and CO_2 (5 mL/min). The reaction was performed enough time in order to achieve steady state performance.

Results and discussion

The size of the NiGa nanoparticles is in the range 4-6 nm (Fig 1), showing that microemulsion method can be successfully applied for synthesizing these bimetallic catalysts. The Ni/Ga molar ratio used in the preparation influences the size of the nanoparticles obtained. As shown in figure 2, the mean particle size determined by TEM changed from ca. 6 nm for catalysts rich in Ga (Ni/Ga = 1.67) to ca. 4 nm for Ni/Ga = 4. Higher Ni/Ga ratios did not influence the size of the resulting nanoparticles. Interestingly, the two trends observed in Figure 2 can be correlated to the phase formed. Catalysts with Ni/Ga ratios of 4 and lower formed the phase β-NiGa whereas higher Ni/Ga ratios resulted in the formation of α'-Ni_3Ga phase. Even for the higher ratios employed in this study, we could not detect pure Ni or Ga-containing phases such as Ga_2O_3. If they exist, their amount should be reduced or, in the case of Ga_2O_3 it could be aggregated as amorphous structures.

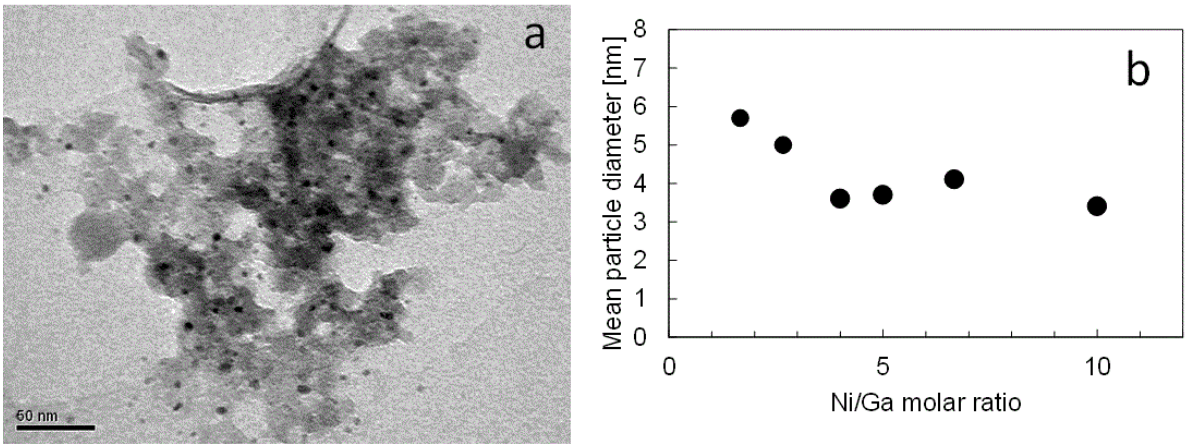

Figure 1: a) TEM micrograph of NiGa catalyst (Ni/Ga molar ratio = 1.67) prepared by microemulsion and reduced at 700°C for 2h. b) Effect of Ni/Ga molar ratio on the average size of NiGa nanoparticles as measured by TEM.

Under CO_2 hydrogenation conditions, the selectivity depends on the phase formed. Catalysts with high Ni content, where α'-Ni_3Ga was the predominant phase, produced mainly CO with traces of CH_4. The rate of CO formation was near 300 μmol/g/h at 220°C and 8 bar and for CH_4 it was less than 20 μmol/g/h. It is important to notice that in spite of having a nominal Ni/Ga ratio of 10, which is higher than the stoichiometric (Ni/Ga = 3), the catalytic properties of Ni were dramatically changed upon Ga addition. Catalysts with lower Ni/Ga ratios, which showed the presence of β-NiGa (Ni/Ga = 2.67 or 1.67) produced methanol with rates ca. 60 μmol/g/h, although were more selective to CO (150 μmol/g/h).

In order to increase the selectivity we studied the effect of reduction pretreatment on a NiGa catalyst prepared with a starting Ni/Ga ratio equal to 1.5 in order to ensure the formation of β-NiGa. Samples were reduced at 600°C during 2h or 12h. The reduction for 2h was beneficial for the catalytic activity, with a rate of methanol formation at 220°C of 75 μmol/g/h and CO of 110 μmol/g/h. When the reduction time was increased to 12h, the rate of methanol formation increased to 85 μmol/g/h but that of CO increased more markedly, to 288 μmol/g/h. This result shows that for NiGa catalysts prepared by microemulsion, reduction at lower temperature (600°C) and for shorter times is beneficial for favoring methanol formation.

Conclusions

We show that water-in-oil microemulsions can be successfully applied to prepare NiGa catalysts for methanol synthesis. We explored the effect of Ni/Ga molar ration and found that β-NiGa phase correlated to the formation of methanol and CO whereas catalysts in which α'-Ni_3Ga predominates were more active to CO and CH_4 formation. Mild reductive treatments are beneficial for attaining lower CO formation rates and thus higher methanol selectivity.

Acknowledgements

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