Bimetallic Ni-Co/SBA-15 catalysts for reforming of ethanol: How cobalt modifies the nickel metal phase and product distribution

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A B S T R A C T

In this study, five mono and bimetallic xNi-(10-x)Co/SBA-15 catalysts (x = 10, 8, 5, 2 and 0, with a total metallic content of 10 wt%) have been synthesized using a deposition-precipitation (DP) methodology. Catalytic performances on the steam reforming of ethanol reaction (SRE) have been determined and correlated with their physical and chemical state. A nickel content of 5% or higher yields catalytic systems with good activity, high selectivity to hydrogen and a low production of acetaldehyde (less than 5%). However, in the systems where the cobalt is the main component of the metallic phase (8–10%), the selectivity changes, mainly due to the production of an excess of acetaldehyde, which is also reflected in the larger H_2/CO_2 ratio. In agreement with previous findings, this important modification in the selectivity comes from the formation of a cobalt carbide phase, where only takes place in the cobalt enriched systems, and is inhibited with nickel content larger than 5%. The formation of this carbide phase seems to be responsible for the decrease of cobalt particle size during the SRE reaction. Even though this cobalt carbide phase is thermodynamically metastable against decomposition to metallic cobalt and graphite carbon, our results have shown that it only reacts and decomposes after a hydrogen treatment at 600 °C.

1. Introduction

Although methane steam reforming is currently the most industrial competitive process for obtaining hydrogen [1–3], the impact on climate of using fossil fuels, and the limited availability of methane due to the remote locations of some of the major natural gas fields makes the use of renewable chemicals as bioethanol a very interesting alternative to reduce the environmental impact [4,5]. This product of the biomass processing is easily available, with low toxicity and also very important, the existing infrastructure for storage and transportation is spread worldwide [6–8]. Ethanol steam reforming has been extensively studied in the last decades. As in other reactions such as the methane reforming, the use of noble metals yields good catalytic performance with high selectivity to hydrogen and a limited amount of carbon deposits poisoning the catalyst [9–14]. Once again, the high price and poor availability of metals as Ru, Pt, Rh or Pd, advises the use of cheaper alternatives, especially Ni, but also Co and/or Cu [15–19], even though these metals favor the deposition of carbonaceous deposits. The carbon deposition processes can be mitigated in several ways, as changing the ethanol/water ratio, introducing oxygen in the feed mixture or using different kind of supports [20,21]. An alternative strategy to overcome this issue involves the use of bimetallic systems, where the synergistic effects of the two metals can improve their catalytic performances. In this sense Ni-Co is one of the most popular couple being used for this SRE reaction but also for reforming of methane [19,22–26]. It has been previously reported that the combining effect of this two metals is able to produce less amount but also less harmful carbon deposits [6].

In this work we have synthesized five catalysts containing nickel and/or cobalt supported on the mesoporous silica SBA-15. The catalytic systems, with a total metal loading of 10 wt%, has been prepared by means of a deposition-precipitation method (xNi-(10-x)Co/SBA-15 catalysts, x = 10, 8, 5, 2 and 0). We have measured the catalytic performances of these systems, and characterized their states after calcination, hydrogen reduction and steam reforming of ethanol reaction conditions using among others, XPS, XAS and TEM. The results have allowed correlating the catalytic performances with the initial state of metallic phases and its evolution under catalytic conditions. The formation of a Ni-Co bimetallic phase and the stabilization of a cobalt carbide phase in the Co-enriched systems are the major factors determining the catalytic performances of these Ni-Co/SBA-15 catalysts.

Table 1
Characterization data of the Ni-Co/SBA-15 catalytic systems.

	S_{BET} ($m^2 g^{-1}$)	Average pore size (nm)[a]	Ni/Co$_{surf.}$ by XPS (%$_{at}$)	Crystallite size (XRD[b]) [Calc/Red]	Average metallic particle size (TEM[c]) [Red/SRE]
SBA-15	738	6.7	–	–	–
SBA-15 treated with urea	249	9.1	–	–	–
10Ni/SBA-15	283	10.3	11.3/0.0	5.4/4.1	4.3/4.2
8Ni-2Co/SBA-15	272	11.1	7.8/2.6	7.6/4.1	4.4/4.0
5Ni-5Co/SBA-15	261	12.0	4.2/3.1	7.0/4.5	5.9/8.6
2Ni-8Co/SBA-15	269	10.3	1.9/7.1	6.5/8.2	8.6/7.0
10Co/SBA-15 DP	280	9.8	0.0/7.1	5.1/13.2	14.4/9.6

[a] Obtained by the BJH method.
[b] Calculated from the Scherrer equation.
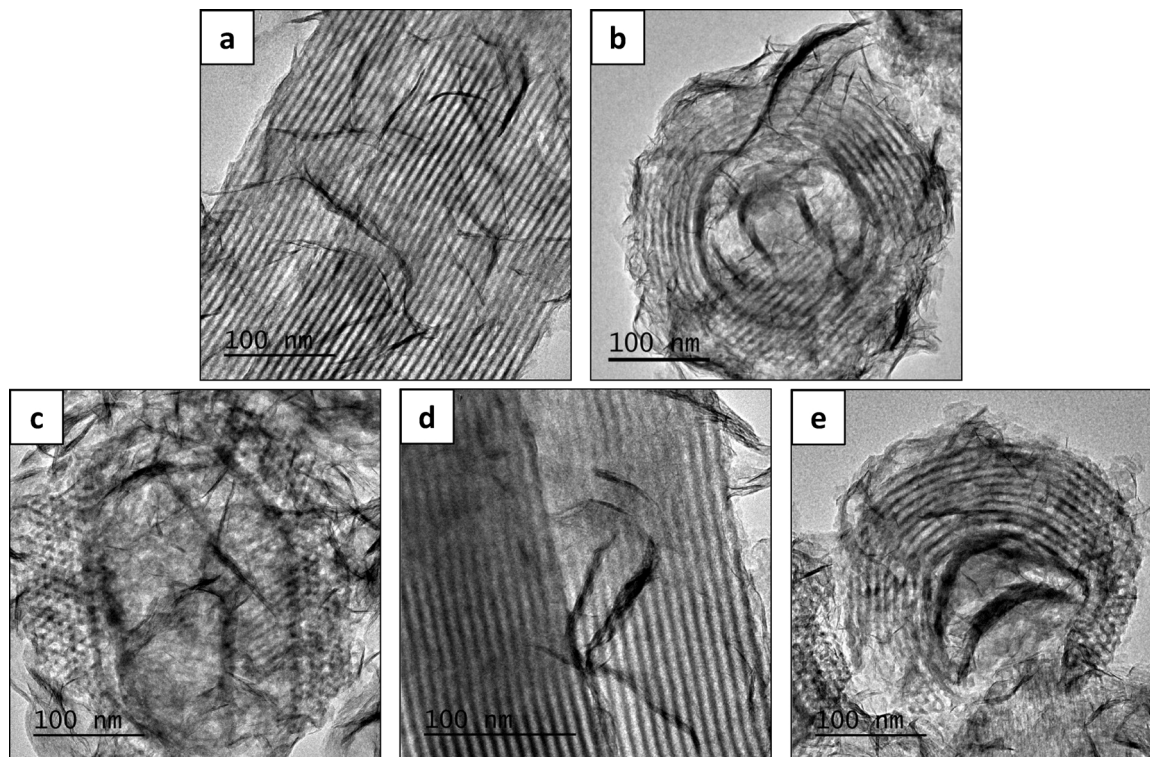[c] Obtained by sampling 150 particles.

Fig. 1. TEM images for calcined 10Ni/SBA-15 (a), 8Ni-2Co/SBA-15 (b), 5Ni-5Co/SBA-15 (c), 2Ni-8Co/SBA-15 (d) and 10Co/SBA-15 (e) catalysts.

2. Experimental

2.1. Preparation of the catalysts

Ni-Co catalytic systems were synthesized by a deposition-precipitation method over a mesoporous support of SBA-15 which was prepared by the Zhao et al. protocol [27] using a TEOS/P123/HCl/H$_2$O (TEOS: Sigma-Aldrich, CAS: 78-10-4; HCl: Sigma-Aldrich, CAS: 7647-01-0; Pluronic® P-123: Sigma-Aldrich, CAS: 9003-11-6) molar relation of 1/0.02/9.91/320. Typically, 3 g of PEG-PPG-PEG (P123) were dissolved in 140 mL of HCl 1.8 M. After total solution, the mix was heated up to 50 °C and 5.9 mL of TEOS were added with stirring. The solution was kept on static at 50 °C for 18 h, and the gel obtained was filtered and washed several times with distilled water. The product was dried and calcined on static air for 3 h at 550 °C. The metallic phase was loaded by heating up to 105 °C during 2 h a solution containing 1 g of as-prepared SBA-15, 150 mL of HNO$_3$ 0.01 M (Sigma-Aldrich, CAS: 7697-37-2), the metal precursors [Ni(NO$_3$)$_2$·6H$_2$O (Panreac, CAS: 13478-00-7) or/and Co(NO$_3$)$_2$·6H$_2$O (Panreac, CAS: 10026-22-9)] and 11.37 g of urea (Alfa Aesar, CAS: 57-13-6), for a total metallic charge of 10% and different xNi/(10-x)Co ratio (x = 0, 2, 5, 8, 10). After this

time, the resulting solution was filtered and washed with distilled water, dried at 110 °C and calcined on static air for 3 h at 550 °C.

2.2. Catalytic test

SRE catalytic tests were performed over 100 mg of catalyst held in a tubular quartz reactor. Samples were pre-reduced in hydrogen at 750 °C for 1 h using a heating ramp of 10 °C min^{-1} and reaction was carried out at 500 °C by injecting 0.02 mL min^{-1} of a H$_2$O/EtOH solution (3.7 molar ratio) and 100 mL min^{-1} of helium as carrier gas. Products were analyzed by gas chromatography using an Agilent's 490 microGC equipment, connected on-line with the reactor, provided with three columns and TCD detectors: two molecular sieves for the analysis of lighter molecules as H$_2$, CO, CH$_4$ and CO, and a capillary column (PoraPLOT-U) for the analysis of CO$_2$, H$_2$O, ethanol and acetaldehyde. Quantitative calculations were as follows:

Ethanol conversion (%):

$$X_{EtOH} = \frac{F_{EtOH\ in} - F_{EtOH\ out}}{F_{EtOH\ in}} \cdot 100,$$

being F_{EtOHin} and $F_{EtOHout}$ the ethanol molar flow in the inlet and