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Understanding the differences in catalytic performance for hydrogen production of Ni and Co supported on mesoporous SBA-15

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ABSTRACT

Three mono and bimetallic $\text{Ni}_x\text{Co}_{1-x}/\text{SBA-15}$ catalysts ($x = 1, 0.5$ and 0) with a total metallic content of 10 wt% have been prepared by a deposition–precipitation (DP) method. The catalytic performances on the dry reforming of methane reaction (DRM) have been determined and correlated with their physical and chemical state before and after the catalytic reaction. So, while the nickel monometallic system presents a high activity and stability in the DRM reaction, the $\text{Co}/\text{SBA-15}$ catalytic system turns out completely inactive. For its part, the $\text{Ni}_{0.5}\text{Co}_{0.5}/\text{SBA-15}$ has initially a catalytic performance similar to the $\text{Ni}/\text{SBA-15}$ monometallic system, but rapidly evolving to an inactive system, therefore resembling the behavior of the cobalt-based catalyst. The characterization by TEM and *in situ* XPS techniques has allowed us to ascribe these differences to the initial state of metallic particles after reduction and their different evolution under reaction conditions. So, while after reduction both nickel containing $\text{Ni}_x\text{Co}_{1-x}/\text{SBA-15}$ catalysts ($x = 1$ and 0.5) present a well dispersed metallic phase, the cobalt monometallic catalyst yields big metallic particles with a heterogeneous distribution of sizes. Additionally, unlike the $\text{Ni}/\text{SBA-15}$, the $\text{NiCo}/\text{SBA-15}$ system increases during reaction the metallic particle sizes.

Besides indicating that the particle size is a major reason determining the catalytic performances, these results suggest that in the Ni–Co system both metals form after reduction a bimetallic phase mainly located inside the mesoporous channels of SBA-15 support. Under DRM reaction conditions, the cobalt is segregated to the surface of the bimetallic particles, which seems to determine the interaction with the support surface SBA-15. This feature gives rise to a much less stable metallic phase which suffers an important sintering process under DRM catalytic conditions.

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1. Introduction

Supported nickel catalytic systems are currently one of the most important industrial heterogeneous catalysts because its remarkable performance in a number of economically strategic processes [1–5]. Among them, the steam reforming of methane (SRM, $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO}$) can be outlined as the main industrial process for obtaining hydrogen and synthesis gas, used to synthesize various important chemicals and fuels [6–9]. Although it is not yet commercially exploited, the dry reforming of methane (DRM, $\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO}$) is an especially interesting reaction that transforms two of the most harmful greenhouse gases, methane and carbon dioxide, into a mixture of hydrogen and carbon monoxide [10–12]. Once again, Ni-based catalysts are the most

widely tested in the literature for this reforming reaction, even though noble metal based catalysts such as Pt, Ru and Rh are much more performance toward methane conversion. The principal issue comes from the fact that Ni typically undergoes severe deactivation processes, mainly due to coke formation, but also due to sintering of the metallic phase, generating big metallic particles which at the same time, favors the coke formation processes [13–17]. As an alternative to overcome these issues, a number of publications have shown as the use of bimetallic systems, as the combination of nickel and cobalt modified the catalytic performance in steam and dry reforming of methane [18–23]. But, depending on the support or the preparation methods both effects, improvements and worsening of the efficiency, have been reported. Main reasons explaining these contradictory findings are probably related with differences in the interaction of metals with support surface, which has been recognized as an essential factor affecting the stability of metal [24–26]. So, a strategy to avoid the growth of metallic particles is the use of special supports, and in particular mesoporous supports.

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These supports typically have high surface area and a tailored size of the porosity, which can be used to control the size of the metallic particles [27–29].

In this work we have prepared three 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 ($\text{Ni}_x\text{Co}_{1-x}/\text{SBA-15}$ catalysts, $x = 1, 0.5$ and 0). As the catalytic behavior of these systems are pretty different, we have characterized the catalytic systems after hydrogen reduction and after dry reforming reaction conditions using among others, *in situ* XPS and TEM. The obtained results have allowed us to correlate the catalytic performances with both, the initial state of metallic phases after reduction, and the final state of these metallic particles after DRM reaction. The interaction of the metallic phase with the SBA-15 inner surface appears as a major factor determining the catalytic stability of these $\text{Ni}_x\text{Co}_{1-x}/\text{SBA-15}$ catalysts.

2. Experimental

2.1. Catalysts preparation

The mesoporous silica SBA-15 used as support was prepared according to a method previously described in the literature [30,31]. Summarizing, 18 g of P123 was dissolved in 270 mL of distilled water and afterwards a solution of 675 mL of HCl 2.5 M was added and heated up to 50 °C. Next, an amount of TEOS was added and kept at 50 °C for 18 h. The product obtained was filtered, washed with boiling distilled water, dried under vacuum at 70 °C and calcined on for 3 h at 550 °C.

The cobalt and nickel metal phases were supported on SBA-15 by a deposition–precipitation method (DP) using urea as a precipitant agent according to the method described by Liu et al. [32]. 1 g of calcined SBA-15 was dispersed in HNO_3 0.01 M with the required amount of metal precursors $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. On stirring, an amount of urea was added and the temperature increased up to 105 °C. After 2 h, the mix was cooled down to room temperature and the powder filtered and dried at 110 °C for 24 h. Finally, it was submitted to a calcination treatment on air at 550 °C. The resulting products were labeled as 10%Ni/SBA-15, 10%Co/SBA-15 and 5%Ni–5%Co/SBA-15. In order to clarify the effect of the preparation treatment, a similar procedure was accomplished without metals addition, and the sample was labeled as SBA-15-DP.

2.2. X-ray diffraction (XRD)

The XRD analysis of calcined and reduced samples were recorded in a PANalytical X-Pert PRO diffractometer with a Cu source ($\lambda = 1.5418 \text{ \AA}$, Cu $K\alpha$), working in a Bragg-Brentano configuration and equipped with an X'Celerator Detector (active range of $2\theta = 2.18^\circ$). The data acquisition was carry out in a 2θ range of 10–80°, a step of 0.05° and an acquisition time of 240 s.

2.3. Temperature programmed reduction (TPR)

The temperature-programmed reduction profiles were obtained using a thermal conductivity detector based in a Wheatstone bridge. The hydrogen consumption was previously calibrated using commercial CuO. A 5% H_2/Ar calibrated mix was used as both carrier and reference gas, with a typical flow rate of 50 mL min^{-1} . Following the recommendation to avoid peak coalescence [33], the experimental conditions were chosen to assure a total hydrogen consumption of approximately 100 μmol of H_2 .

Typically, the experiment was carried out from room temperature up to 1000 °C using a heating ramp of 10 °C min^{-1} .

2.4. Transmission electronic microscopy (TEM)

TEM images were obtained in a Philips CM200 microscope operating at 200 kV. Samples were dispersed on ethanol and deposited onto a copper grid coated with a lacey carbon film. Histograms for particle size distribution were obtained by sampling around 150 particles.

2.5. X-ray absorption spectroscopy (XAS)

XAS (EXAFS and XANES regions) were recorded at the BL22 beamline (CLAESS) of ALBA synchrotron and the BM25A beamline (SPLINE) of ESRF synchrotron facilities. The required amount of sample to maximize the signal/noise ratio was pelletized and XAS spectra collected at RT after calcination. Standards Ni and Co foils were measured and used for energy calibration. The XAS spectra of Ni K-edge and Co K-edge were recorded for a 1000 eV interval, with a step of 0.5 eV step across the XANES region. Once extracted from the XAS spectra, the EXAFS oscillations were Fourier transformed (F.T.) in the range 2.4–11.0 \AA^{-1} . Spectra were analyzed using the software package IFEFFIT [34].

2.6. X-ray photoelectron spectroscopy (XPS)

XPS experiments were carried out in a VG-ESCALAB 210 equipment over pelletized samples. Samples were introduced in a pre-chamber at 10^{-7} Torr. Acquisition was performed in an appendant analysis chamber equipped with a SPECS Phoibos 100 hemispheric analyzer at 10^{-9} Torr using Mg $K\alpha$ radiation ($E = 1.5418 \text{ keV}$) with 20 mA of anode current and 12 kV of potential acceleration. Before acquisition, each sample was treated *in situ* at different temperatures (RT, 350, 500 and 750 °C) in a flow of 5% H_2/Ar at atmospheric pressure using a cell chamber attached to the abovementioned pre-chamber.

2.7. Catalytic activity tests

Dry reforming of methane (DRM) tests were performed using 20 mg of catalyst held in a tubular quartz reactor through wool quartz. The catalytic systems were pre-treated in 5% H_2/Ar at 750 °C for 1 h with a heating ramp of 10 °C min^{-1} . Reaction was carried out with a not diluted mix (1:1) of 40 mL min^{-1} of CH_4 and 40 mL min^{-1} of CO_2 at 750 °C during 42 h. Reaction products were analyzed by GC using an Agilent's 490 microGC equipped with three micro-columns and TCD detectors.

3. Results and discussion

3.1. Characterization of fresh calcined systems

The three catalytic systems were characterized by N_2 adsorption analysis (BET, BJH), XRD, TEM, TPR, XAS and XPS. As expected for mesoporous materials, all samples exhibited type-IV adsorption isotherms. However, as reflected in Table 1, they undergo a significant change in BET surface area and mean porous size as a consequence of the alkaline treatment during the DP preparation methodology. Every sample, including a blank SBA-15 support submitted to the DP treatment without metal salts in solution (SBA-15-DP), suffers a decrease in surface area of around 65%, from 738 $\text{m}^2 \text{ g}^{-1}$ of the pristine SBA-15 to 250–280 $\text{m}^2 \text{ g}^{-1}$. Simultaneously, the smaller porosity collapses (mean size increasing from 6.7 to 10–12 nm). Despite this loss of surface area, the analysis by TEM (Fig. 1) shows that the channeled structure of the SBA-15 support

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