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New insights into the synergistic effect in bimetallic-boron catalysts for hydrogen generation: The Co–Ru–B system as a case study

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This paper is dedicated to Prof. Jean Marie Hermann at the occasion of his retirement from his fruitful carrier and strong promotion of international and multicultural exchange of researchers and knowledge.

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ABSTRACT

Catalysed sodium borohydride hydrolysis is a high-potential method to produce hydrogen for portable applications. Co–B catalysts are the most chosen because they are easily prepared, cheap and efficient. The addition of small amounts of Ru produces a significant enhancement in catalytic activity.

In the present work a series of Co–Ru–B catalysts with variable Ru content was prepared, isolated and characterized. The comprehension of the synergistic effect was achieved trough the incorporation of the nanostructural dimension to the study of surface and bulk chemical states of the involved atoms along the series. It was found that up to 70% (of total metal) atomic content of Ru the catalysts can be considered isostructural to the single Co–B catalyst in the nanoscale. A structural transition occurs in the case of the pure Ru–B material to produce a boron deficient material with higher nanoparticle size. This structural transition together with Co segregation and Ru dispersion play a key role when explaining a $[OH^-]$ dependent effect.

The inexistence of borate layers in Ru rich catalysts is suggestive in the research for non deactivating catalysts.

1. Introduction

Catalysed sodium borohydride ($NaBH_4$, SBH) hydrolysis is a promising method to store and supply hydrogen to PEMFCs (Polymer Exchange Membrane Fuel Cells) for portable applications. H_2 production occurs according to reaction (1):

$$NaBH_4 + (2+X)H_2O \rightarrow 4H_2 + NaBO_2 \cdot XH_2O \qquad X = 2, 4 \qquad (1)$$

This reaction is being extensively studied and main results and current challenges are summarized in recent review articles [1,2]. The efficiency of hydrogen release can be enhanced using appropriate catalysts. Within catalysts, M–B (M = metal) based materials are widely used and can be prepared by chemical reduction of aqueous solutions of metal precursors by SBH. Cobalt is definitely the most selected metal because its efficiency/cost relationship and it has been prepared, characterized and discussed in many works [3–17].

It is well known that the addition of a second metal M′ to form an M–M′–B material permits to increase significantly the catalytic activity respect to the initial M–B alloy. This enhancement has been proven not only for (1) but also for reactions such us ammonia synthesis, hydrogenation of benzene, CO and acetonitrile hydrogenation [18–22].

Recently, a combinatorial technique was employed to test the catalytic activity of in situ prepared M–Ru–B materials (M = Co, Ni, Fe, Pd, Ag, Cu) for reaction (1) [23]. It was found that the addition of ruthenium (20 mass wt%) to cobalt produces 250% enhancement in the activity in comparison to the Co–B mono catalyst. The comprehension of the effect has remained largely descriptive and phenomenological because of the complexity of catalysts composition and microstructure.

In the present work a series of Co–Ru–B catalysts with variable Ru content was prepared and characterized. The synergistic effect is explained by the incorporation of surface characterization as well as chemical and structural description in the nanoscale at the same extent it was done before for a single Co–B catalyst [24]. The comprehension of the effect was interpreted according to the chemical composition and nanostructural evolution along the Co–Ru–B catalysts series which was investigated through: TEM/EELS (Transmission Electron Microscopy/Electron Energy Loss Spectroscopy), TEM/SAED (Selected Area Electron Diffraction), SEM/EDX (Scanning Electron Microscopy/Energy Dispersive X-ray Emission) and XPS (X-ray Photoelectron Spectroscopy) analysis.

2. Experimental

2.1. Catalysts preparation

Catalysts were prepared using a modification of the technique employed before [24]. A discussion about the relationship between

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preparation, handling, storage conditions and final product is found in references therein.

Ultrafine Co–Ru–B powder catalysts were prepared by chemical reduction of an aqueous solution of $CoCl_2 6H_2O$ and $RuCl_3 3H_2O$ with variable x_{Ru} (where x_{Ru} is considered as $n_{mol\,Ru}/(n_{mol\,Ru}+n_{mol\,Co})$ by aqueous $NaBH_4$. 15 ml of a 0.424 M total metal solution (6.37 mmol) acidified with 150 μl of HCl (c) was vigorously stirred in a 0 °C ice bath while 16.4 ml of a $NaBH_4$ 9 wt% solution (43 mmol) was added during 5′. The reaction was left stirring for another 30′ and the solid was filtered and washed thoroughly with water, ethanol and an ethanol/acetone 3:1 mixture. Solvent dry solids are highly pyrophoric especially when $x_{Ru} \geq 0.5$. As a passivation procedure, solvent wet solids were dried slowly in air during 24 h and then were dried in vacuum during 24 h. After this treatment, the products were handled without any particular precautions. Powder catalysts were stored under N_2 in a glove box for characterization and in aerobic conditions to assess the stability against oxidation.

Samples are identified by the theoretical Ru content (w) as defined above, by indicating: "x_{Ru} w sample".

2.2. *Catalytic measurements: hydrogen generation (HG) test*

In a typical experiment, 38 mg of $NaBH_4$ was mixed in a mortar with 3.8 mg of the selected catalyst. The mixture was placed at the bottom of a three necked heart-shaped flask. The flask was immersed in a water bath maintained at (23 ± 0.5) °C. The reaction started by injecting 1 ml of a MilliQ® water or 4.5 wt% NaOH solution. The flask was connected to a 100 ml gas burette and the amount of hydrogen evolved was measured by reading the displacement of a piston (gas-tight by a mercury o-ring) as a function of time. No stirring was used for the experiments, except for the stirring effect of the evolved hydrogen. The HGR (hydrogen generation rate, ml min^{-1}) was obtained from the slope of the plot of the volume of hydrogen evolved vs. time in linear regime. HGR_{cat} was obtained dividing HGR by mass of catalyst employed. Experiments were done by duplicate, and showed to be reproducible.

2.3. *Catalysts characterization*

X-ray diffraction measurements were performed using Cu Kα radiation in a Siemens D5000 diffractometer in a Bragg-Brentano configuration in the 2θ angle range of 40–80°.

XPS spectra were recorded with a Leybold Heraus LH electron spectrometer using Al Ka radiation with 40 eV pass energy at normal emission take off angle. Calibration of Ru containing samples is a difficult task because of the superposition of C (1s) and Ru (3d) signals. In case of Co–Ru containing samples, the position of the $2p_{3/2}$ peak of the oxidized cobalt, at 781.2 eV was used as an internal reference for calibration. In the case of x_{Ru} = 1 sample, the absence of BO_2^- species permitted to assign the O (1s) singlet to Ru–O species, and was taken as second reference peak at 529.2 eV by comparison to ruthenium oxide commercial samples. Reference samples, RuO_2 powder and Ru foil were calibrated according to literature data [25]. Before measurements, the Ru foil was Ar^+ treated (10^{-5} Torr Ar, 3.5 kV during 8 min) to eliminate the oxide layer.

BET measurements were carried out with a Micromeritics Tristar II equipment.

For microscopy studies, the powder samples were impregnated on a copper grid coated with a holey –carbon film. The studies have been performed using two microscopes: A Philips CM 200 with a 2.4 Å resolution equipped with a PEELS spectrometer (GATAN 766-2K) and a high resolution SEM-FEG microscope Hitachi S4800 operating at 5 keV where the EDX detector allows the registration of individual elemental mapping.

Table 1
Catalysts characteristics.

Catalyst	Experimental[a] x_{Ru}	$[B]^b/[M]_{tot}$ ratio	%[c] mass Co	S_{BET} ($m^2\,g^{-1}$)
x_{Ru} = 0	0	0.5	78.04	24
x_{Ru} = 0.13	0.12	0.43	61.62	22
x_{Ru} = 0.5	0.42	0.33	32.85	29
x_{Ru} = 0.7	0.63	0.10	16.19	32
x_{Ru} = 1	1	0.04	0	26

[a] Obtained with experimental measurements of mass percentage of Co and Ru measured by ICP.

[b] $[B]/[M]_{tot}$ ratio represents the ratio between Boron atomic percent and total metal (Ru + Co) atomic percent obtained by ICP.

[c] Obtained by plasma ICP measurements

3. Results and discussion

3.1. *Chemical and nanostructural characterization*

Chemical analyses by plasma ICP (Inductive Coupled Plasma) are shown in Table 1.

The S_{BET} (Table 1) indicate that the prepared catalysts are ultrafine powders with similar surface areas for the extreme compositions and variations along the series that show an increase in surface area for samples x_{Ru} = 0.5 and 0.7.

Powder X-ray diffraction studies were carried out for the Co–Ru–B series and the results are shown in Fig. 1. Up to x_{Ru} = 0.13, powder catalysts are highly amorphous and for higher Ru content, broad diffraction peaks appear in the expected positions for Co and Ru metallic phases indicating the growth of very small crystalline domains.

Fig. 2 shows SEM images of powder catalysts x_{Ru} = 0, 0.13, 0.7 and 1. At this scale, the structure of the series can be considered equal, homogeneous and morphologically described as "cowliflower like". The catalysts appear to be porous and formed by 10–20 nm spherical particles with a degree of coalescence. SEM-EDX mapping of Ru and Co permits to verify that both metals are homogeneously distributed although the resolution is not enough to give further information in the nano-scale.

TEM images are shown in Fig. 3. For x_{Ru} = 0, 0.13 and 0.7 samples, the structure can be described as made up by spherical grains of around 20–40 nm diameter size, forming agglomerates with a degree of interconnection. These spherical grains are as well constituted by smaller dark contrast grains embedded in a light contrast matrix. Besides, the whole structure is surrounded by a lighter layer or veil. A difference to previously studied Co–B catalyst [24] is that

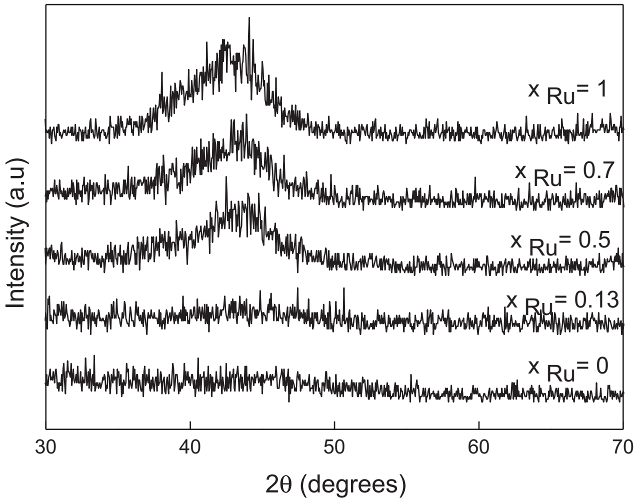

Fig. 1. XRD pattern for the Co–Ru–B prepared catalysts.