A stable catalyst for fuel cell grade hydrogen production from CH_4 decomposition

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Introduction

The catalytic decomposition of methane (CDM) is an attractive alternative for the production of COx-free hydrogen for use in fuel cells. Numerous supported metal catalysts have been tested for this process. Among them, Ni, Co and noble metals can catalyze the decomposition of methane forming carbon nanofibers under relative mild conditions. However, these catalysts rapidly deactivate [1-2]. Thus, in order to stabilize the active metal, lanthana alone or combined with silica is used in this work.

Materials and Methods

The La_2O_3-SiO_2 support was prepared by incipient wetness impregnation of SiO_2 (Aerosil 200) calcined at 900 ºC with $La(NO_3)_3$. La loading was 27.0 wt.% of La_2O_3. Metal deposition was performed with $RhCl_3$. $3H_2O$, $Ni(NO_3)_2$. $6H_2O$ or $Co(NO_3)_2$. $6H_2O$ used as precursor compounds. The Me/La_2O_3-SiO_2 and Me/La_2O_3 (Me= Rh, Ni, Co) catalysts were prepared by incipient wetness impregnation and wet impregnation, respectively. The Me/La_2O_3 solids were obtained by wet impregnation of La_2O_3. The loadings were 2 wt.% of Co and Ni and 0.6 wt.% of Rh. All the catalysts were calcined in flowing air at 550 ºC during 6 h. The surface area of the binary oxide catalysts is ca. 100 m^2g^{-1} while the lanthana supported solids have ca. 8 m^2g^{-1}. The catalysts precursors were characterized by different techniques, including X-ray diffraction (XRD), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). Before reaction, the precursors were reduced for 2 hours at 600 ºC using a 10% H_2/N_2 mixture. Activity measurements were carried out in a fixed-bed quartz tube reactor.

Results and Discussion

Fig. 1 shows the evolution of methane conversion with reaction temperature for the six catalysts. Note that Ni and Rh supported on the binary oxides are the best performing formulations. All the catalysts show stable conversion after being on stream for 24 hs. Furthermore, the best formulation (NiLasi) maintained the activity after 96 hours on stream (Fig. 1B). We have not found in the literature any catalyst for this reaction with such stability.

The TPR data (not shown) indicates that the three metals supported on both types of oxides were completely reduced below 600 ºC. CoLa and CoLaSi exhibit a single broad peak at 340ºC, assigned to dispersed Co_xO_y species. RhLa and RhLaSi show one peak each centered at 250ºC and 196 ºC, respectively. They are assigned to Rh^0 with different metal-support interaction. NiLa shows peaks at 150, 330 and 565ºC, while NiLaSi does so at 200, 470 and 600ºC. The DRX patterns of M-LaSi catalysts show broad reflections at 2θ= 28.5º and 44.5º assigned to $La_2Si_2O_7$. In the calcined M-La_2O_3 solids only the reflections of $La(OH)_3$ are observed. After reduction $La(OH)_3$, La_2O_3 and metal reflections are recorded (Table 1).
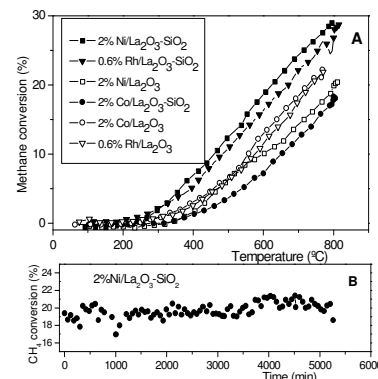

Figure 1. (A) CH_4 conversion vs T(ºC) and (B) Stability of NiLaSi at 600ºC. Reaction conditions: 60 mg of catalysts, 3% of CH_4 in N_2, 200 ml min^{-1}.

The Raman spectra of CoLa shows a small band at 700 cm^{-1}, while CoLaSi exhibits a broad signal centered at 626 cm^{-1}. They are assigned to the main shifts of Co_3O_4 and to highly dispersed Co_xO_y, respectively. The bands recorded with calcined NiLa are seen at 457 and 352 cm^{-1} while for NiLaSi they shift to 513 and 340 cm^{-1}, indicating the different extent of the metal support interaction. After 24 hs on stream all the catalysts containing either Rh or Ni show the caracteristic bands of graphite at 1595 and 1335 cm^{-1}. They were not observed in the Co containing solids.

Table 1 also shows some selected XPS data. Note that the B.E. of La $3d_{5/2}$ in $La(OH)_3$ is 835.6 eV and in La_2O_3 is 833.5 eV. The data shown in Table 1 combined with the XRD information are consistent with the above B.E. values. The higher Ni/La surface ratios in the NiLaSi catalysts are also consistent with the higher activity of this formulation.

Table 1. Characterization data of selected catalysts

Catalysts	Pretreatment	DRX	Binding energy (eV) La 3d $_{5/2}$	Surface ratio Ni2p$_{1/2}$/La3d$_{5/2}$
NiLa	calcined	$La(OH)_3$	835.0	0.26
	reduced	$La(OH)_3$, Ni^0, La_2O_3	834.0	0.22
NiLaSi	calcined	$La_2Si_2O_7$	835.3	0.40
	reduced	$La_2Si_2O_7$	834.9	0.55

Significance

The strong metal support interaction of NiLaSi seems to contribute to the excellent stability of the most active catalyst. In brief, the characterization data support the main catalytic findings.

References

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