ZEOLITE CATALYST FOR CO_2 REFORMING OF METHANE

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Abstract

Methane reforming with carbon dioxide to synthesis gas was investigated over a series of HNiY catalysts modified by Al and La .These catalysts were characterized by XRD, BET, FT-IR, and the nickel contents of the catalysts have been determined by chemical analysis.
The HNiY/La catalysts showed the highest carbon resistance and the most stable catalytic performance.

Keywords: CO_2/CH_4 reforming, zeolite, synthesis gas, carbon deposition.

Introduction

The catalytic reforming of methane with carbon dioxide to synthesis gas has attracted much attention, because it can produce synthesis gas having a low H_2/CO ratio (1:1) that is desirable for direct use as a feed stock for the production of oxygenated derivatives.This reaction is also of great importance in an environmental point of view, because methane and

carbon dioxide, well-known green house gases, can be converted into a valuable feed stock [1, 2].

The CO_2/CH_4 reforming has been studied over numerous supported metal catalysts, such as Ni-based [3-5] and noble metal catalyst [6] .Due to its low cost and ubiquity, Ni is often suggested as the most suitable metal to be dispersed on support.

One of the serious problems in the methane reforming with carbon dioxide is the carbon deposition formed via the Boudouard reaction ($2CO \longrightarrow C+CO_2$) or methane decomposition ($CH_4 \longrightarrow C+2H_2$) [7], whith eventually leads to catalyst deactivation, plugging of the reactor, and break down of the catalyst [8-10].It is known that noble metal catalysts are less sensitive to carbon deposition compared to nickel-based catalyst.

The catalyst support is also an important parameter for carbon dioxide reforming of methane. Several studies have shown that the nature of support employed in terms of surface area, acid-basic sites and metal support interaction influences the catalytic activity .Materials tradionally used as support are SiO_2[11],Al_2O_3 [12],peroviskite,La_2O_3,CeO_2 [13-14].Zeolites have been investigated as support for the carbon dioxide reforming of methane,zeolites may have potential properties for being support in reforming reaction such as their micropore structure, high surface area and high affinity for CO_2 as adsorbent [15-17].A mong the type of zeolites investigated, the zeolites Fau and MFI have been frequently investigated as support. The use of Ni support on zeolites in the dry reforming of CH_4 has been studied by Chang et al [17].They found that Ni supported on ZSM-5 zeolite showed high activity with high resistance to coke formation for CO2 reforming of CH4.This is due to its large specific surface area and its well-defined structure. Bhat and Sachtler [8].Have studied Rh in NaY and obtained catalysts combining stability with high activity and selectivity. Moreover, Jeong et al [18] investigated a series of Ni/HY catalysts modified by Mg, Mn, K, and Ca.It was observed that the Ni-Mg/HY catalyst showed the highest carbon resistance and the most stable catalytic performance.Reported in this work are characterization, catalytic activity, and stability of HY catalysts modified by Al and La promoters in the methane reforming with carbon dioxide.

2. Experimental

2.1Catalyst Preparation

The zeolite supported catalysts have been prepared from the commercial HY (HUSY) from Union Carbide with Si/Al= 3,5.The catalysts were prepared by an incipient wetness impregnation using Ni $(NO_3)_2.6H_2O$ (Prolabo) as the metal precursors.After impregnation,the catalyst sample were dried at 85°C and calcined at 700°C for 8h.

2.2 Characterization of Catalysts

The Ni content of the calcined catalysts has been determined by ICP flame spectroscopy, and the specific surface areas have been determined by the BET method.The results are summarized in Table 1.

Table 1: Properties of the samples studied in dry reforming of methane.

Sample	Ni,%Wt	S_{BET},m^2/g
HNiY	6,40	350,05
HNiY+Al	7,00	303,45
HNiY+La	7,12	318,69

The X-ray powder diffraction (XRD) for calcined catalysts was carried out in a Philips PW1050/81 automated powder goniometer (λ Cu(K α) = 1.54184 Å).Phase is identification was carried out using the reference database (JCPDS-files).The FT-IR spectra were recorder at room temperature with **PHILIPS 9800-FTIR** spectrometer,in the 4000-400 cm^{-1}range.

2.3 Catalytic Testing

The CO_2 reforming reaction of CH_4 was carried out in a continuous flow quartz U - tube reactor at 1 atm pressure and reaction temperature 600°C, with a constant feed composition with equimolar stoichiometric mixture of CH_4 and CO_2 and total flow rate of 20 ml/min, with 0,1g of catalyst.

The catalytic activities were investigad between 400 and 700°C.The reactants (CH_4, CO_2) and products (CO, CO_2, H_2) were analyzed on line using TCD gas chromatograph equipped with a Carbosieve -B column.

3. Results and discussion

3.1. XRD study

Typical XRD patterns for all fresh Ni supported on zeolite catalysts were recorded and illustrated as shown in Fig 1.

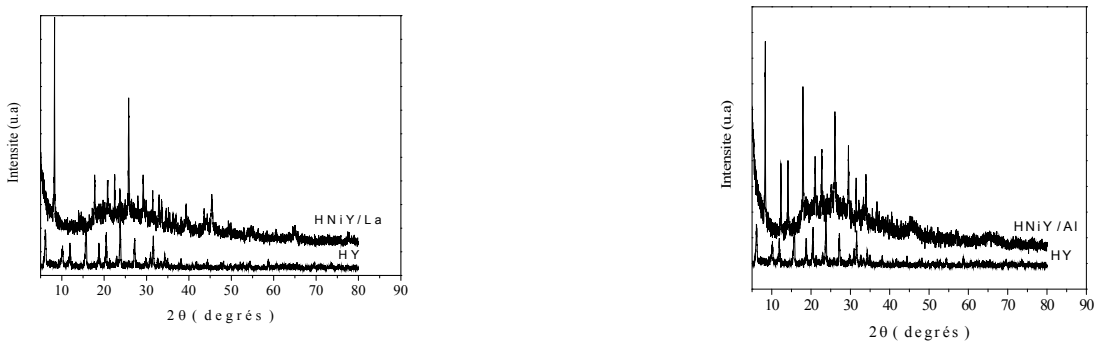

Fig.1. XRD patterns of freshly calcined catalysts

It appears in this case a clear reduction in the intensity of the most intense peaks of spectrum of zeolite HY, this result suggests that the crystalline structure of the starting zeolite is somewhat faded following the operations of successive impregnations and two operations of calcination. NiO crystalline phases were observed at 2θ = 37.2, 43.2, and 62.8° are clearly detected for all samples.

3.2. Spectroscopic studies

The FT-IR spectra of the prepared materials are illustrated in Fig 2.

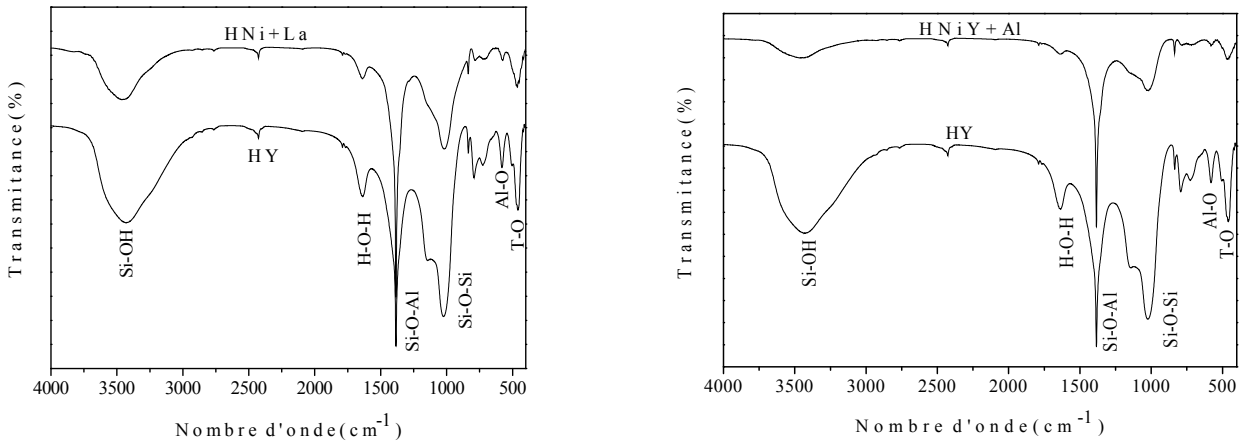

Fig. 2. FTIR spectra of HY, HNiY/La and HNiY/Al.

3.3. Reactivity

We have studied the reaction of dry reforming of methane by carbon dioxide in the presence of various catalysts at temperatures ranging from 400-700C°.CH_4 conversions and CO_2 variation with temperature is shown in Figs.3a and 3b for different catalysts.

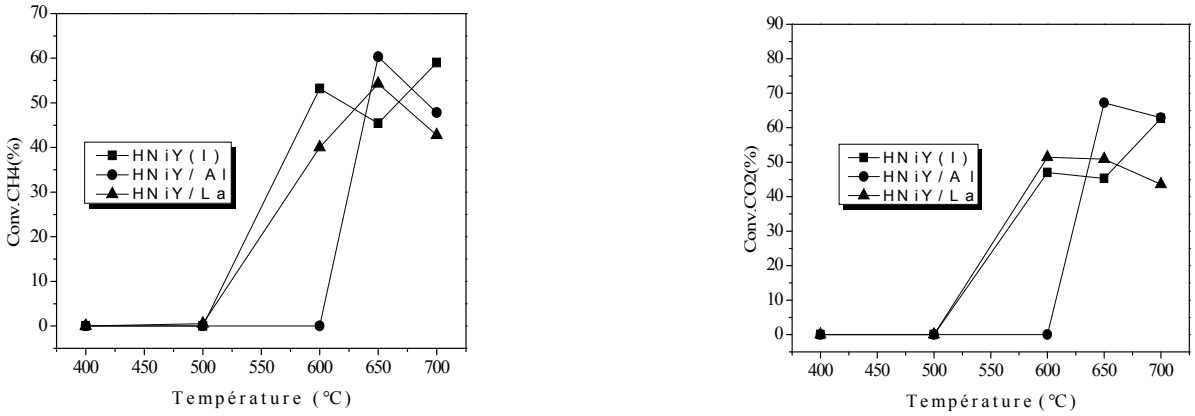

Fig.3. (a) Evolution of CH_4 conversion vs. temperature for different catalysts (P=1atm, CO_2/CH_4=1, F=1,2Lh^{-1}). (b) Evolution of CO_2 conversion vs.

At 700C°,the CO_2 conversion is similar to or higher than that of CH_4 because the reverse water gas shift (RWGS) reaction occurs simultaneously to CO_2 reforming of CH_4[19].There for, this reaction consume more CO_2 and produce more CO,as indicated by Bradford and Vannice [20].Wang and Au [21] attributed this result to CO_2 complete dissociation.The carbon monoxide formation rates equal 26,7.10^{-2} mol/h.g, 14,5.10^{-2} mol/h.g and 11,5.10^{-2} mol/h.g respectively on HNiY/La, HNiY(I) and HNiY/Al catalysts at 650C°.

To summarize, the studied catalysts exhibit catalytic performances at 650C°, whith vary in the following sequence: HNiY/La> HNiY> HNiY/Al.

Conclusion:

Methane reforming with carbon dioxide to synthesis gas was investigated over a series of HNiY catalysts modified by Al and La .These catalysts were characterized by different methods. The catalytic testing of these materials in the reaction of methane reforming by dioxide at various temperatures 400 to 700C° has evidenced differences in catalytic activity, according to the sequence HNiY/La> HNiY> HNiY/Al at 650C°.This study has shown the occurrence of many secondary reactions such as the reversed water gas shift reaction.

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