

Preparation and characterization of NiO/ZrO₂ catalyst prepared by impregnation for hydrogen production by methane steam reforming.

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Abstract—The activity and stability of NiO (4wt%) catalysts supported on ZrO₂ were investigated for the methane steam reforming between 475 and 700 °C at atmospheric pressure. The catalysts were prepared by the impregnation method. They have been characterized by various physical methods like atomic absorption, BET technique, X-ray diffraction. The results of XRD analyses carried out showed the presence of the NiO phase for the solid. The reaction of steam reforming of methane, in the presence of nickel-based catalysts (4% nickel) deposited on ZrO₂, is carried out at atmospheric pressure between 475 and 700 °C. According to the catalyst, the activity can be due, not only to the interaction nickel-support but also to the physico-chemical properties of the support.

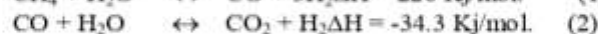
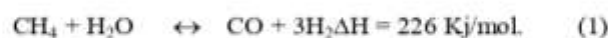
Keywords— Methane, steam reforming, nickel/ supports oxides, Hydrogen, coke.

I. INTRODUCTION

Today, alternative and sustainable solutions are proposed to replace fossil fuels. Hydrogen is an alternative energy source for the future. It can be produced by electrolysis (4%) and essentially by reforming of fossil fuels (95%). Natural gas, consisting mainly of methane, propane and butane, is a fairly abundant and widely available raw material in the world. The preferred route of its recovery is its transformation into synthesis gas (CO + H₂). It can be converted into many products usually derived from petrochemistry (ammonia, methanol, higher alcohols, aldehydes, carboxylic acids, gasoline...

Steam methane reforming is the most common and economical way to make hydrogen. There are two primary reactions: the reforming reaction (1) and the water gas shift

reaction (2) to produce synthesis gas according to the following reactions:



Due to the endothermic reaction, it operates that under severe conditions pressure and temperature (15 - 30 bar and 850-900°C) in order to increase the conversion to methane. The syngas (CO + H₂) obtained has a defect in carbon monoxide. In these reactions, the supported catalysts are largely used. The support is not necessarily inert, there are metal-support interactions that exalt the activity of the catalysts [1]. The reactivity and stability of Ni/SiO₂ catalysts are investigated in the steam reforming reaction at 565 °C. The results showed a great dependence on the steam-reforming according to the ratio $R = \text{H}_2\text{O} / \text{CH}_4$.

Among the advanced research and the existing processes in the area of chemical conversion of natural gas, the classical methane steam reforming (MSR) is an indirect conversion via synthesis gas and remains extensively used [2]. The hydrogen is a clean energy that could play a key role as energetic source for fuel cells and for the environmental protection [3].

Among the catalysts based on transition elements, used in the steam reforming of methane, nickel is the most studied element [4]. It has been reported that nickel presents good catalytic performances when supported on Al₂O₃ doped by MgO and CaO [5]. Mixed oxides such as Al₂O₃-ZrO₂, prepared by sol-gel method, or by grafting zirconium on the surface of the alumina.

The major problem with nickel based catalysts, is carbon deposition to form coke which deactivates the catalysts. To remedy this inconvenient, some authors

examined the use of the nickel promoted by an alkaline oxide [6] in sweeter conditions.

The aim of the present work is to compare the activity, the selectivity and the carbon formation of nickel based catalyst (4 wt. %) supported on ZrO_2 during the MSR reaction. The catalysts have been characterized after calcination and reaction by BET, atomic absorption, X-ray diffraction (XRD).

II. EXPERIMENTAL

A. Catalysts preparation

The solids Ni/ ZrO_2 were prepared by impregnation of the support ZrO_2 with $Ni(NO_3)_2 \cdot 6H_2O$ (1 M) (Merck). The solution was stirred during 2 h, and then evaporated at 80 °C under agitation. The solid was dried at 80 °C (12 h), calcined during 2 h at 300 °C and 2 h at 500 °C at a heating rate of 4 °C/min, in air flow (1.2 L h⁻¹). The catalysts were then sieved to have a particle diameter less than 0.16 mm.

B. Catalysts characterization

The solids were analyzed by atomic absorption thanks to a spectrometer type Perkin-Elmer 1100 B. The specific surface areas were determined by the BET method using an analyzer of surface type (Coultronics 2100E). The crystal structures were identified by XRD with a diffractometer ($\theta/2\theta$ CGF) provided with a proportional detector and using $K\alpha$ molybdenum anticathode ($\lambda=0.70930$ Å). The X-ray patterns were obtained for 2θ values ranging from 20° to 70°. The apparent size of nickel oxide (nickel) particles was calculated by the Scherrer formula, $L = 0.9\lambda/\beta\cos\theta$, where β is the width of the most intense NiO peak at half-height, and θ is the corresponding Bragg angle.

C. Reactivity

The catalytic tests were carried out in a quartz reactor fixed bed ($L=65$ cm, $\varnothing=1$ cm) under atmospheric pressure. The catalyst (0.1 g) is pre-reduced at 500 °C under hydrogen flow (1.2 L h⁻¹) before introduction of the gas mixture ($H_2O/CH_4 = 3.3$) diluted in argon flow and obtained by crossing of a mixture CH_4 (10 %)/Ar, in a saturator with a thermostated bath (65 °C, 1.2 L h⁻¹). The reactants and the products (CO , CO_2 and CH_4) were analyzed by gas chromatography thanks to TCD chromatograph (Hewlett-Packard 5730) on a carboxieve B column, 100-200 mesh, of 2 m of length, using hydrogen as vector gas.

Before each analysis, the reactants and products pass through a water-trap at 0 °C to remove water. The conversion of CH_4 and product selectivities are calculated using following formulas:

$$Conversion_{CH_4} (\%) = \frac{n_{CH_4}^{in} - n_{CH_4}^{out}}{n_{CH_4}^{in}} \times 100$$

$$Selectivity_{CO} (\%) = \frac{n_{CO}^{out}}{n_{CH_4}^{in} - n_{CH_4}^{out}} \times 100$$

$$Selectivity_{CO_2} (\%) = \frac{n_{CO_2}^{out}}{n_{CH_4}^{in} - n_{CH_4}^{out}} \times 100$$

$$\%C = (n_{CH_4}^{in} - (n_{CH_4}^{out} + n_{CO}^{out} + n_{CO_2}^{out})) \times 100$$

n : number of moles

III. RESULTS AND DISCUSSION

A. Catalytic systems characterization

The physical characteristics of the solids are summarised in Table1.

TABLE I
CHARACTERISTICS OF Ni/SUPPORT SYSTEMS

Samples	SBE m ² /g	Ni _{app} wt%	Ni _{meas} wt %	XRD results			
				d ^o (nm) NiO	d ^o (nm) Ni	before reaction	After reaction
ZrO ₂	93						ZrO ₂
4% Ni/ZrO ₂	86	4.3	4	35.8	21.5	NiO, ZrO ₂	Ni ^o , ZrO ₂

[a]: Evaluated from the full width β at half maximum of the most intense XRD peak using the Scherrer relation.

The atomic absorption analysis shows that the composition of the systems is very close to the theoretical one.

The specific surface areas of 4wt %Ni/ZrO₂ are 86 m²/g, slightly lower than that of the ZrO₂ support (93m²/g).

The crystallite size was calculated from X-ray line broadening of NiO and that of Ni peaks ($2\theta=19.5^\circ$ and 20° respectively) using the Scherrer equation. The results show that the support influence significantly the average size of Ni particles with ca. 22 nm for Ni/ZrO₂, while for the NiO particles, the value is ca. 36 nm for carriers.

After calcination at 500 °C, the XRD pattern of 4 wt% and after MSR reaction, the presence of Ni^o metallic species and that of support are visible in the patterns of Ni/ZrO₂ (Table 1). The absence of peaks corresponding to carbon in presence of Ni/ZrO₂ catalyst could be due to an amorphous form of carbon.

B. Methane Steam reforming reaction

The catalytic performances of supported Ni systems in the MSR reaction were examined in the temperature range (475–700 °C), after reduction pretreatment under hydrogen flow at 500 °C (1.2 L/h).

Moreover, we noticed no diffusional limitation (effect of mass, flow etc...). The experimental conditions of the

reaction are chosen so that they are as optimal as possible. It appears that the catalyst is more active. This is can be due to a better dispersion of the active phase for the weakly charged catalyst, a result in agreement with the literature data.

The MSR reaction over the catalysts leads to the formation of CO, CO₂, H₂ and carbon and the results are reported in Figures 2, 3

C. Variation of the catalytic activity over the reaction time

For the preparation of 4%Ni/ZrO₂ sample, two calcination temperatures (500 and 700°C) were used to examine their effect on the catalytic performance.

After reduction pre-treatment (H₂/500 °C/overnight), 4%Ni/ZrO₂ system leads to similar evolution of the methane conversion with reaction temperature for calcinations temperatures 500 and 700 °C. when the catalyst is calcined at 500 °C, the CO₂ formation is favoured at low reaction temperatures (> 650 °C), the CO selectivity is favoured at high temperatures (< 550 °C). This result shows that the used calcination temperature, during the catalyst preparation, does not have a significant effect on the conversion whereas CO formation is favored when the calcination temperature is 500 °C. So, the calcination temperature was fixed at 500°C for all studied systems.

Table 2 and Figure 1 show methane conversion as a function of reaction temperature.

TABLE II
CATALYTIC ACTIVITIES OF NiO/ZrO₂

Catalysts	Temp (°C)	Conv (%)	Select CO (%)	Select CO ₂ (%)	% C	H ₂ 10 ⁻⁴ (mol/g h)
4%Ni/ZrO ₂	475	22	12	42	46	-
	500	33	30	23	47	17.0
	550	49	46	6	48	17.2
	600	62	42	traces	58	17.4
	650	75	41	0	59	17.5
	700	82	41	0	59	17.5

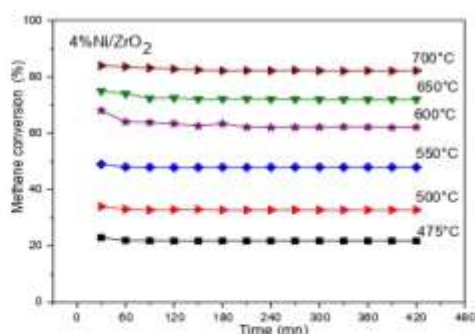


Fig. 1: Methane conversion vs. reaction time, for catalysts 4% Ni/ZrO₂ at different temperatures, m= 0.1 g, Tred= 500 °C/H₂/overnight, d= 1.2 L h⁻¹, H₂O/CH₄= 3.3.

The catalytic activity of 4%wt NiO/ZrO₂ in the MSR reaction was examined in the temperature range (475–700 °C) after in-situ pre-treatment of the catalyst under hydrogen flow at 500 °C overnight. Similar evolutions of the methane conversion as a function of time-on-stream were obtained at different temperatures for 4%wt NiO/ZrO₂ catalyst. Steady-state was reached at the beginning of reaction for all temperatures indicating a good stability of this system. The catalytic activity of 4%wt NiO/ZrO₂ became stable in less than 3 h for reaction temperatures below 700 °C. The methane conversion increases from ca.20 to ca. 85% in presence of 4%wt NiO/ZrO₂ with increasing of reaction temperature from 475 to 700 °C, reflecting the endothermic nature of MSR reaction.

The evolution of the methane conversion with time shows that a stationary regime is reached after ~ 3 h (Fig. 1). The setting in mode is accompanied by the formation of CO₂ which strongly decreases with the profit of the CO formation as one approaches the stationary regime. This indicates an incomplete reduction of catalysts during the pre-treatment in H₂ (500 °C) and thus the reactional mixture produces species on surfaces more reduced than hydrogen itself [7]. We note an important carbon deposition at 600 °C on the catalysts.

The methane conversion is represented in figure2.

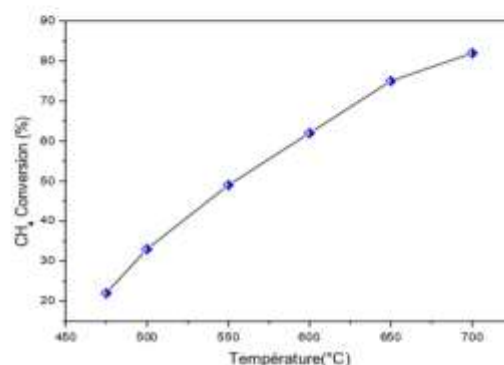


Fig. 2 Conversion of the methane versus temperature for nickel-based catalysts with ratios of 4% NiO/ZrO₂ at different temperatures, m= 0.1 g, Tred= 500 °C/H₂/overnight, d= 1.2 L h⁻¹, H₂O/CH₄= 3.3.

This result is agreement with the literature, according to Nielsen [8] who found that carbon deposition, on nickel catalyst has different temperature regimes: usually, ~ 550 °C, the activation energy of coke formation changes to a negative value.

Regarding the activation energy we plotted the log TTG = f (1 / T) (Fig3) the slope gave us a value of - 850 KJ/mole; this value being negative it goes in the same direction as the literature [8].

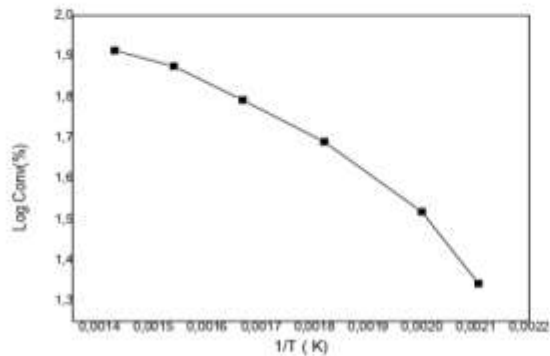


Fig. 3 Log Conv= f (1/T) of the methane for nickel-based catalysts with ratios of 4% NiO/ZrO₂ at different temperatures, m= 0.1 g, T_{red}= 500 °C/H₂/overnight, d= 1.2 L h⁻¹, H₂O/CH₄= 3.3.

The methane selectivity as a function of reaction temperature shows in figure 3.

The testing results show that catalytic performances of Ni/ZrO₂ are very sensitive to temperature from 500 to 700 °C, and conversions varying between 22 - 82 % (Fig 2) and CO selectivity varying between 12 - 41% (table II and Fig 3). On the other hand, we note that the selectivity of CO₂ move towards zero around 600 °C (table II and Fig 3). We notice an important carbon deposition at 600 °C on catalyst (table II).

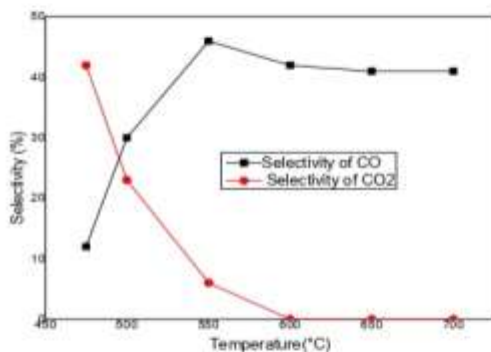


Fig 3: Methane selectivity versus temperature catalysts for nickel-based catalysts with ratios of 4% NiO/ZrO₂ at different temperatures, m= 0.1 g, T_{red}= 500 °C/H₂/overnight, d=1.2 L h⁻¹, H₂O/CH₄= 3.3.

The Production of hydrogen according to the temperature on the nickel-based catalysts is presented in Fig4.

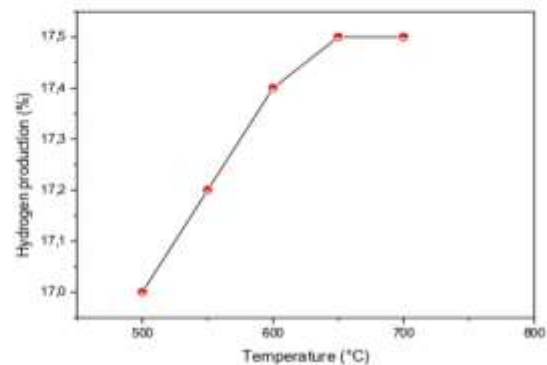


Fig 4 : Production of hydrogen according to the temperature on the nickel-based catalysts, with ratios of 4% NiO/ZrO₂ at different temperatures, m= 0.1 g, T_{red}= 500 °C/H₂/overnight, d= 1.2 L h⁻¹, H₂O/CH₄= 3.3.

The best hydrogen production is at temperature between 650-700°C (17.5%) (Fig 4).

IV. CONCLUSIONS

In the present work we showed the reactivity, of CH₄/H₂ reaction, for synthesized Ni-based catalysts (4 % of NiO) supported on ZrO₂ at temperatures ranging from 475 to 700 °C facilitated the formation of synthesis gas(production of hydrogen).

The catalyst is more active. This result can be explained by a better dispersion of the active phase for the lower nickel charged catalysts.

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