

## **Methane catalytic decomposition over Cu-Ni-Al catalyst: reaction rate and catalyst regeneration**

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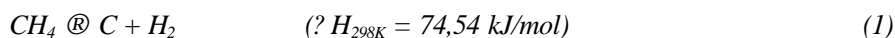
### **Abstract**

The objective of this work is the kinetic study and the reaction rate determination of methane catalytic decomposition over Cu-Ni-Al catalyst for pure hydrogen production. First the rate limiting step was investigated. To do so, reaction was carried out using four catalyst particle size ranges and the Mears criterion was applied. They showed that the external diffusion effects and diffusion in porous catalysts step do not influence significantly the reaction rate in the studied conditions. Then the reaction was carried out in a thermobalance with different temperatures (500 to 600°C) and methane concentrations (0.5 to 1.2 mol m<sup>-3</sup>) in order to determine the reaction rate. It was observed that this is a first order reaction, with activation energy of 50655 J mol<sup>-1</sup>. The reaction also forms carbon, which is deposited on the catalyst surface causing deactivation. The carbon oxidation for catalyst regeneration was also investigated. Repeated reaction-regeneration cycles were carried out, being the regeneration composed by oxidation or by oxidation and reduction. The oxidation was carried out at different temperatures (500 to 600°C) and times (20 to 75min), with the reaction happening in severe conditions (600°C and methane concentration of 1.2 mol m<sup>-3</sup>). The best regeneration condition, that is, the condition that allows a larger number of cycles with low activity loss, was determined. It was also observed that the deposited carbon is in the nanotubes form, which was analyzed by Scanning Electron Microscopy (SEM).

Keywords: hydrogen production; natural gas; methane decomposition; co-precipitated catalyst; carbon nanotubes.

### **1. Introduction**

Hydrogen has been considered as an ideal energy source because its combustion generates only water. Methane is the usual hydrogen source (Takenaka et al., 2004) and natural gas steam reforming is currently the most economic way to produce hydrogen (Guil-López et al., 2006). Others pathways are partial oxidation, autothermal reforming and dry reforming. These processes provide hydrogen in a mixture with carbon monoxide, which is a strong poison for fuel cells (Chen et al., 2004). This way, an interesting alternative process for hydrogen production is methane catalytic decomposition:



The methane decomposition produces high purity hydrogen, which can be utilized directly as the fuel of H<sub>2</sub>-O<sub>2</sub> fuel cell (Suelves *et al.*, 2006). Besides, carbon may be produced in the nanotubes form (Villacampa *et al.*, 2003; Perez-Lopez *et al.*, 2004a, 2004b, 2005). The carbon nanotubes properties (Serp *et al.*, 2003), make them suitable for many applications such as polymer reinforcements for composites or materials for energy storage, electronics and catalysis (Paradise *et al.*, 2006).

The catalysts used in the methane decomposition are mostly based on transition metals (Ni, Fe, Co etc.) (Paradise *et al.*, 2005), especially, Ni catalysts, due to its high catalytic activity and capacity of producing carbon nanotubes in moderate temperatures, of 500-700°C (Aiello *et al.*, 2000). When Ni catalyst is modified with other metals, an increase in its stability is expected (Takenaka *et al.*, 2003).

The main problem of Ni-based catalysts is its deactivation due to carbon deposition on its surface, covering the Ni active centre. However, catalyst deactivation may be overcome by regeneration of the catalyst (Takenaka *et al.*, 2004; Guil-López *et al.*, 2006; Villacampa *et al.*, 2003; Aiello *et al.*, 200; Otsuka *et al.*, 2004).

In this work, the kinetics parameters of methane decomposition reaction over Cu-Ni-Al co-precipitated catalyst were determined and the regeneration of the deactivated catalyst was studied.

## 2. Experimental

### 2.1. Catalyst preparation

The Cu-Ni-Al catalyst was prepared by a co-precipitation of a solution containing metallic nitrates (Cu, Ni and Al) with Na<sub>2</sub>CO<sub>3</sub>, at constant pH (8±0,1) and temperature (60°C). The precipitate was crystallized, filtered and dried. The catalyst obtained was submitted to thermal treatment with synthetic air at 600°C for 6h.

### 2.2. Catalytic Tests

The catalytic tests were carried out in a TA thermobalance (model SDT Q600). The catalyst samples were firstly activated with a N<sub>2</sub>/H<sub>2</sub> (80/20) mixture at 500°C and at a heating rate of 5°C/min. The methane decomposition reaction was carried out (2 h) with a CH<sub>4</sub>/N<sub>2</sub> mixture at different methane compositions (0.5-1.25 gmol.m<sup>-3</sup>) and temperatures(500-600°C).

Reaction-regeneration cycles were carried out with different temperatures and regeneration times. After the reaction (600°C and 1.25 gmol.m<sup>-3</sup> CH<sub>4</sub> concentration) the methane was removed by purge with nitrogen and the synthetic air was added in order to do carbon oxidation. The reaction-regeneration sequence was repeated several times. Regeneration was carried out in temperatures between 500 and 600°C for 30 min and in different times (20, 30 and 45 min) at 560°C. An additional experiment was carried out including an activation step (N<sub>2</sub>/H<sub>2</sub> at 500°C for 1 h) after regeneration with air (560°C for 30min).

## 3. Results and discussion

### 3.1. Influence of the methane concentration

Figure 1 shows the reaction rates obtained at 600°C and different methane concentrations. It is shown that the reaction rate increases quickly in the initial minutes, which is called the nucleation period. The rate enhances until reach a constant value called the growth filaments period (Villacampa *et al.*, 2003; Snoeck *et al.*, 1997a, 1997b; Toebes *et al.*, 2002). However, if the rate continues to increase after the nucleation period, it means that there is still formation of new nucleation points.

The increase of the reaction rate after the nucleation period is ascribed to further reduction of the remained NiO phase (after activation), due to the presence of methane or hydrogen produced in the reaction. In our case, it is reasonable to suppose that after the activation step the reduction of NiO was not complete due to the low reduction temperature used. Similar behavior was observed by Snoeck et al. (1997) and Zhang and Smith (2005). A four hours test showed that the reaction rate became constant at about 140 minutes.

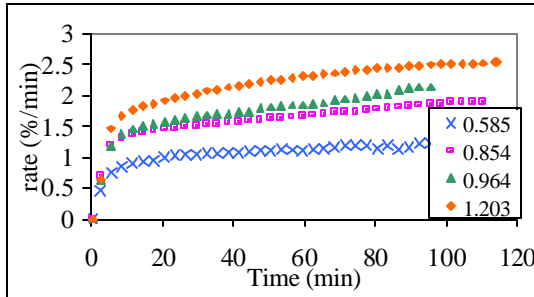


Figure 1. Methane concentration effect ( $\text{gmol.m}^{-3}$ ) on the reaction rate.

Like described in the literature (Fogler, 1999):

$$r'_c = k' C_{\text{CH}_4}^n \quad (1)$$

In equation 1,  $r'_c$  is the carbon generation rate ( $\text{gmol.g}_{\text{cat}}^{-1}\text{min}^{-1}$ ),  $k'$  is the specific reaction rate ( $\text{m}^3\text{g}_{\text{cat}}^{-1}\text{min}^{-1}$ ),  $C_{\text{CH}_4}$  is the feed methane concentration ( $\text{mol m}^{-3}$ ) and  $n$  is the reaction order. The plot  $\ln(r'_c)$  versus  $\ln(C_{\text{CH}_4})$  allowed to calculate  $k'$  for  $600^\circ\text{C}$  and the reaction order,  $n$ . The kinetic parameters found by linear regression ( $R^2=0.998$ ) were:  $k'=0.00181\text{m}^3\text{g}_{\text{cat}}^{-1}\text{min}^{-1}$  and  $n=0.94$ .

### 3.2. Effect of the Temperature

In order to determine the activation energy, the reaction rates for different temperatures were obtained (Figure 2). Considering a first order reaction,  $k'$  for each temperature is calculated by equation 1. Starting from equation 2, the  $k_0$  (pre-exponential factor,  $\text{m}^3\text{g}_{\text{cat}}^{-1}\text{min}^{-1}$ ) and  $E_a$  (activation energy,  $\text{Jmol}^{-1}$ ) found by linear regression ( $R^2=0.995$ ) were  $2.0\text{m}^3\text{g}_{\text{cat}}^{-1}\text{min}^{-1}$  and  $50655\text{Jmol}^{-1}$ , respectively.

$$k' = k_0 e^{-\frac{E_a}{RT}} \quad (2)$$

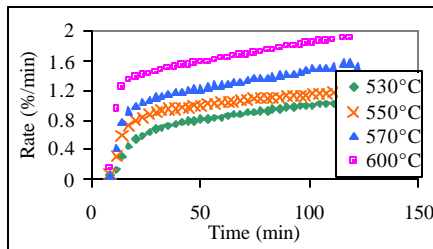


Figure 2. Reaction temperature effect on the reaction rate.

Villacampa et al. (2003) obtained carbon formation activation energy over Ni-Al co-precipitated catalyst of  $14.440\text{Jmol}^{-1}$  in the nucleation step. Constant reaction rates for a 400 min time-on-stream were observed by Li et al. (1997) using supported nickel catalysts.

Zavarukhin and Kuvshinov (2004) studied the methane decomposition over Ni-Al coprecipitated catalyst using a fluidized bed microreactor. The rates initially reached a maximum and later happened quickly deactivation. Similar behavior was observed by Villacampa *et al.* (2003); Piao *et al.* (2002); Otsuka *et al.* (2004).

### 3.3. Effect of Regeneration Cycles

The catalyst was submitted to reaction-regeneration cycles, being the reaction carried out with a larger methane concentration ( $1.203 \text{ gmol m}^{-3}$ ). Figure 3 shows the results for several reaction-regeneration cycles. As it can be seen, three regenerations were performed without significant loss of activity and the initial nucleation period was observed only in the first reaction. The reaction rate is approximately constant after the first regeneration and, in sequence, a decline is observed, showing the loss of stability of the catalyst. This decrease in the reaction rate can be attributed to a partial oxidation of the active phase (Ni<sub>0</sub> metallic) during the regeneration stage.

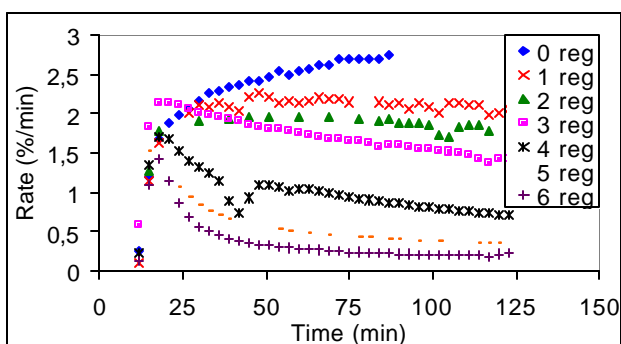


Fig. 3. Regeneration cycle effect on the reaction rate (regeneration at  $560^\circ\text{C}$  for 30 min).

The ratios between reaction rates after regeneration and the initial rates (fresh catalyst), for several regeneration temperatures, are presented in Table 1. As it can be seen, the optimum regeneration temperature is  $560^\circ\text{C}$ , since the first three regenerations the maximum rate is approximately 80% of the initial rate. After the third regeneration, the rate suffers an abrupt fall and its maximum value is half of the initial value. On the other hand, when regeneration is carried out at temperatures smaller than  $560^\circ\text{C}$  the produced carbon was not totally eliminated, accumulating after each regeneration, and a strong decrease in the reaction rate was observed after each cycle.

Table 1. Regeneration conditions effect on the  $r/r_0$  ratio after the regeneration cycles.

Number of reg.	500°C	530°C	560°C			600°C
	30min	30min	20min	30min	45min	30min
1	0.52	0.74	0.78	0.80	0.83	0.73
2	0.375	0.61	0.70	0.75	0.75	0.71
3		0.54		0.78		
4		0.48		0.62		
5		0.47		0.57		
6		0.47		0.52		

Table 1 also shows 20, 30 and 45 minutes regenerations that are carried out at 560°C. It can be observed, that there aren't significant differences among them. As pointed out previously, Ni metallic can be partially converted to the oxide form when regeneration is carried out with air and therefore a new reduction stage may be necessary after carbon elimination with air. Figure 4 shows the results of runs carried out with the inclusion of a  $H_2/N_2$  reduction step after each regeneration (30min at 560°C).

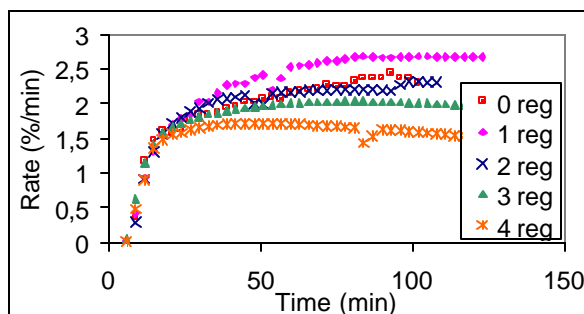


Fig. 4. Influence of regeneration cycle, with reduction step, on the reaction rate.

As it can be seen, the obtained results were better and the catalyst was more active after the first regeneration than the fresh catalyst. Similar behavior was observed by Guil-López et al., (2006). These results proved that the catalyst was not totally activated in the reduction step, explaining also the increase in the reaction rate of the fresh catalyst with the time-on-stream. This behavior is due to the complete activation of the catalyst that takes place only after the first cycle of regeneration.

#### 4. Conclusions

It was possible concluded that the methane decomposition over Cu-Ni-Al catalyst is an alternative route for hydrogen production from natural gas. Also:

- when fixed temperatures was used, the reaction rate increases until it reaches a constant value, which occurs above a 140 min time-on-stream. The catalyst was shown quite stable in the studied period;
- the kinetic parameters have been correlated satisfactorily. The reaction is first order, and the activation energy is of 50.6 kJ/mol;
- the results of regeneration will be better when carried out at 560°C during 30 min. If the  $H_2/N_2$  reduction step is made after each regeneration, the catalyst can be regenerated more times with smaller activity loss in the same conditions.

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