

Partial Regeneration of Ni-Based Catalysts for Hydrogen Production via Methane Cracking

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Methane cracking has the potential to produce high purity, carbon monoxide-free hydrogen suitable for application in PEM fuel cells. The 2 products of the reaction are molecular hydrogen and solid carbon. The carbon appears in the form of carbon filaments whose growth is hindered by carbon encapsulation leading to total deactivation of the catalyst. Several attempts have been made to regenerate the catalyst, mainly by gasifying the carbon filament in air or steam. Our work on 5-wt% $Ni/\gamma-Al_2O_3$ indicated that after complete gasification of the carbon the catalyst lost nearly all its activity toward methane cracking. However, if the gasification proceeds to only a certain extent, it is possible to recover significant activity of the catalyst. This technique, also known as partial regeneration, is a promising strategy to overcome the challenge of catalyst deactivation in catalytic decomposition of methane. Optimization of the partial regeneration method is presented here, in particular the extent to which the gasification should take place. Activity of the catalyst and the extent of gasification have been monitored through thermogravimetric analysis.

Regeneration of catalyst is still a much-questioned field to maintain not only a continuous and also an economical process. That is why this experimental study focused on regeneration of nickel supported on alumina. As an overview of this study: The effects of percentage of nickel, application of reduction, reaction temperature, and the amount of gasified carbon on weight gain are stated as the rate of carbon formation per gram of nickel present in catalyst.

Key Words: Methane cracking, hydrogen, filamentous carbon, partial regeneration, $Ni/\gamma-Al_2O_3$ catalyst.

Introduction

Hydrogen, being a clean source of energy, is predicted to be the “fuel of the future”.¹⁻³ Hydrogen also plays an important role in many other processes like chemical processes, electronics, food processing,

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and metal manufacturing. It is generally accepted that in the near-to-medium term future hydrogen production will continue to rely on fossil fuels, primarily natural gas.⁴ Natural gas—mostly methane—is the most obvious source for hydrogen because it has the highest H/C ratio among all fossil fuels and is relatively abundant.^{5,6} Advanced processes for hydrogen production (high-temperature water electrolysis, thermochemical and hybrid water splitting cycles, photoelectrochemical and photobiological decomposition of water, solar/photovoltaic water electrolysis, etc.) will not yield significant reductions in hydrogen costs in the near future (10-20 years).⁵ Steam reforming of methane remains the technology of choice for hydrogen production. Other important methods of hydrogen production include autothermal reforming and partial oxidation. However, all these processes involve the formation of a large amount of CO₂ as a by-product. CO₂, which is a major greenhouse gas, is of environmental concern,⁷ and the hydrogen purity obtained from these conventional methods is not suitable for hydrogen in PEM fuel cells and a further purification step would be required to remove CO.⁵

The catalytic cracking of methane over supported nickel catalysts is a potential route for the production of molecular hydrogen and solid carbon.⁸ Thermocatalytic cracking of natural gas is a simple one-step process without energy and material intensive gas separation stages and has the potential to be a CO₂-free hydrogen production process.⁴ If not used in PEM fuel cells, the unseparated mixture of hydrogen and methane is a more effective fuel for internal combustion engines and gas turbine power plants than natural gas or oil.

As a reaction product, solid carbon, in the form of pyrolytic carbon, carbon black, and filamentous carbon, can be used in various industrial processes. It possesses a variety of unique properties with prospective applications such as catalyst supports, reinforcement material, selective adsorption agents, and energy storage devices.¹ Therefore, in the last few years a great deal of effort has been directed towards the optimization of process conditions for carbon filament (CF) formation and the tuning of the CF properties for desired applications.

The growth of carbon filaments is a result of the following processes:^{1,5,9} Decomposition of the hydrocarbon at the gas–metal interface followed by dissolution of carbon into the metal and diffusion through the particle. The carbon then precipitates at the metal–support interface, detaches the metal particle from the support, and forms a filament with an exposed metal particle at its tip. The rate-determining step of this process is thought to be the diffusion of carbon through the metal particle. This mode of carbon accumulation allows the catalyst to maintain its activity for an extended period of time without deactivation.⁸

If methane cracking is to be utilized for the production of hydrogen in a continuous process (similar to the one introduced by UOP in the 1960s) catalyst regeneration has to be improved.⁸ Such regeneration is still being investigated in order to render the process continuous and economically viable. That is why the present experimental study focused on regeneration of nickel supported on alumina. Our work on 5-wt% Ni/ γ -Al₂O₃ indicated that, after complete gasification of the carbon, the catalyst lost nearly all its activity toward methane cracking.⁵ Instead of complete gasification, partial gasification of the deposited carbon is a strategy that we propose to maintain significant activity of the catalyst. This technique, also known as partial regeneration, is a promising strategy to overcome the challenge of catalyst deactivation in the catalytic decomposition of methane. This study investigates the effects of percentage of nickel, application of reduction, reaction temperature and amount of gasified carbon, on catalyst activity.

Experimental

Catalyst Preparation

The catalysts used for thermocatalytic cracking of methane were 5, 10, and 15 wt% Ni/ γ -Al₂O₃ (30-40 mesh) prepared by incipient wetness impregnation of γ -alumina support in powder form (Alfa Aesor, 99.94%). The metal precursor was Ni (NO₃)₂.6H₂O salt (Aldrich, crystalline). The required amount of nickel nitrate was dissolved to obtain a homogeneous solution and this solution was impregnated with support (Al₂O₃) and dried overnight. The resulting solution was stirred for 2 h (rpm: 120, T = 19 °C). The resulting solution was then heated at 80 °C for 1 h with stirring until the solution became viscous. The catalyst was dried at 130 °C overnight. The dried catalyst was pressed and crushed for sieve analysis.

Pretreatment and Activity Measurement

Calcination, reduction, and methane cracking reactions were performed in situ in a thermo-gravimetric analyzer (Cahn TG 151, Thermo Cahn). The calcination temperature was chosen as 50 °C higher than the cracking temperature and reduction was performed at the same temperature as that of the cracking reaction. The reactor temperature was increased under N₂ (99.998% - PRAXAIRTM) using 120 mL/min at a heating rate of 10 °C/min up to 550 °C. The catalyst was calcined in situ with 100% compressed air (zero grade - PRAXAIRTM) using 120 mL/min under isothermal condition (550 °C) for 30 min. The reactor temperature was then cooled down to 500 °C at the same temperature ramping rate with N₂ (120 mL/min) and nitrogen was switched to a H₂ (10% vol)/N₂ mixture for reduction at 500 °C for 30 min using a total gas flow of 120 mL/min (hydrogen was grade 4.5 – 99.995% PRAXAIRTM). (The same procedure was repeated for a reaction temperature of 600 °C) The reaction took place at 1 atm pressure and temperatures of 500 and 600 °C. The initial sample weight was 20 mg and the feed was pure methane with a flow rate of 120 mL/min.

Results and Discussion

The catalytic activity of the Ni supported on γ -Al₂O₃ catalyst for the decomposition of methane into gaseous hydrogen and solid carbon was measured in grams of carbon formed per gram of nickel in the catalyst. The experiments were run at 500 and 600 °C. The furnace temperature is accurate within 1 °C and the accuracy of the thermobalance is 1 μ g at atmospheric pressure. The reaction gas was pure methane. The mass flow controller accuracy is within $\pm 0.2\%$ full scale at ambient temperature. Most experiments have been repeated (same batch of catalyst, same activation procedure, same reaction conditions) to be able to obtain reproducible data. No significant difference between replicated experiments was observed. The weight of the catalyst will increase as long as the catalyst is active. No more weight gain indicates deactivation. In the following sections, the influence of percentage of nickel, of the application of a reduction step prior to cracking, of the amount of gasified carbon, and of reaction temperature on regeneration and stability of catalyst activity will be discussed.

Effect of Nickel Percentage and Reduction

As seen in Figure 1, the nickel content can strongly affect the catalytic activity. An important result from Figure 1 is that, while nickel percentage has a strong effect on catalytic activity, reduction—as a pretreatment

for catalyst preparation—has a minor effect here. Experiments with reduction show slightly higher rates of carbon deposition with marginal increases in total carbon deposited after complete deactivation. Although the initial rate of carbon formation is quite independent of the Ni content (especially for 10 and 15 wt %), the maximum specific weight of carbon (mg C/mg Ni) increases drastically as the Ni content increases. Figure 1 also shows that the nickel content can change the life time of the catalyst; the reaction continued for 165, 275, and 440 min with reduction and 180, 285, and 440 min without reduction for 5, 10, and 15 wt % Ni, respectively. In summary, methane cracking can be sustained for a longer period of time when nickel content is higher. The results in Figure 1, therefore, indicate that the Ni content affects directly the deactivation of the catalyst.

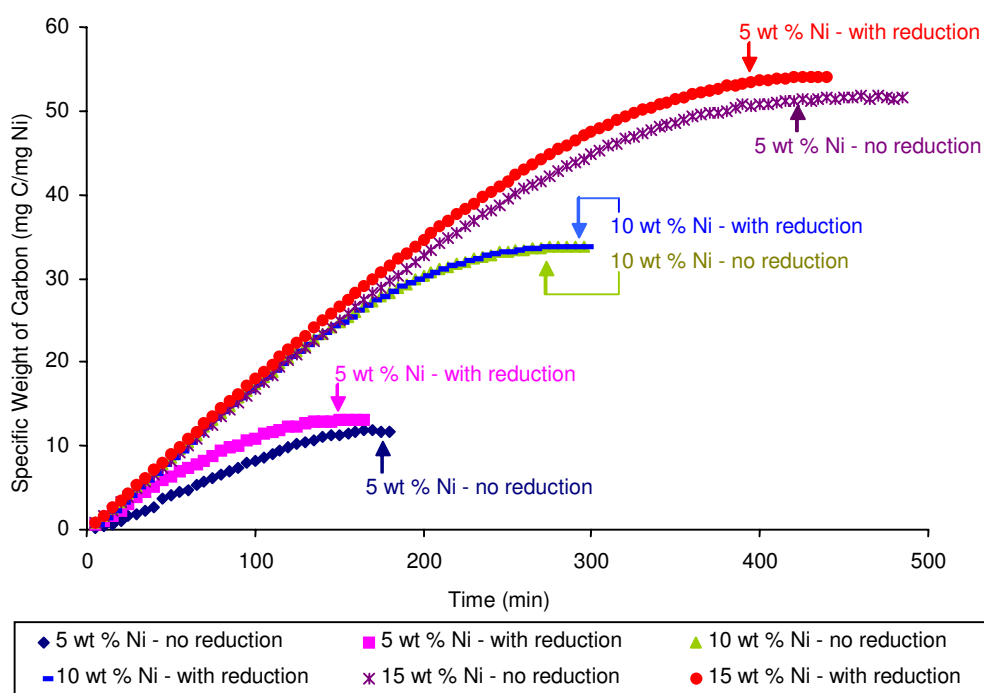


Figure 1. Specific weight of carbon for different Ni contents with and without reduction. Initial sample mass of 20 mg, temperature of 500 °C. Feed is pure methane.

In addition, we conclude that a pre-reduction step has a minor influence on the catalyst activity. This might be due to possible reduction by the H₂ produced during the early stage of the cracking reaction. Avoiding a reduction step is of practical significance since it will simplify the process operation and reduce the consumption of hydrogen. As such, for the cyclic experiments with catalyst regeneration, we decided not to apply a reduction step before methane cracking.

Effect of Gasified Carbon Percentage on Partial Regeneration Method

To be able to develop an effective way for regeneration, the mechanism of thermocatalytic cracking of methane and deactivation should be analyzed. A detailed mechanism of the catalytic decomposition of methane has been proposed by Snoeck et al.¹⁰ The mechanism involves the dissociative chemisorption of methane, which produces a methyl group, with the abstraction of the first hydrogen atom, which gradually

dehydrogenates on the surface to adsorbed carbon atom and atomic hydrogen. These surface reactions are followed by dissolution/segregation reactions. The carbon dissolved in a nickel particle at the front end side diffuses to the rear end side of the particle (i.e. metal/carbon filament interface) due to the driving force resulting from the concentration difference. The carbon that diffused through the metal particle from the front end to the rear end segregates at the interface between the metal and the carbon filament and builds up the carbon deposition as filaments. The initial carbon deposition (nucleation) takes the nickel particle away from the support. As the methane decomposes to carbon and hydrogen, carbon filaments continues to grow as hollow channels. At the end, the catalyst deactivates due to encapsulation. According to Trimm,¹¹ the reason for deactivation is carbon encapsulation, which hinders the interaction between active metal particles and methane, not the detachment of the metal particle. By combining all of the information above, it was attempted to retrieve the activity of the deactivated catalyst by total regeneration (gasification of all carbon deposited on the catalyst) in a previous work.¹² However, the rate of carbon formation of the regenerated catalyst was extremely low compared to that of the fresh catalyst.

In order to surmount the regeneration problem, we have applied a different gasification strategy to regenerate the catalyst by partially oxidizing the filament. The carbon filament is very strong and more difficult to oxidize than the encapsulating carbon. We tried to remove the encapsulated carbon first without modifying significantly the structure of the existing filament. The filament could then continue to grow. The structure of the filaments is important for holding the metal particle at the tip of the filaments through which carbon diffuses to the support for precipitation. The complete regeneration destroys the filament structure; thus it is not certain whether the metal particle sits on the support with the same surface orientation as before regeneration. That is why, in the present approach, the idea of partial regeneration was employed, where the main skeletal body of the filament remains intact.¹²

In this investigation, all experiments were carried out with 20 mg of catalyst. The catalyst was calcined in situ at 550 °C for 30 min in air for each run. Figure 2 represents the sequence that we followed during deactivation and regeneration cycles of 5-wt% Ni/ γ -Al₂O₃ at 500 °C. Pure methane as reaction gas (CH₄) passes over the catalyst until no more weight gain is observed as evidence of complete catalyst deactivation. Before regeneration, nitrogen (N₂) as purge gas carries all products and unreacted gases out. Partial regeneration has been implemented by gasifying solid carbon with air. Subsequently, nitrogen passes through the furnace to sweep CO_x gases. We repeated this sequence of gas flow (CH₄ - N₂ - Air - N₂) 4 times. In Figure 2, the amount of gasified carbon after each deactivation represents 10% of the mass of carbon that was deposited after the first deactivation.

Gasification has been performed in 2 ways. One is to remove nearly the same amount of carbon (as in Figure 2); the other is to gasify carbon until the same weight for each cycle. In the first procedure the weight loss gasification is constant, while in the second procedure the mass before cracking remains constant. Figure 3 illustrates these 2 procedures: Exp. 5 represents the first procedure, while Exp. 6 illustrates the second one. Specifications (total weight gain, percentage of gasified carbon – burn off %) for each experiment are given in the Table.

The influence of the weight of gasified carbon on the rate of carbon filament formation by methane cracking at 500 °C is shown in Figures 3 to 6.

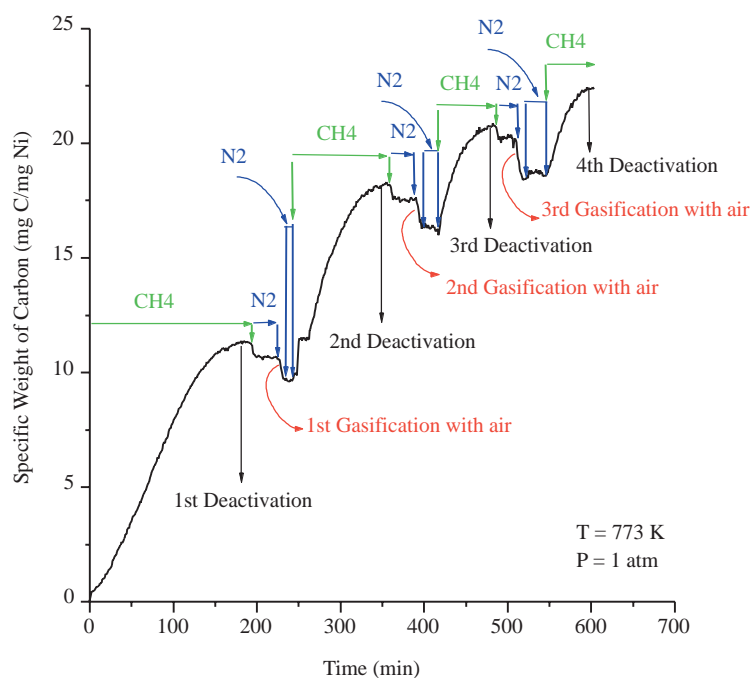


Figure 2. Deactivation-regeneration cycles of 5-wt% Ni/ γ -Al₂O₃ with 10-wt% initial carbon gasified.

Within each figure (Figures 3 to 6), the only parameter that changed from one experiment to another is the weight of gasified carbon. All other conditions like nickel percentage, reaction temperature, and pressure remained the same. According to the results shown in the Table and Figures 3 to 6, the more carbon we gasified to regenerate the catalyst, the higher the activity. Note that the range of percentage of carbon gasified was from around 5% (exp. 11) to just over 90% (exp. 6).

The reason for increasing activity (weight gain) with increasing gasified carbon can be explained by Baker et al.'s suggestion.¹³ They suggested that the core of the carbon filament has less structural order than the filament skin. Therefore, during oxidation, the central core is removed first, while the relatively more oxidation-resistant outer skin takes a longer time to be gasified during partial oxidation. According to Trimm,¹¹ during gasification (i.e. partial oxidation) the carbon diffuses through the nickel particle in the reverse direction of that during methane decomposition. Then after partial regeneration of the catalyst the carbon from methane decomposition diffuses back through the nickel particle and deposits once again inside the core of the filaments without affecting the structure. After detachment of the metal from the support, the mean temperature of the metal particle increases because it is no longer in contact with the support, which acts as the heat sink; instead, it is in contact with the filaments, which act collectively as an insulator. Because of the higher temperature, the carbon solubility increases and, as a result, the rate of carbon transport through the particle also increases and leads to a higher growth rate.

Effect of Temperature on Partial Regeneration Method

In Figures 7 and 8 the reaction temperature was changed (500 and 600°C). As a general conclusion, higher temperatures give higher reaction rates but the catalyst deactivates faster, yet still yielding a higher amount of carbon deposited after complete deactivation.

Table. Sample properties and deactivation and regeneration specifications.

No.	Sample	Total Specific Weight Gain (mg C/mg Ni)	Average of % Burn off
1	5-wt% Ni, T= 500 °C (with reduction)	13.09	No Gasification (one deactivation)
2	10-wt% Ni, T= 500 °C (with reduction)	33.79	No Gasification (one deactivation)
3	15-wt% Ni, T= 500 °C (with reduction)	54.12	No Gasification (one deactivation)
4	10-wt% Ni, T= 600 °C	35.83	No Gasification (one deactivation)
5	5-wt% Ni, T= 500 °C	26.59	8.63
6	5-wt% Ni, T= 500 °C	113.97	91.27
7	10-wt% Ni, T= 500 °C	51.59	8.43
8	10-wt% Ni, T= 500 °C	62.71	11.04
9	10-wt% Ni, T= 500 °C	105.65	49.08
10	10-wt% Ni, T= 500 °C	135.94	61.38
11	15-wt% Ni, T= 500 °C	66.43	4.25
12	15-wt% Ni, T= 500 °C	152.14	52.29
13	15-wt% Ni, T= 500 °C	184.52	72.89
14	15-wt% Ni, T= 500 °C	221.19	83.00
15	15-wt% Ni, T= 500 °C	233.23	88.41
16	10-wt% Ni, T= 600 °C	172.56	57.35
17	15-wt% Ni, T= 600 °C	299.11	87.00

*5-wt% Ni means 5:100 ratio of Ni: γ -Al₂O₃ by weight; T is reaction temperature; Total specific weight gain is the sum of accumulated carbon weight in 4 deactivation cycles; % Burn off is calculated by dividing the amount of carbon gasified during the current regeneration by the latest weight gain of the catalyst.

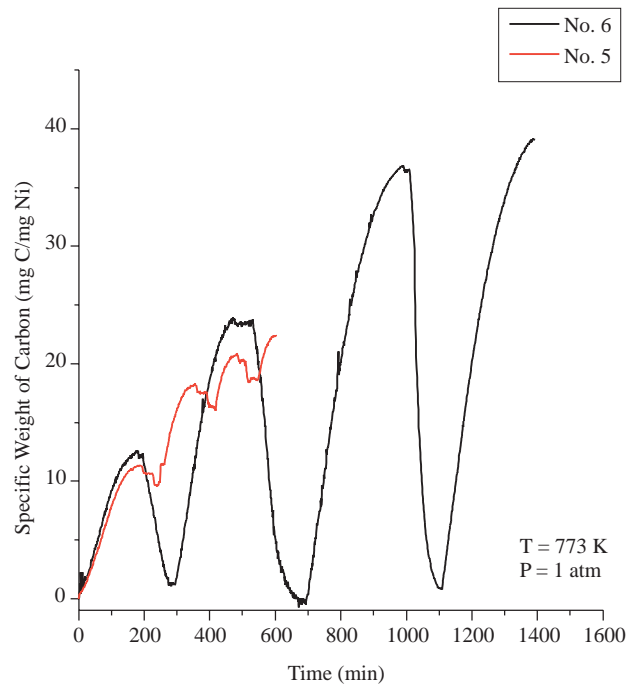


Figure 3. Specific weight of carbon over time for deactivation-regeneration cycles of 5-wt% Ni/ γ -Al₂O₃.

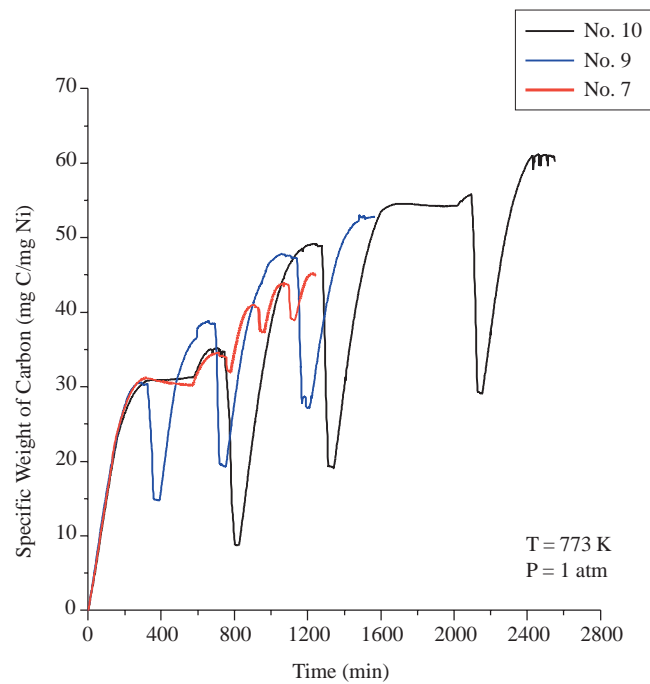


Figure 4. Specific weight of carbon over time for deactivation-regeneration cycles of 10-wt% Ni/ γ -Al₂O₃ (Same amount of carbon is gasified for all cycles).

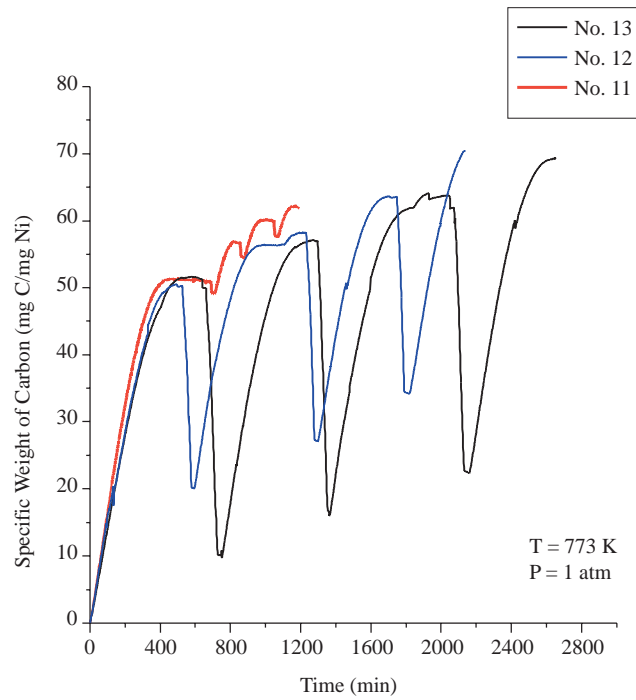


Figure 5. Specific weight of carbon over time for deactivation-regeneration cycles of 15-wt% γ -Al₂O₃ (Same amount of carbon is gasified for all cycles).

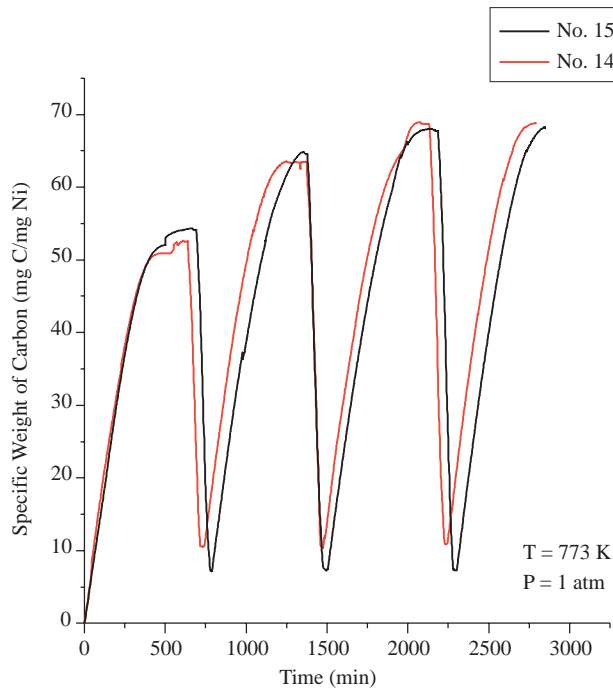


Figure 6. Specific weight of carbon over time for deactivation-regeneration cycles of 15-wt% γ -Al₂O₃ (Amount of gasified carbon is increased for each cycle).

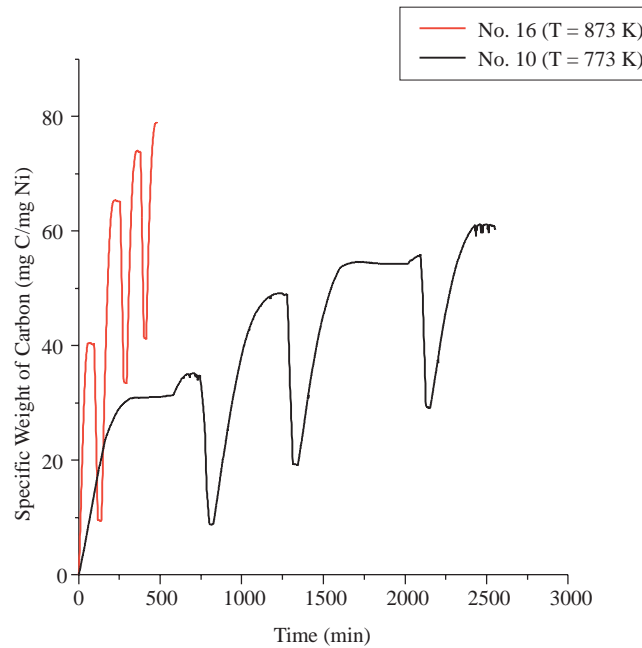


Figure 7. Influence of reaction temperature on deactivation-regeneration cycles of 10-wt% Ni/ γ -Al₂O₃.

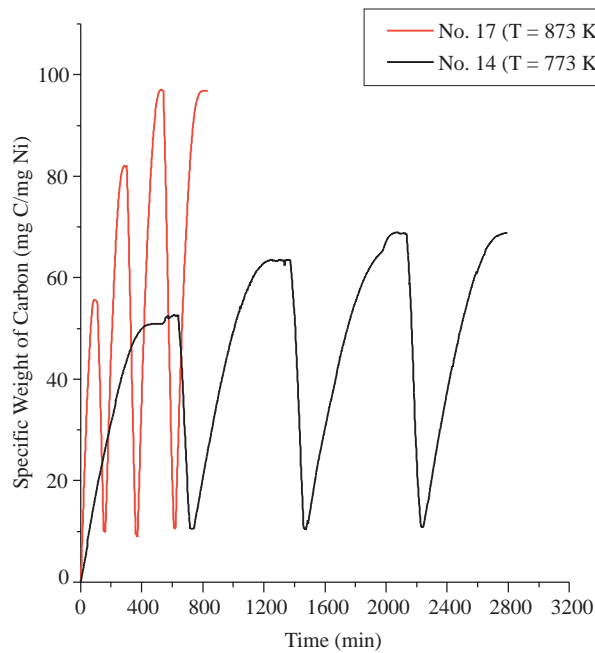


Figure 8. Influence of reaction temperature on deactivation-regeneration cycles of 15-wt% Ni/ γ -Al₂O₃.

Surface Analyses

SEM micrographs can be used to explain the formation of carbon filaments on the surface. SEM micrographs of the deactivated samples with different percentages of nickel are given in Figure 9. The sharp distinction is the difference in diameters of the filaments. The diameters of the filaments increase with increasing nickel

content. Moreover, nickel percentage influences the length of the filaments. Filaments of 5-wt% Ni/ γ -Al₂O₃ are longer than the filaments of 10 and 15-wt% Ni/ γ -Al₂O₃.

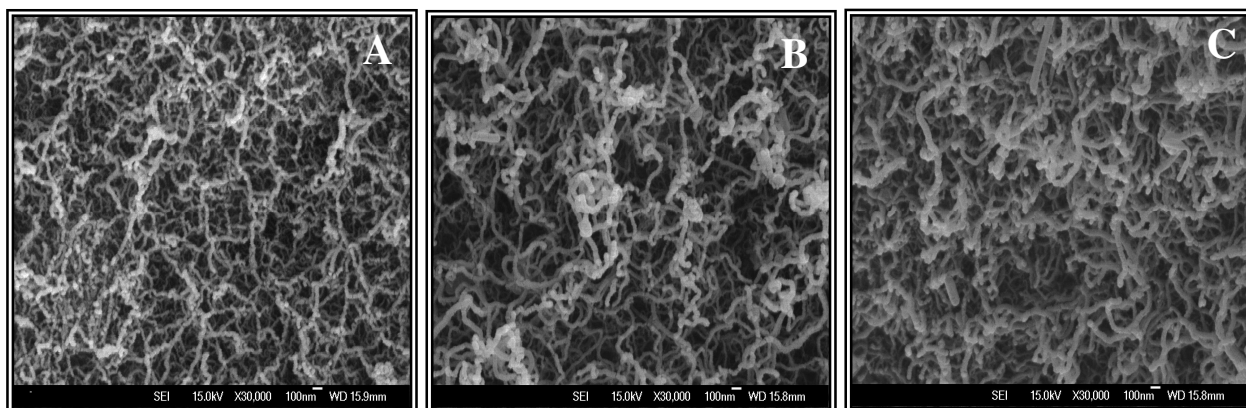


Figure 9. SEM micrographs of the catalysts after one deactivation. (Micrographs correspond to the data shown in Figure 1 without reduction.) (A) Surface of deactivated 5-wt% Ni/ γ -Al₂O₃ (\times 30,000); (B) Surface of deactivated 10-wt% Ni/ γ -Al₂O₃ (\times 30,000); (C) Surface of deactivated 15-wt% Ni/ γ -Al₂O₃ (\times 30,000).

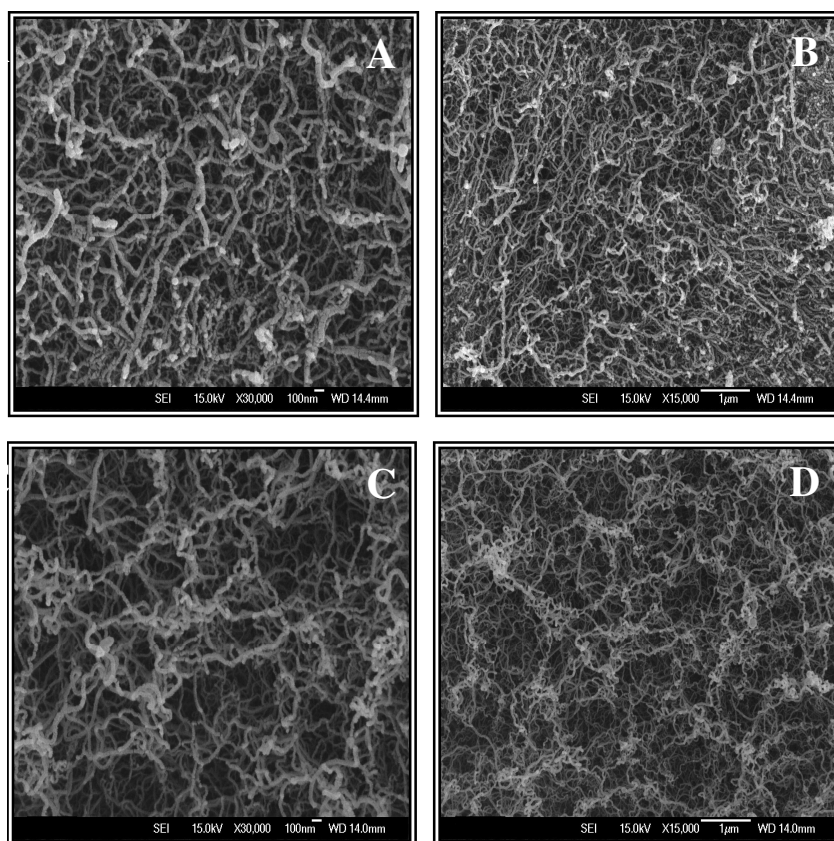


Figure 10. SEM micrographs of regenerated catalysts after 4 deactivation steps: (A) Surface of regenerated 15-wt% Ni/ γ -Al₂O₃ at 773 K (\times 30,000); (B) Surface of regenerated 15-wt% Ni/ γ -Al₂O₃ at 773 K (\times 15,000); (C) Surface of regenerated 15-wt% Ni/ γ -Al₂O₃ at 873 K (\times 30,000); (D) Surface of regenerated 15-wt% Ni/ γ -Al₂O₃ at 873 K (\times 15,000).

As a general conclusion, when we increased the percentage of the nickel the diameter of the carbon filament increased but the length of the filament decreased.

SEM micrographs for samples after 4 deactivation steps with 15-wt% Ni/ γ -Al₂O₃ at 500 and 600 °C are given in Figure 10 (A and B belong to the sample with No.14 and C and D belong to the sample with No.17 in the Table). Micrographs of the regenerated catalysts at different temperatures showed the emphasis on the diameter and length of the carbon filaments. The rate of carbon formation is slower and filaments grow athwart rather than lengthways at lower temperatures (i.e. at 500 °C).

Conclusion

Thermocatalytic cracking of methane over 5, 10 and 15 wt% Ni/ γ -Al₂O₃ is studied by collecting data as carbon formed over time using thermogravimetric analysis. Carbon yield of the cracking reaction increased with increasing nickel content of the catalyst. Reduction prior to cracking had no significant effect on weight gain; it was concluded that the reduction took place during the early stage of the methane cracking reaction.

Partial regeneration of methane with air can overcome the challenge of deactivation of the catalyst. Increasing the amount of gasified carbon—but not until total removal of carbon—allowed for higher weight gain.

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