

Preparation and Activity of Precipitated Ni-MgO/Al₂O₃ Catalysts for the Partial Oxidation of Methane

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The effect of catalyst preparation methods, NiO/MgO molar ratio and reaction temperature on the performance of Ni-MgO catalysts supported on Al₂O₃ in the partial oxidation of methane to syngas were investigated in a fixed-bed flow reactor. Three catalyst preparation methods (all slight variants of the precipitation method) produced comparable results in CH₄ conversion, CO and H₂ selectivities. Energy Dispersive X-Ray (EDX) analysis and the color of the catalysts after reaction showed that catalysts produced by simultaneous dissolution of the nickel and magnesium salts may have better carbon deposition resistance. NiO/MgO molar ratio significantly affected the performance of the catalyst. When the NiO/MgO ratio decreased, activity decreased. At a NiO/MgO molar ratio of 1/2 and a reduction temperature of 850°C, CH₄ conversion and CO selectivity increased when reaction temperature increased while H₂ selectivity remained almost the same. The catalyst gave excellent activity and remained stable after 5h time-on-stream.

Keywords: Catalysis, methane, NiO-MgO/Al₂O₃, partial oxidation, precipitation, and syngas.

INTRODUCTION

For synthesis gas production, there are several choices: (a) steam reforming, (b) catalytic partial oxidation, (c) CO₂ reforming; and (d) auto-thermal reforming method, which is the

combination of both partial oxidation and steam reforming in one reactor (Hui et al. 2000). Among these methods, catalytic partial oxidation of methane has been receiving more attention recently because of its mildly exothermic nature and its H₂/CO ratio of about 2, which is appropriate

for methanol synthesis and Fischer-Tropsch synthesis. Because of the weak exothermic nature and simple reactor design, operation and energy costs may be reduced significantly compared with other methods.

Although catalytic partial oxidation of methane (CPOM) is very attractive in terms of economics, industrial application is still a big challenge (Albertazzi et al. 2003). The thermodynamics of the partial oxidation of methane favors the formation of CO and H₂ at high temperature while CO₂ and H₂O are favored at low temperatures (Figure 1). Hence, development of catalysts with high carbon-deposition resistance is of particular interest because carbon deposition becomes significant at higher temperatures (Hu and Ruckenstein 2002).

In recent reviews (Hu and Ruckenstein 2002, 2004), NiO-MgO solid solution catalysts were mentioned as having good potential for

this reaction, demonstrating high conversions and high selectivities. The NiO-MgO catalysts were also mentioned as having good carbon-deposition resistance, even at high-temperatures when used for the CO₂-reforming of methane. In addition to the studies by Hu and Ruckenstein, the studies by Choudhary and Mamman (1997) and Choudhary, Uphade, and Mamman (1997) are the noteworthy predecessors of this paper. An interesting effect described in Ruckenstein and Hu (1999) was that the activity and selectivity essentially remained unchanged even when the NiO/MgO composition was varied between 9.7 and 68 mol%. Two possible explanations were given. The first centered on the possibility that essentially the number of active sites does not increase as the NiO/MgO mole ratio increases because the overall surface area of the catalyst decreases. The alternative explanation was that the reaction reaches thermodynamic equilibrium at the exit of the catalyst bed.

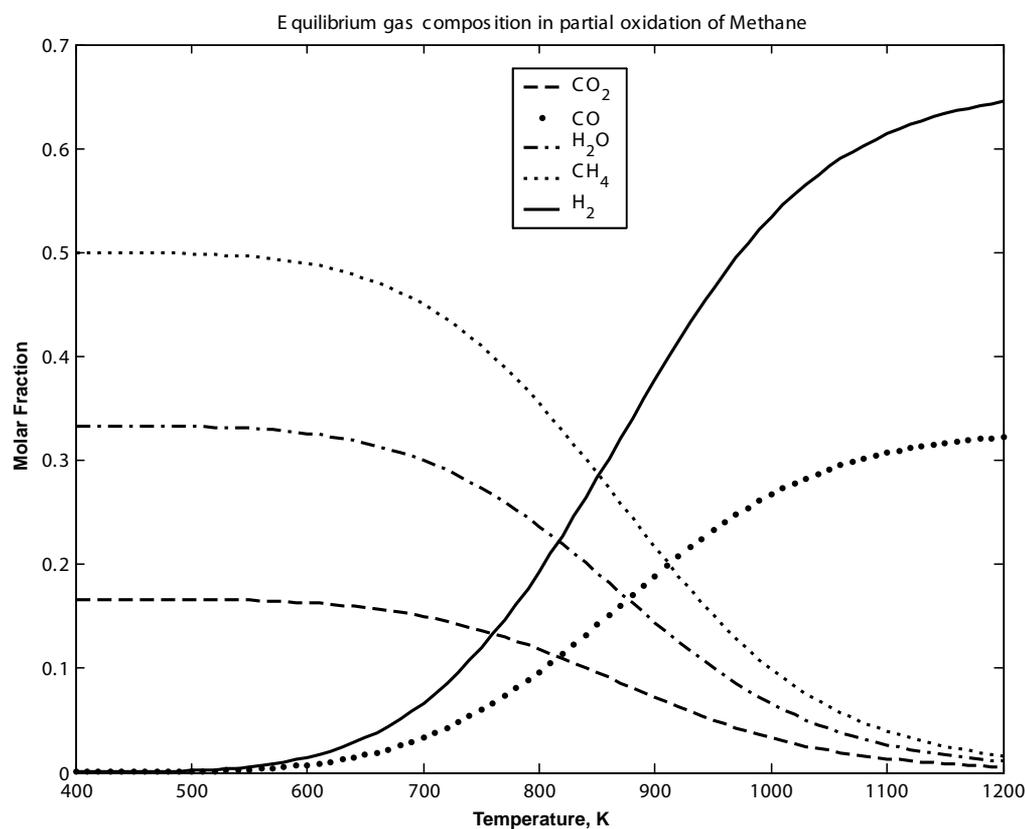


Figure 1. Equilibrium Curves for a CH₄:O₂ Feed Ratio = 2

In this paper, we present results from NiO-MgO catalysts supported on an α -alumina and prepared using variations of the precipitation method. Three variants of preparation were tested. The one that showed better carbon deposition resistance while exhibiting good conversion and selectivity was selected for further tests.

EXPERIMENTAL

Catalyst Preparation

Three variants of the precipitation method were tested. The idea behind the first and the second methods was to investigate the effects of varying the order of steps in precipitation method. Method 3 was inspired by the study of Choudhary Uphade, and Mamman (1997), in which low surface area supports were precoated by MgO before Ni was deposited on the surface by impregnation method. By changing the manner of precipitation, the three catalysts are expected to have differing dispersions of nickel atoms in the MgO lattice.

Method 1 (Simultaneous Dissolution)

Appropriate amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) were dissolved simultaneously in 50 ml of H_2O . Five grams of $\alpha\text{-Al}_2\text{O}_3$ powder (J.T.Baker) was slurried in this solution. Boiling was conducted for 0.5 h. After that, the solution was cooled to 5-10°C. One milliliter of concentrated HNO_3 (Merck) was added. Eighty milliliter dilute NH_4OH solution was made by dissolving 40ml of NH_4OH (J.T.Baker, concentration about 25-28%) into H_2O . After that, the solution was cooled to 5-10°C. While the temperature was being maintained at 5-10°C, dilute NH_4OH solution was added slowly with rapid agitation until a pH of 11 was reached. Decantation was used for washing. The solution was added to 1,000ml of H_2O and suspended for 15min while stirring. After that, the suspension was allowed to settle down and decanted after 4h. The washing procedure was repeated six times. The light green precipitate was filtered in

a funnel and then dried in air at 80°C for 4h. Finally, calcination was conducted in air at 900°C for 4h. In this method, the best dispersion of Ni in the MgO lattice, probably a (Ni, Mg)O solid solution, is expected.

Method 2 (Sequential Dissolution)

An appropriate amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50ml of H_2O . Five grams of $\alpha\text{-Al}_2\text{O}_3$ powder was slurried in this solution. Boiling was conducted for 0.5h. After that, the solution was cooled to 5-10°C. One milliliter of concentrated HNO_3 was added. Dilute NH_4OH was added slowly, using the procedure similar to that used in method 1. An appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 25ml of H_2O , then 1ml of concentrated HNO_3 was added and the solution was cooled to 5-10°C. $\text{Ni}(\text{NO}_3)_2$ solution was added to this solution with vigorous stirring over a period of 0.5-1 h. The same procedure in method 1 was used in the washing, drying, and calcination. Although the precipitation is done sequentially, reasonably good dispersion is expected because the calcination is not done until all of the precipitation is completed.

Method 3 (NiO Supported on Al₂O₃ Precoated with MgO)

An appropriate amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50ml of H_2O . Five grams of $\alpha\text{-Al}_2\text{O}_3$ powder was slurried in this solution. Boiling was conducted for 0.5 h. After that, the solution was cooled to 5-10°C. One milliliter of concentrated HNO_3 was added. Dilute NH_4OH was added slowly, using the procedure similar to that used in method 1. The same procedure for washing, drying and calcination described in method 1 was used. Since the precoated catalyst carriers were available already, $\text{Ni}(\text{NO}_3)_2$ was allowed to precipitate on the particles in the same way. After this, the same procedure for washing, drying, and calcination as described for method 1 was repeated. With this method, the least dispersion of Ni in the MgO lattice is expected. Most probably, an Ni metal supported on MgO is produced.

All of the catalysts were stored in air-tight vials at ambient conditions.

Catalyst Testing

Time-on-Stream Test

The gaseous products were analyzed by gas chromatography. Carbon deposition was assumed to be very small when compared with the quantity of CO and CO₂, so it can be neglected. To facilitate comparison, the definition for CO and H₂ selectivity used in the study made by Pantu and Gavalas (2002) was used:

$$\text{Selectivity of CO} = \frac{\text{mols of CO produced}}{\text{mols of CO} + \text{CO}_2 \text{ produced}}$$

$$\text{Selectivity of H}_2 = \frac{\text{mols of H}_2 \text{ produced}}{2 \times \text{mols of CH}_4 \text{ consumed}}$$

The experiments were conducted with high purity gases (99.99%, CIGI) at atmospheric pressure in a fixed bed quartz micro reactor (internal diameter =10mm; length =350mm) set in a vertical position in an electric furnace (Figure 2). The catalyst sample (0.5g powder) was placed between two ceramic wool plugs in the center of the reactor. A K-type thermocouple was inserted into a thermowell, which was centered within the catalyst bed. The product gases, after removal of all water by an ice trap and a moisture trap, were analyzed with a Trace GC Ultra gas chromatograph (Thermo Electron S.p.A.) equipped with a Thermal Conductivity Detector (TCD). The catalytic tests were initiated by heating the reactor, from ambient to the reduction temperature, under a constant flow of helium. After heating, 120ml/min of H₂ was introduced to reduce the catalyst for 1h. The reduction temperature depended on the catalyst used. Subsequently, H₂ flow was stopped and He flow was used to purge the catalyst bed until no peak of H₂ was detected. During that time, the temperature was adjusted to the reaction temperature. When the furnace temperature

was stabilized, the rest of the reaction mixture (CH₄, O₂, N₂) was allowed to flow through the reactor, with N₂ first and O₂ and CH₄ at the same time. The molar ratio of O₂:CH₄:N₂:He equals to 6:12:14:68 with the total flowrate was 250ml/min. Gas Hourly Space Velocity (GHSV) was 30,000 ml (g cat.)⁻¹ h⁻¹. Typical duration of a catalytic test was 5h. After that, admission of CH₄, O₂ and N₂, was stopped, and the reactor was cooled to room temperature under a constant flow of helium.

Catalyst Characterization

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) results of fresh and used catalysts were obtained by Jeol JSM-5310 Scanning Microscope.

RESULTS AND DISCUSSION

Effect of Catalyst Preparation Methods

In a preliminary set of experiments, the effect of reduction temperature was observed. When the reduction was conducted at 650°C and reaction was conducted at 700°C, catalysts prepared by both methods 2 and 3 produced CO and H₂ in this condition while catalysts prepared by method 1 required an effective reduction temperature greater than 700°C before it could produce CO and H₂. Otherwise, only complete combustion occurs. It may be speculated that in method 1, Mg(OH)₂ precipitated after Ni(OH)₂, since the precipitation pH for Mg(OH)₂ and Ni(OH)₂ are 10.5, 6.7, respectively, so Ni(OH)₂ molecules were covered by Mg(OH)₂ molecules. After calcination, solid solution possibly formed between NiO and MgO. For method 1, the NiO reduction occurs at higher temperatures and so, the degree of reduction is lower because of the incorporation of Ni²⁺ deep in the MgO matrix.

Hence, the condition for the series of experiments on the effect of sequence of dissolution was chosen as follows: a reduction temperature of 800°C, a reaction temperature of 700°C, and a designed NiO/MgO molar ratio of 1.

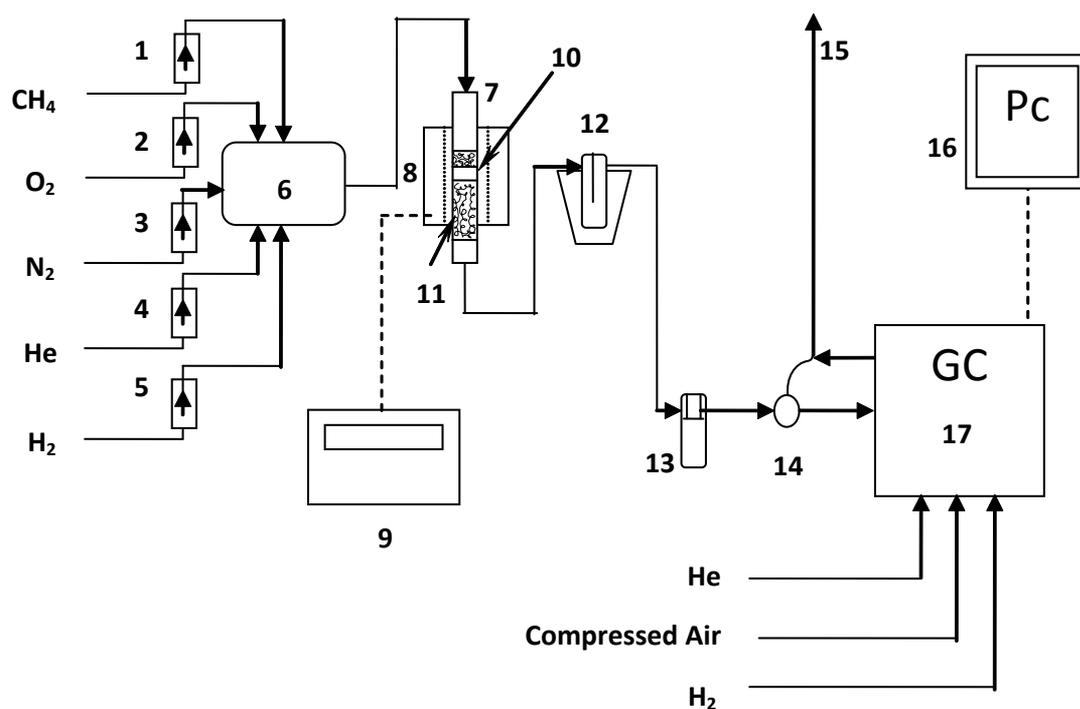


Figure 2. Schematic Diagram of the Experimental Setup

1, 2, 3, 4, 5: flowmeters; 6: mixing tank; 7: reactor; 8: furnace; 9: temperature controller; 10: catalyst bed; 11: ceramic wool; 12: ice trap; 13: moisture trap; 14: two-way valve; 15: ventilation; 16: computer; and, 17: Gas chromatography unit

From Figure 3, it is clear that the CH₄ conversion and CO and H₂ selectivities of method 1 and method 2 are comparable to each other. The catalyst prepared by method 3, however, had a lower CH₄ conversion. It could be speculated that in this catalyst preparation procedure, Ni(OH)₂ precipitated on the surface of Al₂O₃ precoated by MgO. During calcination, the Ni(OH)₂ was perfectly converted to NiO. Since a stable MgO layer already existed, NiO might have partially formed solid solution with MgO, reducing the catalyst activity.

While the activity and selectivity of the catalysts produced by methods 1 and 2 were similar and the catalysts prepared by method 3 gave only slightly lower conversion, there is another evidence that can be shown to determine the right catalyst preparation procedure for the succeeding experiments.

A visual observation showed that the used catalyst from method 1 was pale while others

were black. This might be due to the difference in amount of carbon deposition on the catalyst surface and this is verified by the EDX analysis shown in Figure 4. Method 1 had the smallest carbon deposition. Also, Figure 5 shows that method 1 delivered a NiO/MgO molar ratio on surface very near the designed ratio of 1. Methods 2 and 3 gave surface NiO/MgO ratios greater than the designed ratio. Because of these observations, the method of simultaneous dissolution of the Mg and Ni salts was used for all succeeding experiments.

Effect of NiO/MgO Molar Ratio

Method 1 (simultaneous dissolution) was chosen to prepare the catalysts for the following experiments. When testing with NiO/MgO ratio=1/2 at 700°C with reduction temperature of 800°C, no CO and H₂ were produced. Increasing the reduction temperature to 850°C gave good

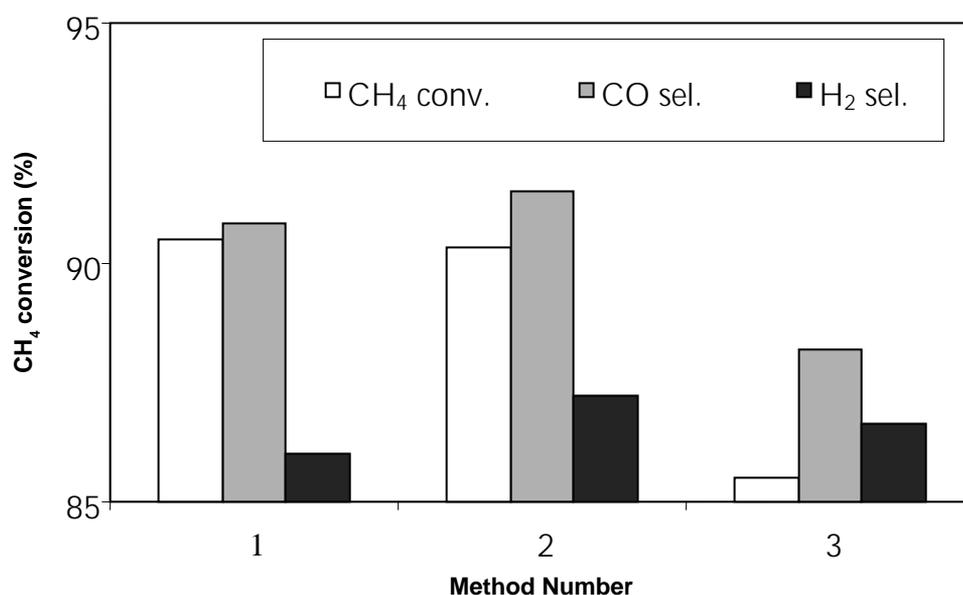


Figure 3. CH₄ Conversion and CO and H₂ Selectivities after 5h of Time-on-Stream at Different Catalyst Preparation Methods for CPOM [NiO/MgO =1; Tred. = 800°C; Treact. = 700°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

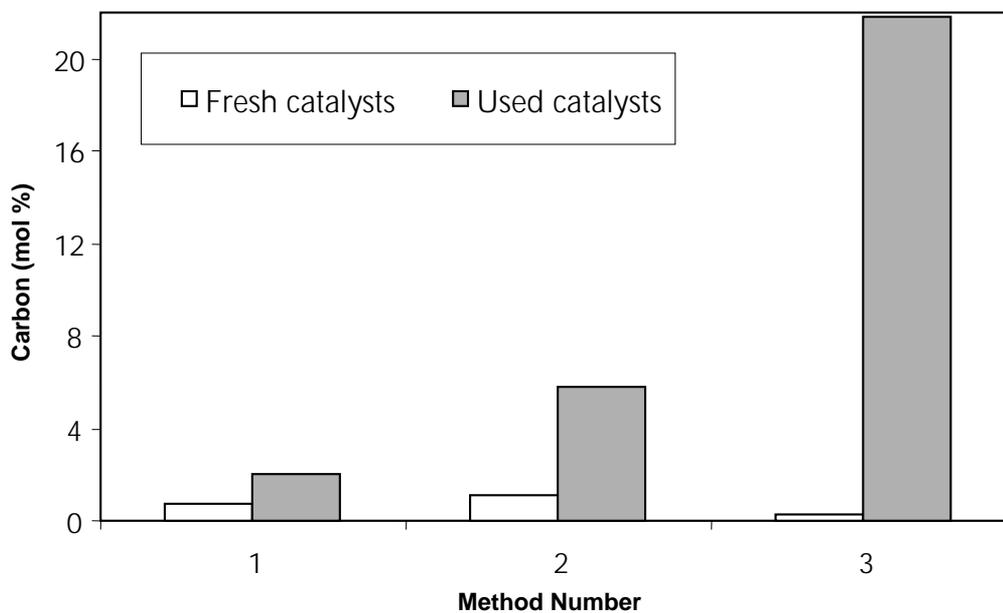


Figure 4. Surface Carbon Content of Fresh and Used Catalysts from Three Catalyst Preparation Methods [EDX analysis) (CPOM conditions: NiO/MgO =1; Tred. = 800°C; Treact. = 700°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

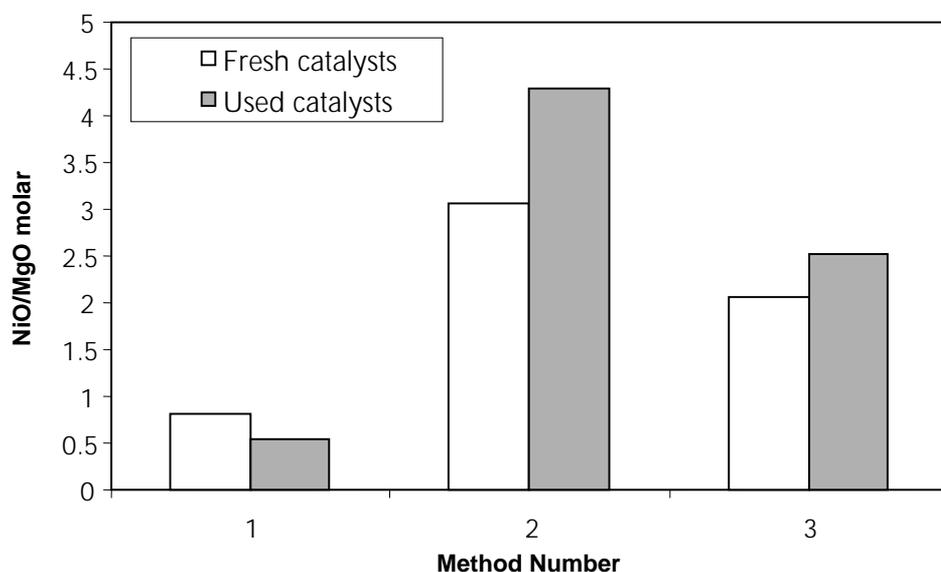


Figure 5. Surface NiO/MgO Molar Ratio of Fresh and Used Catalysts from Three Catalyst Preparation Methods (EDX analysis) [CPOM conditions: NiO/MgO =1; Tred. = 800°C; Treact. = 700°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

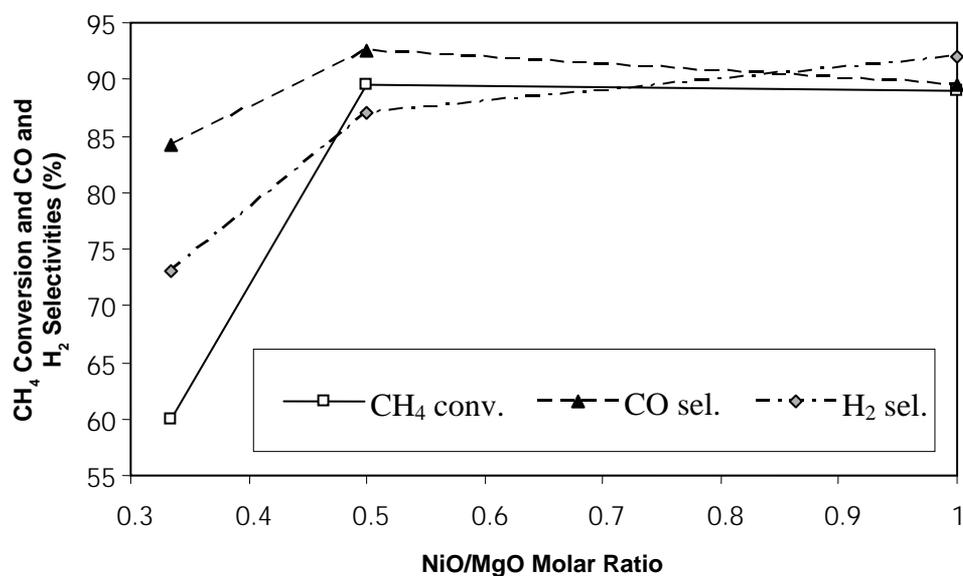


Figure 6. CH₄ Conversion and CO and H₂ Selectivities as a Function of NiO/MgO Molar Ratio for CPOM [Tred. = 850°C; Treact. = 700°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

results. Hence, the following conditions were used for the experiments described in this section: a catalyst reduction temperature of 850°C and a reaction temperature of 700°C. The NiO/MgO molar ratio had been varied as 1, 1/2, 1/3, and 1/4.

Figure 6 shows that when decreasing the NiO/MgO ratio, the conversion and selectivities decreased. For the NiO/MgO molar ratio of 1/4, only complete combustion occurred, no traces of H₂ and CO were detected. When NiO/MgO molar ratio change from 1 to 1/2, the CH₄ conversion had almost the same values. These results differ somewhat from those of Hu and Ruckenstein (1999), who observed in impregnated NiO-MgO catalysts that the activity did not change even when the NiO/MgO ratio was changed considerably. In this work, we observed a change in activity if the NiO/MgO ratio was changed from 1/2 to 1/3.

The electron transfer from NiO to MgO may induce strong interactions between NiO and MgO, which may inhibit the reduction of NiO. At low concentrations of NiO (NiO/MgO molar ratio equal to 1/3), there may be a reduction of only a few NiO molecules, and the small number of

active sites is responsible for the low activity and selectivity. As the amount of NiO increases, the number of Ni⁰ sites might increase both because of the higher concentration of NiO and of the weakening of the interactions with MgO. Mostly, when the NiO/MgO molar ratio was too low, example 1/4, the NiO molecules might be buried in the MgO matrix, leading to the disappearance of the CPOM, due to the lack of Ni⁰.

The almost constant activities between two catalysts, with NiO/MgO molar ratio are 1 and 1/2, might be a result of two factors. The reduction temperature might be big enough to equalize the number of active sites exposed to the chemical atmosphere. Also, since GHSV was not varied, the experiments might not have been sensitive enough to distinguish between the two catalysts since both had already approached equilibrium.

Figure 7 shows that the surface NiO/MgO molar ratio of the fresh and used catalysts prepared by method 1 are almost the same with the designed ratio. This means that for the catalyst preparation by method 1, the precipitation of Ni(OH)₂ and Mg(OH)₂ almost occurred just in the surface.

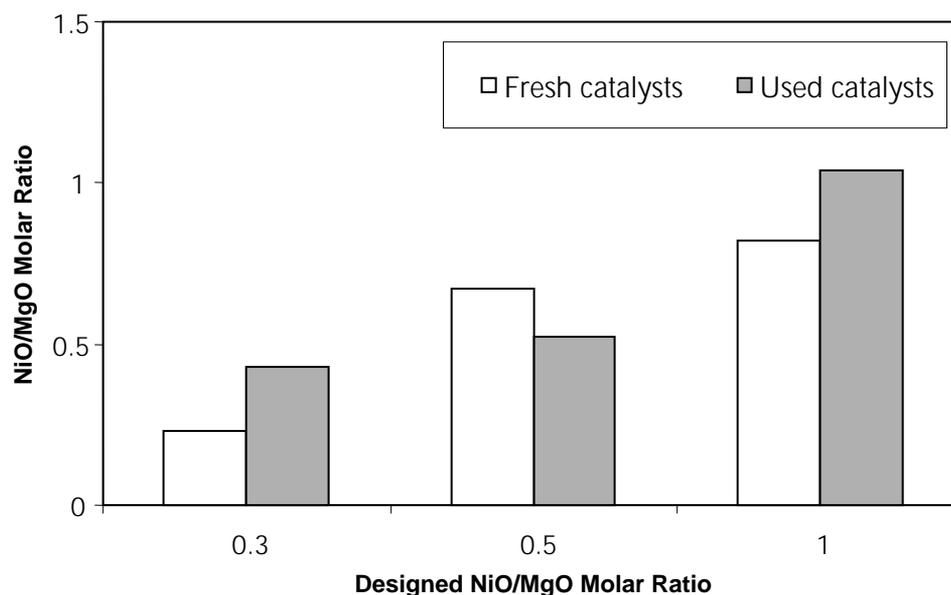


Figure 7. Surface NiO/MgO Molar Ratio of Fresh and Used Catalysts of Three Designed NiO/MgO Molar Ratios (EDX analysis)

[reaction condition: Tred. = 850°C; Treact. = 700°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

Effect of Reaction Temperature

The catalysts prepared by method 1 were also used for this series of experiments. The conditions for this series of experiments were a reduction temperature of 850°C and a NiO/MgO molar ratio of 1/2. The reaction temperature was varied between 600°C and 800°C.

The temperature dependence of the catalyst performance is shown in figures 8, 9, and 10. O₂ conversion of >99% were achieved in all the experiments. CH₄ conversion as well as CO selectivity increased with the temperature. On increasing the temperature from 600 to 800 °C, CH₄ conversion rose from 65 to 98 % and CO selectivity from 65 to 96.5 %. From Figures 7 and 8, it can be seen that CH₄ conversion and CO selectivity increased with the same trend as equilibrium values, even though the experimental were always lower than the equilibrium values. As the reaction temperature increased, the difference of experimental values and equilibrium ones became smaller. At 800°C, CH₄ conversion reached equilibrium and CO selectivity was very near equilibrium value. The flattening of the curve in Figure 7 probably indicates that the

internal-diffusion effects are beginning to become significant at that temperature. This deserves further attention.

The H₂ selectivity was almost constant when the temperature increased from 600 to 800 °C (Figure 10). It just slightly decreased in the range of 2%. It may be because CO shift reaction was thermodynamically favored at low temperatures so the H₂ selectivity remained high (about 90%). Compared with the equilibrium values, the experimental values were significantly lower and kept at a horizontal trend. The equilibrium trend shows the increasing of H₂ selectivity vs. temperature.

The equilibrium lines in figures 8 to 10 were generated by the data obtained from other studies (Pantu and Gavalas 2002, Utaka et al. 2003, and Albertazzi et al. 2003).

CONCLUSIONS

It seems that, when using the precipitation method, simultaneous dissolution (method 1) is the most suitable method for the preparation of these catalysts because it has a surface NiO/MgO molar ratio near the designed one and

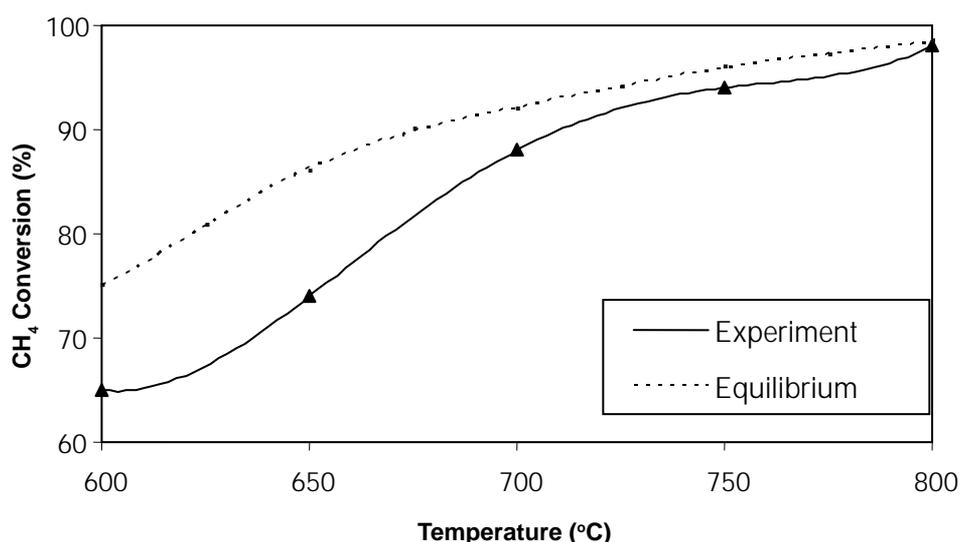


Figure 8. Effect of Reaction Temperature on CH₄ Conversion [NiO/MgO = 1/2; Tred. = 850°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

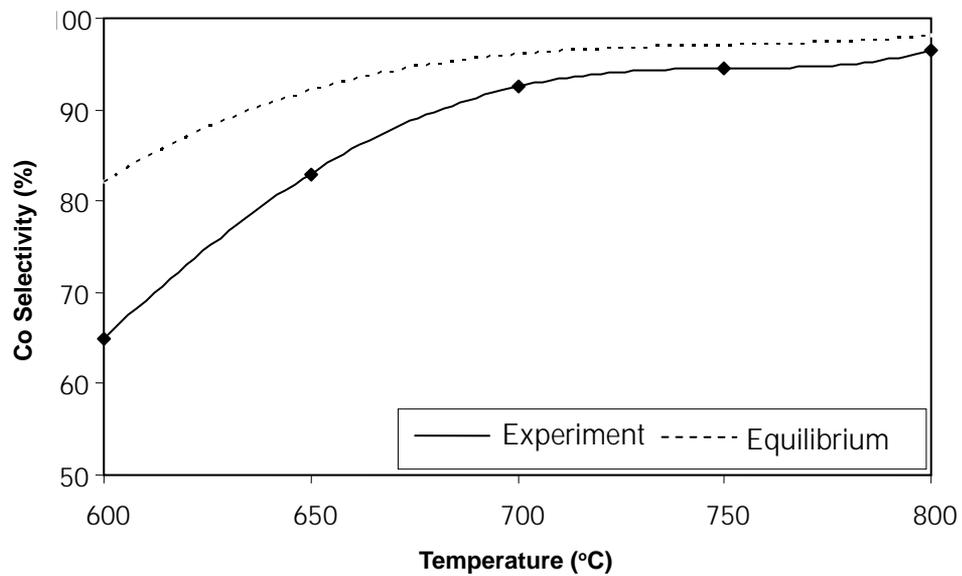


Figure 9. Effect of Reaction Temperature on CO Selectivity [NiO/MgO = 1/2; Tred. = 850°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

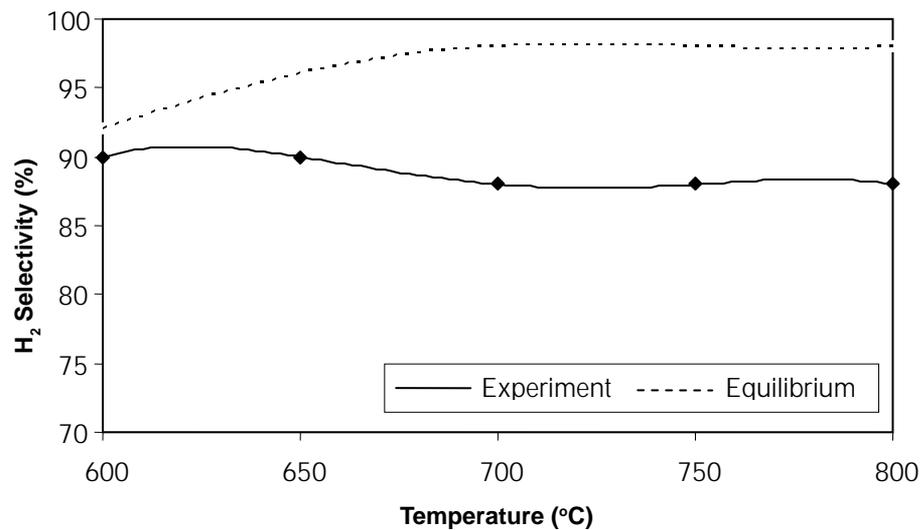
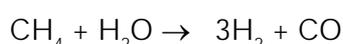
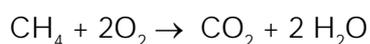


Figure 10. Effect of Reaction Temperature on H₂ Selectivity [NiO/MgO = 1/2; Tred. = 850°C; O₂: CH₄: N₂: He = 6:12:14:68; GHSV = 30,000 ml (g cat.)⁻¹h⁻¹]

has the highest carbon deposition resistance. The carbon deposition was verified using visual observations and EDX analysis. The observations are consistent with the expectation that the nickel dispersion in the MgO lattice may be expected to be greater in Method 1 than in Method 2 and also greater in Method 2 than in Method 3. This is also supported by the observation that catalysts prepared by Method 1 are more difficult to reduce.

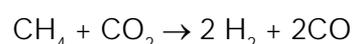
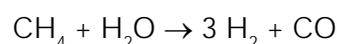
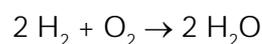
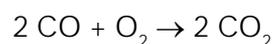
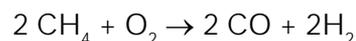
Time-on-stream tests were unable to distinguish between catalysts prepared by these three methods, however. This was probably due to the fact that the reaction was already very close to equilibrium. The NiO/MgO molar ratio of 1 and 1/2 gave the highest activity when using a reduction temperature of 850°C and reaction temperature of 700°C among catalysts with different NiO/MgO molar ratios. Both the CH₄ conversion and CO selectivity increased significantly when reaction temperature was increased while H₂ selectivity is almost independent of reaction temperature. This behavior follows the equilibrium curve. Mass transfer effects will have to be investigated more closely.

Some speculations may be made on the mechanism by which the reaction proceeded. In previous studies, already summarized in the reviews by Hu and Ruckenstein (2002, 2004), two mechanisms have been postulated. One is called the "indirect" or "reforming" mechanism. It would proceed as follows:



If the reaction proceeds in this manner then the ratio of CO₂ to CO may be expected to be higher than the equilibrium ratio if the conversion is below the equilibrium conversion.

On the other hand, another reaction mechanism has been suggested, which is called the "direct" or "pyrolysis" mechanism.



If this mechanism were the dominant mechanism, then the ratio of CO₂ to CO may be expected to be higher than the equilibrium ratio if the conversion is below the equilibrium conversion.

Table 1 shows a comparison of the observed CO₂/CO ratio to the equilibrium value at different temperatures. It can be seen that the observed value is always higher than the equilibrium value. This is most apparent at the higher temperatures when the observed conversion is already very close to the equilibrium conversion. Hence, the most likely mechanism is the indirect or reforming mechanism. This will be explored further in future studies.

Using the catalyst prepared by simultaneous precipitation and a NiO/MgO molar ratio of 1/2 and reduced at 850°C, the highest CH₄ conversion of about 98% was achieved at a reaction temperature of 800°C. The CO and H₂ selectivities were about 96.5 and 88 %, respectively. To the knowledge of the present researchers, this is the first time Ni-MgO/α-Al₂O₃ catalysts prepared by precipitation method were investigated. The catalysts gave good activity and selectivity. This is in contrast to the statement made in Hu and Ruckenstein (2002) that much of the Ni might be buried in the bulk of the solid solution if the precipitation method is used. Since the catalysts gave excellent activity and stability, this study can be considered as a springboard for further research in partial oxidation kinetics and reactor design.

Table 1. Comparison of CO₂/CO ratios at Different Temperatures.

Temperature (°C)	Observed		Equilibrium	
	CO ₂ /CO ratio	Conversion (%)	CO ₂ /CO ratio	Conversion (%)
600	0.54	65	0.22	75
650	0.21	74	0.087	86
700	0.08	88	0.042	92
750	0.05	94	0.031	96
800	0.036	98	0.02	98.5

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