

Nickel Catalysts on Porous Ceramic Supports for the Reaction of Partial Oxidation of Propane to CO and H₂

Miroslav Stanković and Aleksandra Milutinović-Nikolić

Abstract In this paper synthesis, textural and structural properties as well as selectivity of Ni based catalysts for partial oxidation of propane to CO and H₂ are given. The influence of aluminosilicate and magnesia based porous ceramic supports on catalyst performance is emphasized. The influence of concentration of impregnation solution, number of successive impregnations and nature of modifier was investigated. The catalytic test was performed in order to define the catalyst with the highest selectivity toward CO and H₂ while the presence of side-products like CO₂, CH₄, and coke as well as unreacted C₃H₈ are reduced to minimum. All synthesized catalysts samples were dominantly macroporous. The selectivity of catalysts increased with presence of modifiers in the following order: CaO < MgO < Al₂O₃. The selectivity of studied catalysts is governed mainly by two structural parameters: nickel loading and nickel crystallite size. The comparison of the best performing aluminosilicate and magnesia supported catalysts with Al as modifier revealed that the latter express somewhat lower selectivity particularly toward CO.

Keywords Aluminosilicate support • Magnesia support • Ni catalyst • Textural properties • Partial oxidation • CO and H₂

1 Introduction

Gas atmosphere containing dominantly CO and H₂ is commonly used for heat treatment furnaces where reductive atmosphere is required [1]. Conversion of CH₄ to appropriate reduction atmosphere has been studied extensively [2–4]. Although CH₄ is the major component of natural gas, other C₂-C₄ alkanes should also be taken into consideration. Oxidation of these alkanes can lead to complete

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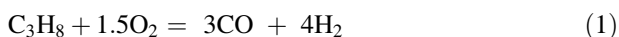
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combustion, partial oxidation to CO and H₂ mixture, cracking and dehydrogenation reactions to olefins, or finally pyrolysis to coke [5]. In order to obtain the desired CO and H₂ gas mixture the partial oxidation of C1-C4 alkanes should be performed under the appropriate process conditions and the catalyst should be as selective as possible toward formation of CO and H₂ mixture.

The most common and economical method of producing this mixture of gasses is to use a mixture of air and natural gas or air and propane and heat it over a nickel coated ceramic catalyst [1]. The various ceramic supports of Ni based catalyst are employed in catalytic partial oxidation to CO and H₂ gas mixture. Aluminosilicate-nickel oxide and magnesia-nickel oxide type of catalysts are the most commonly used ones [6].

The chemical reaction of partial oxidation can be described with following equation:



Basic request for catalyst for conversion of C1-C4 alkanes is thermal stability at high temperatures. Only catalysts that fulfill this request can be applied in process of partial oxidation [7–14]. The high thermal stability of these alkanes demands that the conversion takes place at temperatures higher than 900 °C that on the other hand, lead to fast deactivation of catalyst [15–17]. There is a great variety of different causes that might initiate quick deactivation of catalyst and are usually associated with severe conditions in which the process takes place. During its lifetime the catalyst is exposed to thermal effects which cause changes in its structure, texture, the modifier distribution on the active surface and the other properties. The consequence of which is a decrease in the catalyst activity, i.e. “ageing” or deactivation. During process disturbances the catalyst may be heated up to temperature greatly in excess of 900 °C, both locally or in the bulk, which makes the catalyst activity decline more pronounced. Deactivation may also be caused by deposition of coke obtained in side process reactions such as cracking of alkanes or by contamination of the catalyst with pollutions mainly from sulfuric compounds. Such contamination occurs if the inlet gas has not been desulfurized prior to introduction into the system. The resistance of the nickel based catalyst toward heating i.e., its thermal stability, depends on the chemical composition of the catalyst, the nature of the support, and its original structure and texture. In addition, the nature and the amount of the modifier also have an influence on the thermal stability of the modified catalyst. These important catalyst properties cannot be reliably predicted, hence, it must be experimentally determined for each catalyst. However, the problem of quick deactivation which is caused by the interaction of the supports and the active species can be prevented using an inert support.

Textural properties are significant for variety of applications [18–22], particularly for catalysts [23–28]. The IUPAC has divided pores according to their size into three groups. Micropores have size smaller than 2 nm; mesopores have size between 2 and 50 nm and macropores are with sizes larger than 50 nm [29]. Mercury porosimetry enables the detection from macropores down to larger

mesopores, while physisorption of nitrogen provides the most reliable results for pores in the micro and mesopore regions [30]. These two methods are complementary for a proper evaluation of a porous structure [31].

In this work nickel catalysts with macroporous aluminosilicate and magnesia supports were synthesized. In order to improve catalyst performance and particularly selectivity of catalysts different modifiers were used. Textural properties of these materials as well as the dispersion properties of active metallic nickel were tested and correlated with catalytic activity and selectivity of catalysts.

2 Experimental

2.1 Basic Requirements for Catalyst

The products of partial oxidation should have the following composition (given in vol. %): CO: 20–26, H₂: 30–40, CO₂: 0.2–0.5, CH₄: 0.3–0.5 and N₂ is a rest to 100 %, while the presence of C₃H₈ should be undetectable. Porosity of catalyst should be approx. 70 vol.%, but at the same time with appropriate mechanical durability.

2.2 Synthesis of Aluminosilicate Based Ni Catalysts

The aluminosilicate based support was synthesized using alumina, quartz, kaolin (from domestic sources) and up to 40 mass% of petrol coke. After thermal treatment at 1300 °C the sample having 70 % of porosity was obtained. According to results of the X-ray analysis the obtained catalyst support mainly consisted of aluminosilicate having mullite structure with traces of α -Al₂O₃ and cristobalite [32, 33].

The synthesis of catalysts was performed by wet impregnation of mullite support with aqueous solution of nickel nitrate in concentration range 0.5–2.5 mol dm⁻³. Single or successive impregnations followed by heat treatment were the procedure adopted for catalyst synthesis. Impregnation was carried out at room temperature for 15 min. Each impregnation step was followed by drying at 110 °C for 1 h and calcination at 400 °C for 2 h. For the second impregnation the properties of the surface to take into account were those of the catalyst obtained after previous impregnation. The influence of different process parameters on catalyst selectivity were tested including: initial concentration of impregnation solution, number of successive impregnations and the nature of modifier [33]. The effect of Al, Ca and Mg modifiers on textural and catalytic properties of the synthesized Ni catalyst on porous mullite support was studied. All modifiers were applied in form of nitrate solution. The solid (support) to liquid (aqueous solution of salts) mass ratio was 1:5, while nickel:modifier molar ratio was 10:1.

2.3 *Synthesis of Magnesia Based Ni Catalysts*

Starting material for magnesia based support was raw magnesite. The raw magnesite was converted into sintered magnesia through sintering at high temperature. The chemical composition (given in mass%) of the obtained magnesia support was as follows: 95.5 MgO, 2.06 SiO₂, 2.09 CaO, 0.21 Fe₂O₃, and 0.14 Al₂O₃. The catalyst synthesis consisted of single or successive impregnations with nitrate precursor salts of active nickel and one of selected modifiers (Al, Ca and Mg), followed by thermal catalyst activation. The solid (support) to liquid (aqueous solution of salts) mass ratio was 1:3 [34]. The impregnation conditions were the same as previously given for aluminosilicate support. The above mentioned conditions enable decomposition of applied salts into corresponding oxide forms.

The concentration of Ni in impregnation solution varied from 1.0 to 3.0 mol dm⁻³. In each of impregnation solutions used in catalyst preparation the nickel:modifier molar ratio was 10:1.

Nickel oxide is reduced in situ into active metallic form prior to catalytic test with propane and air mixture.

2.4 *Sample Designation*

In this work different synthesis parameters were studied and accordingly the great number of different samples was obtained. In order to be able to distinguish samples the designation was performed in following manner: the first chemical symbol behind Ni indicates the used modifier, the letters A and M refer to aluminosilicate and the magnesia support, respectively; the first number denotes the nickel concentration in the impregnation solution and second number refers to the number of successive impregnation steps. For example NiAl/M-2-2 refers to nickel catalyst on magnesia support impregnated with solution containing 2.0 mol dm⁻³ Ni (NO₃)₂ + 0.2 mol dm⁻³ Al(NO₃)₃. The impregnation was repeated twice.

2.5 *Sample Characterization*

The content of Ni in catalyst was determined by standard chemical analysis using dimethylglyoxime.

The content of promoters in catalyst samples were determined by atomic absorption spectroscopy (Varian AA 775).

Nitrogen physisorption isotherms were determined on a Sorptomatic 1990, Thermo Finnigan instrument at -196 °C. Samples were outgassed at 160 °C during 20 h. Prior to N₂ physisorption, density of samples was determined using a pycnometer with benzene as the displacement fluid. The specific surface area, S_{BET} , of

the support and synthesized catalysts was evaluated from the adsorption data in the relative pressure range from 0.05 to 0.35 and calculated according to Brunauer, Emmett, Teller method [29]. S_{BET} was obtained using ADP2005 software.

Mercury intrusion porosimetry measurements were performed using a Carlo Erba Porosimeter 2000 (operating in the interval from 0.1 to 200 Mpa) equipped with a Carlo Erba 120 macropore unit. The porosity and the pore size distribution were determined in the range 7.5–100,000 nm. For data acquisition software Milestone 200 was used [30].

The specific surface area of the active nickel (S_{Ni}) was estimated by selective oxygen chemisorption at 0 °C in a flow pulse device with a gas chromatographic analyzer [35, 36]. Chemisorption measurements were carried out under the following conditions: in situ reduction of dried impregnated samples at 450 °C in $60 \text{ cm}^3 \text{ min}^{-1}$ flowing H_2 for 1 h. Cleaning the surface to remove H_2 was performed in $30 \text{ cm}^3 \text{ min}^{-1}$ flowing He. Prior to determining O_2 chemisorption capacities reduced and purged catalysts were cooled to 0 °C. After pretreatment, the saturation of the surface with O_2 was performed by injecting calibrated pulses of pure O_2 at 0 °C. The Ni surface area was calculated assuming a chemisorption stoichiometry $\text{O}:\text{Ni}_s = 1$, and surface nickel atom (Ni_s) average area of 0.065 nm^2 .

The average size of nickel crystallite (d_{Ni}) was calculated according to the following equation, with assumption that crystallites have a form of cube:

$$d_{\text{Ni}} = \frac{5 \times 10^{-3}}{\rho_{\text{Ni}} \cdot S_{\text{Ni}}} \text{ nm} \quad (2)$$

where: ρ_{Ni} is Ni density and S_{Ni} is specific surface area of active metallic Ni.

2.6 Catalytic Test

The high temperature propane oxidation by air, catalyzed by prepared samples, was studied in the temperature range 800–950 °C in a flow fixed-bed quartz reactor online connected with an analytical system. In all catalytic experiments almost equally amount of catalyst of about 40 g, and catalyst fraction granulated from 2 to 3 mm were used. Propane and air mixture with a volume ratio of 1:7.14 were passed over the catalyst at a GHSP of 300 h^{-1} , and at atmospheric pressure. Before the catalytic tests the catalyst samples were carefully reduced in situ with propane and air mixture, at a volume ratio of 1:9.6, respectively.

Analysis of C_3H_8 , O_2 , CO , H_2 and CH_4 in gas mixture in the inlet as well as in the outlet of the reactor was performed using a Perkin Elmer gas chromatograph (columns: $4 \text{ m} \times 3 \text{ mm}$ 60/80 Porapak Q, and $2 \text{ m} \times 3 \text{ mm}$ MS-5A, both at 150 °C). A calibration mixture (Messer-Griesheim) was used as the reference in quantitative analysis of products. The water content in the reaction products was determined by online connected hygrometer (Prolabo). Mass balance accurate to $\pm 1 \%$ was obtained for all analyses.

The scheme of assembly for catalytic test is given in Fig. 1.

The assembly for catalytic tests has three major sections: A—system for gas dosage, B—reactor and C—system for quantitate detection of gases in inlet and outlet.

The conversion of propane was defined as moles of propane converted per mole of propane introduced into reaction chamber (X):

$$X_{C_3H_8} = \frac{n_{C_3H_8}^0 - n_{C_3H_8}}{n_{C_3H_8}} \quad (3)$$

where: $n_{C_3H_8}^0$ is the molar flow-rate of propane to the reactor and $n_{C_3H_8}$ is the molar flow-rate of propane at the outlet of the reactor.

The selectivity for main products of reaction (CO and H₂) was calculated using the following equations:

$$S_{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2} + n_{CH_4}} \quad (4)$$

$$S_{CO} = \frac{n_{H_2}}{n_{H_2} + n_{H_2O} + n_{CH_4}} \quad (5)$$

where n_i is molar flow rate of the product “i” [37].

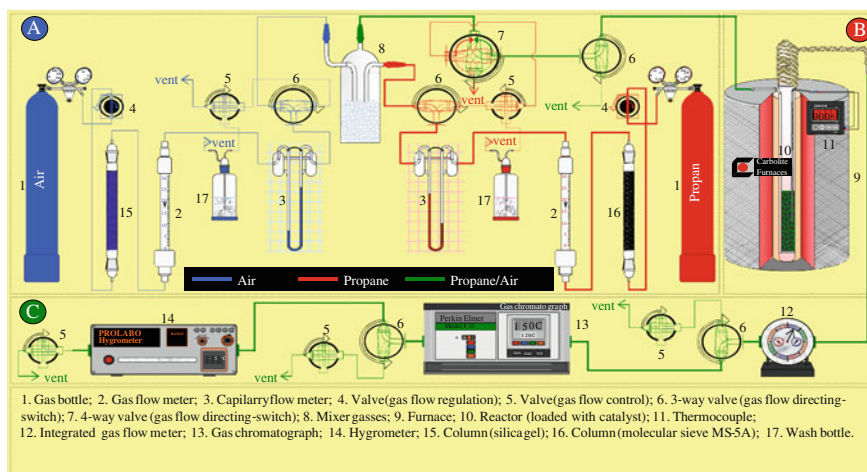


Fig. 1 Laboratory apparatus for testing of catalytic partial oxidation process

3 Results and Discussion

3.1 Textural Properties of Catalyst Supports and Catalysts

The results of mercury intrusion porosimetry and specific surface area S_{BET} obtained from low temperature N_2 -physisorption are presented in Tables 1 and 2 [32–34, 38, 39].

Table 1 Selected textural properties of aluminosilicate supported catalysts

Sample	Mercury intrusion porosimetry			N ₂ -physisorption
	V_p (cm ³ g ⁻¹)	$D_{\text{max-1}}$ (nm)	$D_{\text{max-2}}$ (nm)	S_{BET} (m ² g ⁻¹)
A	0.730	29,500	1000	2.9
Ni/A-0.75-1	0.670	25,500	1000	4.0
Ni/A-1-1	0.660	21,500	1000	4.2
Ni/A-2-1	0.640	16,000	1000	7.5
Ni/A-2.5-1	0.630	10,000	1000	8.3
Ni/A-0.75-6	0.495	21,500	680	9.6
Ni/A-1-4	0.525	17,000	940	11.5
Ni/A-2-2	0.525	16,000	1700	13.2

Table 2 Selected textural properties of magnesia supported catalysts

Sample	Mercury intrusion porosimetry			N ₂ -physisorption
	V_p (cm ³ g ⁻¹)	$Dv/2$ (nm)	D (nm) _{max}	S_{BET} (m ² g ⁻¹)
M	0.145	7030	7940	0.2
NiAl/M-1-1	0.139	6840	8020	0.3
NiAl/M-1-2	0.138	6610	8130	0.6
NiAl/M-1-3	0.134	6290	7760	0.8
NiAl/M-1-4	0.130	5330	7760	1.0
NiAl/M-1-5	0.124	4800	7240	1.2
NiAl/M-1-6	0.116	4600	6030	1.3
NiAl/M-2-1	0.136	4790	7760	1.1
NiAl/M-2-2	0.134	4540	7240	1.2
NiAl/M-2-3	0.128	3920	6020	2.1
NiAl/M-2-4	0.117	3520	5750	2.2
NiAl/M-3-1	0.132	4560	8330	1.5
NiAl/M-3-2	0.126	4080	8130	1.6
NiAl/M-3-3	0.113	3440	6310	1.7
NiAl/M-3-4	0.103	2630	3470	1.9
NiMg/M-2-2	0.125	4700	7320	1.4
NiCa/M-2-2	0.136	4630	7420	1.3

Differential pore distribution curves for aluminosilicate (A) support and all catalysts obtained using this support revealed bimodal distribution having two maxima ($D_{\max-1}$ and $D_{\max-2}$). On the other hand when magnesia (M) support is used the differential pore distribution curves have only one maximum. Different modifiers had insignificant impact on textural properties of A-based catalyst and therefore were omitted from Table 1.

The following observations apply to both aluminosilicate and magnesia base materials. All samples were dominantly macroporous. The pores in mesoporous region were slightly developed resulting in low values of S_{BET} . Impregnation process led to decrease of total pore volume and increase of S_{BET} . The same trend was obtained with increasing the number of impregnation steps and increased concentration of impregnation solution. Observed changes in catalyst textural properties can be attributed to additional developed porosity originated from nickel oxide deposits within the support structure.

The pore diameter at maximum of differential pore size distribution curve (D_{\max}) decreased with increasing the number of impregnation steps, i.e. with the increasing of the reached Ni loading (Table 3). The pore size distribution curves for catalyst samples show a significant broadening to the pores with smaller diameters. The

Table 3 Loading of nickel and modifiers and dispersion of nickel

Sample	Nickel properties			Modifier loading mass (%)
	Loading mass (%)	S_{Ni} ($\text{m}^2 \text{g}_{\text{Ni}}^{-1}$)	d_{Ni} (nm)	
NiAl/A-1-4	7.6	13.8	40	–
NiMg/A-1-4	7.5	10.9	52	0.8
NiCa/A-1-4	7.6	10.2	54	0.8
NiAl/M-1-1	0.56	15.7	36	0.06
NiAl/M-1-2	1.10	15.1	37	0.10
NiAl/M-1-3	1.62	12.8	44	0.14
NiAl/M-1-4	2.13	12.6	45	0.19
NiAl/M-1-5	2.63	11.6	48	0.23
NiAl/M-1-6	3.13	11.2	50	0.27
NiAl/M-2-1	1.13	9.0	62	0.10
NiAl/M-2-2	2.12	8.7	65	0.18
NiAl/M-2-3	3.04	8.4	67	0.26
NiAl/M-2-4	3.87	8.1	69	0.34
NiAl/M-3-1	1.79	6.3	89	0.16
NiAl/M-3-2	3.19	5.7	100	0.28
NiAl/M-3-3	4.15	5.5	103	0.36
NiAl/M-3-4	4.95	5.2	107	0.43
NiMg/M-2-2	3.24	11.1	51	–
NiCa/M-2-2	3.32	7.7	73	0.30

– Due to the presence of modifier in the support the identification of introduced modifier was not determined

observed changes in the pore structure of catalyst samples are more intense for the samples prepared from impregnation solution with greater Ni^{2+} concentration than for the ones prepared from the diluted solution. These effects are more expressed for D_{max-1} than D_{max-2} and for M-based catalysts in comparison to A-based catalysts.

3.2 Dispersion of the Active Nickel

Table 3 presents nickel and promoter loadings as well as specific surface of metallic nickel and calculated average nickel crystallite size according to Eq. 2 [32–34, 38, 39]. For aluminosilicate based catalysts only the influence of nature of modifier is selected to be presented.

As expected the incorporation of nickel increased proportionally with the increase of applied Ni concentration in the impregnation solution. The nickel loading and calculated average size of nickel crystallite increased with number of the impregnation steps. It can be explained by growth of the Ni crystallites as a result of deposit of Ni^{2+} from impregnation solution on the Ni crystallites formed in the previous impregnation steps. Raising the Ni concentration in impregnation solution decreased the Ni surface area and increased the mean Ni crystallite size in the obtained magnesia supported nickel catalysts [33].

The influence of modifiers used on the Ni surface area and the average Ni crystallite size is observed for both catalyst supports in same manner. The mean Ni crystallite size increased according to the following order of applied modifiers: $\text{Al}_2\text{O}_3 < \text{MgO} < \text{CaO}$. The observed effect could be explained with the respect to literature data for particle radius for pure modifier oxides [40]. Since these oxides do not reduce to metallic form the average Ni crystallite size is in a good agreement with an increasing particle size of the applied modifiers [32–34].

3.3 Results of Catalytic Test

In order to analyze performance of synthesized catalysts the catalytic test was performed on different temperatures. The conversion for propane oxidation in the air at temperatures in the studied range for all catalysts was studied by measuring the outlet gas for detectable products i.e. CO, H_2 , CH_4 , CO_2 and H_2O . Since no presence of C_3H_8 was detected in the outlet, the conversion of propane was 100 % for all investigated catalysts.

The selectivity toward CO and H_2 were the criteria for evaluating all catalysts. It was observed that the concentration of impregnation solution, number of successive impregnations and nature of modifier have high impact on catalyst selectivity.

For each type of porous ceramic support the series of experiments were performed. The influence of synthesis parameters on the aluminosilicate support based catalysts is given in Figs. 2 and 3.

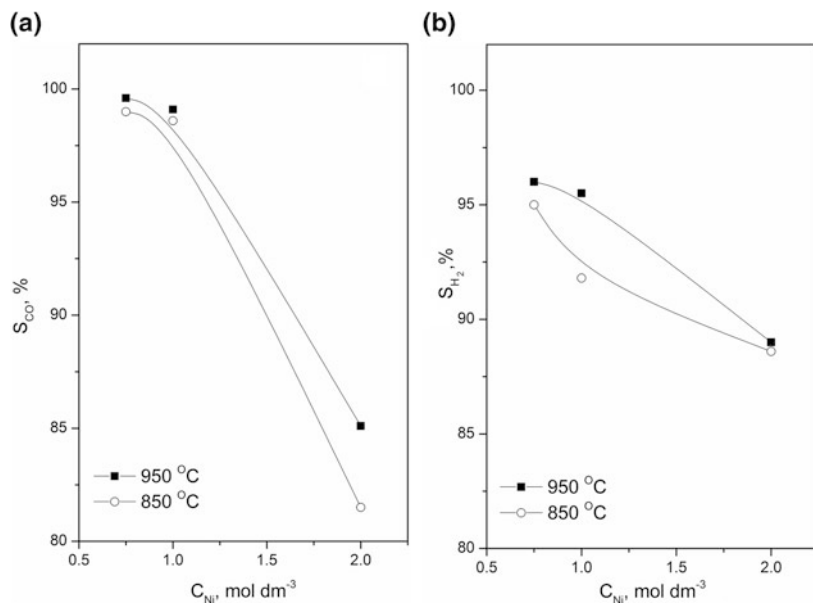


Fig. 2 Dependence of selectivity of aluminosilicate based catalysts in partial oxidation of propane on concentration on impregnation solution used for synthesis of catalysts: **a** CO; **b** H₂

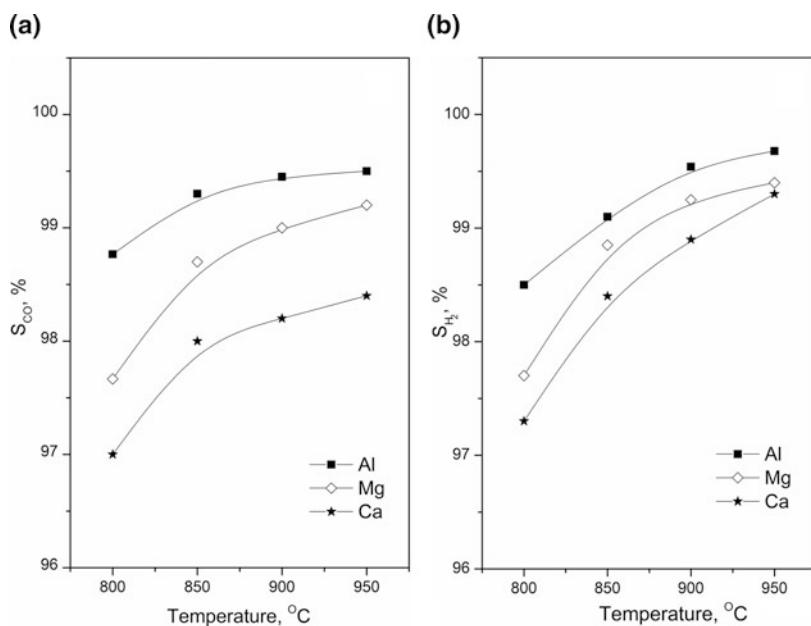


Fig. 3 Dependence of selectivity of aluminosilicate based catalysts in partial oxidation of propane on nature of modifier: **a** CO; **b** H₂

In Fig. 2 the influence of concentration of nickel in impregnation solution on selectivity for CO (Fig. 2a) and H₂ (Fig. 2b) on different temperatures is given. For comparison purpose the catalysts with approx. same nickel loading (7.6 mass%) were selected. In order to achieve the same amount of nickel in catalyst the number of successive impregnation was different. Therefore, the samples Ni/A-0.75-6, Ni/A-1-4 and Ni/A-2-2 are presented in Fig. 2.

The selectivity toward CO and H₂ formation in the propane oxidation on catalyst samples had same trend, although the S_{H₂} was less sensitive to applied concentration of impregnation solution. The samples obtained by impregnation with more concentrated solutions had lower selectivity for both major products of oxidation than the one observed on samples synthesized using more dilute impregnation solutions.

The effect of different modifiers on selectivity of aluminosilicate based catalysts on different temperatures is given in Fig. 3a, b for CO and H₂, respectively. All samples were prepared using the same concentration of impregnation solution (1.0 mol dm⁻³ Ni(NO₃)₂). Four successive impregnations were performed for each sample. Therefore, Fig. 3 shows the catalytic properties of NiAl/A-1-4, NiMg/A-1-4 and NiCa/A-1-4. The nickel loading for all these samples was ≈ 7.6 mass%.

All investigated catalysts showed high selectivity toward both CO and H₂. Even at 800 °C their selectivity was higher than 97 %. The best selectivity was obtained when Al was used as modifier. The selectivity rose in following order: CaO < MgO < Al₂O₃.

The applied modifiers had the same influence on magnesia supported catalysts (Fig. 4). For comparison the catalysts with the same nickel loading of approx. 3.2 mass% are given.

The magnesia supported catalysts were more temperature sensitive than corresponding aluminosilicate supported catalysts. Also the influence of modifiers on M-based catalyst is more expressed. Since magnesia supported catalysts had smaller values of S_{BET} than aluminosilicate supported catalysts, the nickel loading under same experimental conditions led to higher values of nickel loading for latter.

Since magnesia supported Ni catalyst with Al modifier expressed significantly better selectivity than magnesia supported Ni catalysts with other modifiers only this group of catalysts will further be discussed. Besides temperature on selectivity of these catalysts two structural parameters have great impact: nickel loading and size of nickel crystallite. Theoretically the higher nickel loading should provide better selectivity while smaller crystallite size led to selectivity improvement. Since those two parameters are not independent a compromise should be made. Figure 5 shows the influence of Ni crystallite size on selectivity of NiAl/M catalyst. In Fig. 6 the influence of Ni loading on selectivity of NiAl/M catalyst is given. The values of crystallite size and nickel loading are given in Table 3.

In Fig. 5 three groups of results can be observed. In first group of results the samples impregnated with 1.0 mol dm⁻³ Ni²⁺ solution with Ni crystallite size in range 44–50 nm. The samples NiAl/M-1-1 and NiAl/M-1-2 with smaller crystallite

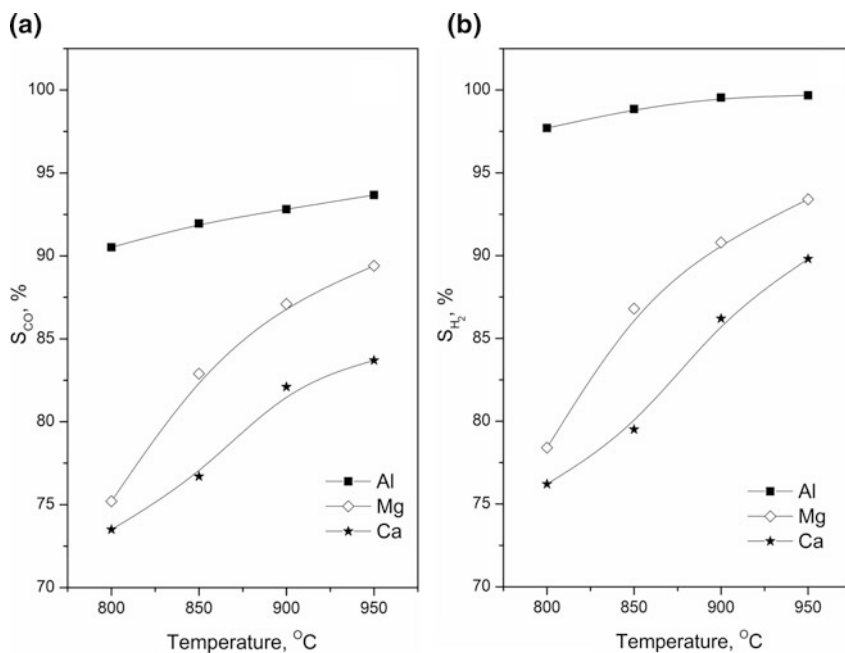


Fig. 4 Dependence of selectivity of magnesia based catalysts with different modifiers in partial oxidation of propane on nature of modifier: **a** CO; **b** H_2

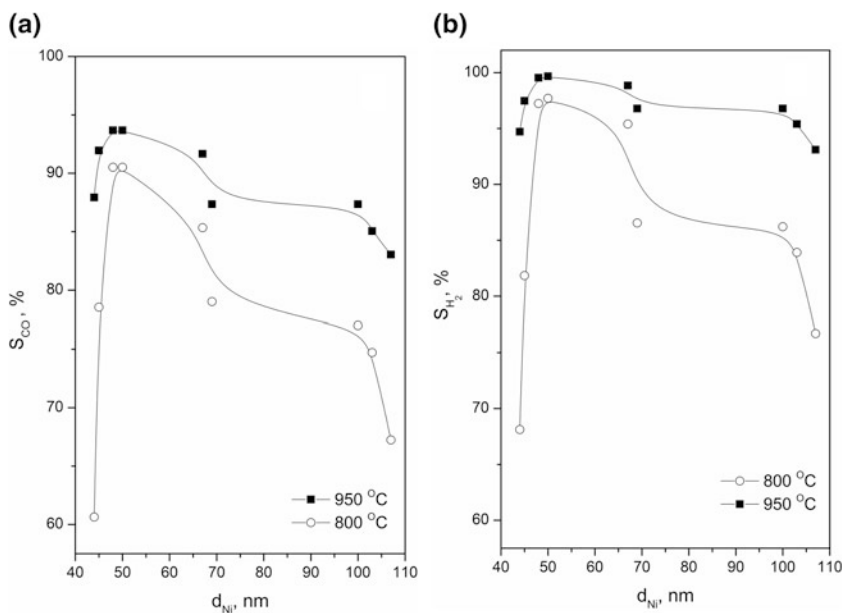


Fig. 5 Dependence of selectivity of NiAl/M catalysts in partial oxidation of propane on nickel crystallite size: **a** CO; **b** H_2

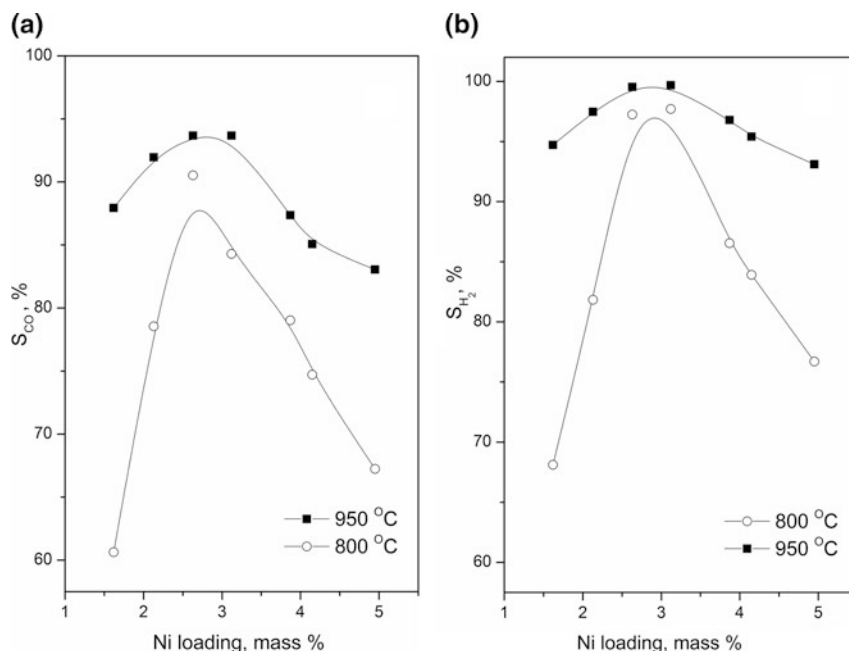


Fig. 6 Dependence of selectivity of NiAl/M catalysts in partial oxidation of propane on nickel loading: **a** CO; **b** H_2

sizes (36 and 37 nm, respectively) had nickel content smaller than 1.6 mass% and consequently were unable to perform efficient catalysis. For this group of catalysts it appears that selectivity was improved with increase of crystallite size, but improvement was actually caused by increase in Ni loading (Fig. 6).

The second group of results was obtained with samples impregnated with 2.0 mol dm^{-3} $Ni(NO_3)_2$ solution with Ni crystallite size in range 65–69 nm. The third group of results illustrates behavior of NiAl/M-3 catalyst ($100 < d_{Ni} < 107 \text{ nm}$). Since samples NiAl/M-2-1 and NiAl/M-3-1 had insufficient nickel content their selectivity was not analyzed. For all catalysts prepared with impregnation solution having concentration higher than 1.0 mol dm^{-3} selectivity decreased with the increase of nickel crystallite size even when nickel content increased. Summarizing the results in Figs. 5 and 6 it can be concluded that under the investigated synthesis conditions the best selectivity toward both CO and H_2 was obtained for catalyst having nickel loading around 3 mass% and $d_{Ni} \approx 50 \text{ nm}$. The magnesia supported catalyst NiAl/M-1-6 i.e. catalyst obtained by six fold impregnation with 1.0 mol dm^{-3} was the catalyst with the best selectivity in partial oxidation of propane to CO and H_2 .

The comparison of the best performing aluminosilicate and magnesia supported catalysts with Al as modifier revealed that the latter express somewhat lower selectivity particularly toward CO. For both catalysts (NiAl/A-1-4 and NiAl/M-1-6) the temperature increase had small impact on the increase of selectivity, suggesting that both catalysts exhibit high performance even at 800 °C. However, due to

higher porosity the aluminosilicate support enabled higher nickel uptake than magnesia support resulting in higher selectivity ($98.8 < S_{CO} < 99.5$ and $98.5 < S_{H_2} < 99.7$ for NiAl/A-1-4 and $90.5 < S_{CO} < 93.7$ and $97.7 < S_{H_2} < 99.7$ for NiAl/M-1-6 for temperatures between 800 and 950 °C).

4 Conclusions

Nickel catalysts on porous ceramic aluminosilicate and magnesia supports were synthesized by single or successive impregnations with nitrate precursor salts of active nickel and one of selected modifiers (Al, Ca and Mg). After thermal catalyst activation the obtained catalysts were tested in the reaction of partial oxidation of propane to CO and H₂. The textural properties, nickel loading and nickel crystallite size were correlated with selectivity toward CO and H₂.

All synthesized catalysts samples were dominantly macroporous. Impregnation process led to decrease of total pore volume and increase of S_{BET} in comparison to support. The same trend was obtained with increasing the number of impregnation steps and increased concentration of impregnation solution.

The calculated average size of nickel crystallite increased in the same manner as the incorporated nickel i.e. increased with the increase of Ni concentration in the impregnation solution as well as with number of successive impregnations.

The selectivity of catalysts increased with presence of modifiers. The selectivity rose in following order: CaO < MgO < Al₂O₃.

Selectivity toward CO and H₂ of studied catalysts is governed mainly by two structural parameters: nickel loading and nickel crystallite size. Theoretically the higher nickel loading should provide better selectivity while smaller crystallite size led to selectivity improvement. Since those two parameters are not independent a compromise should be made. For Al₂O₃ modified magnesia supported Ni catalysts was found that around 3 mass% of Ni in catalyst with crystallite size approx. 50 nm provided the best selectivity among this type of catalysts.

The comparison of the best performing aluminosilicate and magnesia supported catalysts with Al as modifier revealed that the latter express somewhat lower selectivity particularly toward CO.

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