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Influences of synthesis methods and modifier addition on the properties of Ni-based catalysts supported on reticulated ceramic foams

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Abstract: A method of synthesizing Ni-based catalysts supported on α-Al_2O_3-based foams was developed. The foams were impregnated with aqueous solutions of metal chlorides under an air atmosphere using an aerosol route. Separate procedures involved calcination to form oxides and drying to obtain chlorides on the foam surface. The synthesized samples were subsequently reduced with hydrogen. With respect to the Ni/Al_2O_3 catalysts, the chloride reduction route enabled the formation of a Ni coating without agglomerates or cracks. Further research included catalyst modification by the addition of Pd, Cu, and Fe. The influences of the additives on the degree of reduction and on the low-temperature reduction effectiveness (533 and 633 K) were examined and compared for the catalysts obtained from oxides and chlorides. Greater degrees of reduction were achieved with chlorides, whereas Pd was the most effective modifier among those investigated. The reduction process was nearly complete at 533 K in the sample that contained 0.1wt% Pd. A lower reduction temperature was utilized, and the calcination step was avoided, which may enhance the economical and technological aspects of the developed catalyst production method.

Keywords: catalysts; nickel; ceramic foams; modification; aerosol process; catalytic properties

1. Introduction

Catalysts supported on oxides that contain noble or base metals as catalytically active components are widely used in heterogeneous catalysis processes (e.g., hydrocarbon steam reforming) [1–3]. The various support types and forms, onto which metals can be applied, include reticulated α-Al_2O_3 foams and γ-Al_2O_3 powders [3–6]. Although noble-metal-based catalysts exhibit excellent catalytic properties (i.e., activity, stability, and selectivity) [3], their application in industry is expensive [7]. In contrast, Ni is an effective substitute for noble metals because of its high catalytic activity and selectivity [8]. Because of its low cost, Ni is economically favored in industrial applications [6,9–10]. As an example, Ni/Al_2O_3 catalysts are used in the steam reforming of ethanol and other hydrocarbons [6,10–12]. However, Ni-based catalysts are prone to rapid deactivation due to the formation of deposits on the Ni surface and Ni sintering at elevated temperatures. Hence research on the synthesis of Ni-based catalysts with enhanced activity, deactivation resistance, and selectivity is necessary to enable their functionality in long-term applications. This goal can be achieved through the use of different supports, various preparation methods, and the addition of activity modifiers [6,8–10]. The addition of a small amount of Pd (0.1wt%–0.3wt% [10] or 0.01wt%–0.03wt% [12]) as a catalytic activity modifier substantially enhances the stability of Ni-based catalysts such that the catalysts retain their initial activity without deterioration of their properties at elevated temperatures. Notably, the activity and selectivity of the catalysts can drastically decrease due to the inhomogeneous

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dispersion of Ni and Pd on the support material [10,12].

Ni-based catalysts are conventionally synthesized by thermochemical methods that involve calcination and activation by hydrogen reduction. One cause of deactivation is the formation of the highly undesirable $NiAl_2O_4$ spinel phase, which generally occurs in catalysts supported on γ-Al_2O_3 and synthesized by impregnation. The $NiAl_2O_4$ is formed during the calcination process, and its presence hinders the catalyst's reducibility. Consequently, the amount of Ni available for catalytic reactions is diminished [6,10–11]. The $NiAl_2O_4$ is a product of the solid-solid reaction between NiO and acidic Al_2O_3 at the NiO/Al_2O_3 interphase at high temperatures (> 1073 K). An increase in the calcination temperature leads to further $NiAl_2O_4$ growth through the interaction of Ni and Al ions. Its strong bond with Al_2O_3, very high degree of dispersion, and stable structure render $NiAl_2O_4$ a hardly reducible phase [6,11,13–14]. As reported by Cheng *et al.* [11], $NiAl_2O_4$ is also formed at low calcination temperatures (823 K). According to Gayán *et al.* [15], the use of an α-Al_2O_3 support in the production of Ni-based oxygen carriers by impregnation minimizes $NiAl_2O_4$ formation.

Novel methods for the synthesis of submicron-sized catalysts and materials include a step of ultrasonic aerosols generation. These methods enable the formation of fine spherical particles with precise stoichiometry and high purity [16–18]. As an example, nearly spherical and mostly submicron-sized ZnO particles were obtained by the ultrasonic spray pyrolysis method, which is favored in industrial use and in large-scale production [19]. Aerosol routes can be used to synthesize fine metal powders from precursor salt solutions, without a calcination step. Gurmen *et al.* [20] successfully synthesized spherical nanocrystalline Fe–Ni particles by pyrolyzing ultrasonically aerosolized aqueous solutions of $NiCl_2$ and $FeCl_2$ and directly reducing the products with hydrogen in a tubular quartz reactor.

Reticulated ceramic foams are suitable as catalyst supports because of their combination of high pore volumes, low pressure drops during fluid flow, good mass transfer, and good heat conductivity. These properties give ceramic foams advantages over other supports, and their use in industry could be beneficial [4–5,21–22].

The aim of the present research was to develop a method for the synthesis of Ni-based catalysts. α-Al_2O_3-based foams used in the synthesis were prepared by the polymer replication method described in our previous work [23–24]. The catalysts were produced by impregnation of the foams with ultrasonically aerosolized aqueous solutions of metal chlorides in a tubular quartz reactor. The formation of oxides and chlorides on the foams was achieved using two separate procedures that were conducted under air atmosphere. To obtain oxides, we calcined the impregnated samples at 773 K. Pérez-Hernández *et al.* [25] have used $NiCl_2$ as a precursor to synthesize Ni-based catalysts via the impregnation method. Their catalyst preparation method included calcination at 773 K for 2 h in an air atmosphere, followed by reduction with hydrogen for 2 h at the same temperature [25]. To deposit chlorides on the foams, the impregnated samples were dried at 473 K. The samples were subsequently reduced under flowing hydrogen.

In our previous report, we investigated the effects of Pd, Cu, and Fe additives on the extent of $NiCl_2$ reduction by hydrogen [26]. Low-temperature reduction experiments (533–653 K) were conducted. We observed that the addition of 0.1wt% $PdCl_2$ was the most effective and that the greatest degree of reduction (58.16%) was achieved at 653 K for 24 min. Pd exhibited the most pronounced effect because the induction period of $NiCl_2$ reduction was shortened [26], most likely as a result of the hydrogen spillover effect [27].

On the basis of our formerly obtained results [26], the present research included a comparative analysis of the catalysts obtained from oxides and chlorides. The effects of the addition of activity modifiers (M = Pd, Cu, Fe) on the degree of hydrogen reduction of the catalysts were analyzed to enhance their catalytic properties**.** Modification with noble metals (e.g., Pd or Pt) has been reported to improve the catalytic properties of Ni-based catalysts [10,12]. The low-temperature reducibility of the catalysts was investigated with the aim of utilizing a lower reduction temperature. In the developed synthesis route, the calcination step was eliminated, which can enhance the economic and technological efficiency of the catalysts' production process.

2. Experimental

In this work, the experiments included the synthesis of Ni/Al_2O_3 and Ni–M/Al_2O_3 catalysts supported on α-Al_2O_3-based foams. The catalysts contained Ni as their active component and added catalytic activity modifiers (M = Pd, Cu, Fe).

The following materials were used to prepare the catalysts: $NiCl_2\cdot 6H_2O$, $PdCl_2$, $CuCl_2\cdot 2H_2O$, $FeCl_2\cdot 4H_2O$ (MERCK, pro analysis), and previously synthesized reticulated α-Al_2O_3-based foams. The foams were prepared via the polymer replication method, as described in our previous reports [23–24]. Appropriate amounts of $NiCl_2\cdot 6H_2O$ (without additives and with $PdCl_2$, $CuCl_2\cdot 2H_2O$, and $FeCl_2\cdot 4H_2O$) were dissolved in distilled water. The metallic ion concentrations in the prepared precursor solutions were 0.15 mol/L. The amounts of chloride precursors were calculated to achieve a nominal content of 20wt% Ni in the catalysts. The additive loadings were 0.1wt% Pd, 1.0wt% Cu, and 1.0wt% Fe with respect to the Ni content.

The foams were placed into a tubular quartz reactor in an electro-resistant furnace. An ultrasonic nebulizer (PROFI SONIC, PRIZMA) with a resonator frequency of 1.7 MHz was attached to the reactor. Two separate procedures were used to impregnate the foams with aerosolized precursor solutions. The first experimental procedure involved preheating the foam at 773 K, followed by flowing the aerosol through the reactor. After the aerosol generation was complete, the sample was calcined for 60 min at 773 K in air. The calcination enabled the formation of oxides on the foam surface. The second procedure was similar to the first, except that the foam was preheated at 473 K and the sample was dried at 473 K for 60 min in air. The drying treatment was conducted to obtain dehydrated chlorides on the foam surface. A schematic of the apparatus used for this process is presented in Fig. 1.

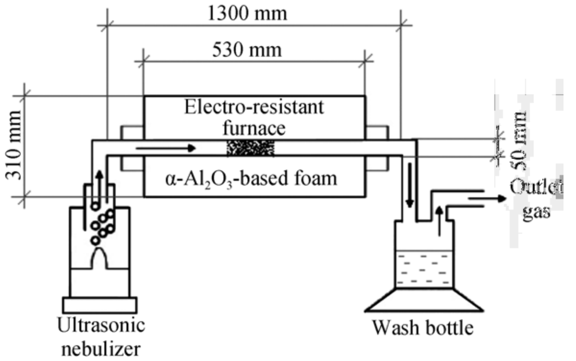

Fig. 1. Experimental setup for the impregnation of α-Al_2O_3-based foams with precursor solutions.

After the calcination and drying procedures, the obtained samples were reduced under flowing H_2 (flow rate: 20 L/h) at 533 or 633 K for 90 min. The samples were reduced under static conditions. The apparatus used for the reduction is detailed elsewhere [26].

In the case of the system without additives, the microstructure of the samples calcined, dried, and reduced at 633 K was investigated using a JEOL JSM–5800LV scanning electron microscope. Phase identification of the samples reduced at 633 K was performed by X-ray diffraction (XRD) on a PHILIPS PW–1710 diffractometer. In the case of the synthesized Ni/Al_2O_3 and Ni–M/Al_2O_3 catalysts, their degree of reduction was also examined. The masses of the calcined and dried samples were measured before and after the reductions at 533 and 633 K. The degrees of reduction were calculated on the basis of the mass differences.

3. Results and discussion

3.1. Ni/Al_2O_3 catalysts

Analyses were performed after the impregnation procedures to compare the Ni/Al_2O_3 catalysts obtained from the oxide and chloride supported on the foams. The calcined and dried samples, before and after hydrogen reduction, were analyzed by scanning electron microscopy (SEM); the results are presented in Figs. 2 and 3.

The SEM micrograph of the sample calcined at 773 K shows the formation of sponge-like agglomerates on the foam surface and inhomogeneous particle distribution (Fig. 2(a)). The most probable explanations for the obtained morphology are the combined complex mechanisms of rapid water evaporation from the aerosol, $NiCl_2·6H_2O$ dehydration, and the transfer of $NiCl_2$ to the oxide phase. Furthermore, the foam acted as a filter, and its cell morphology resulted in it being incompletely covered with the oxide phase.

In contrast to the SEM image in Fig. 2(a), the SEM image of the sample dried at 473 K shows that the foam surface

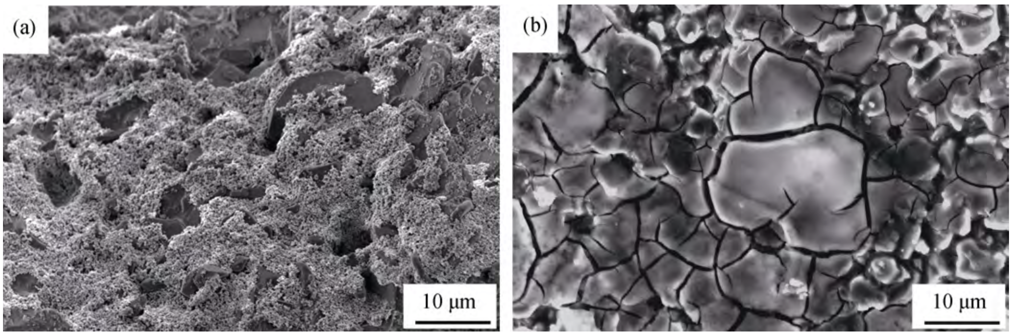

Fig. 2. SEM micrographs of samples after the impregnation procedures: (a) calcined at 773 K for 60 min and (b) dried at 473 K for 60 min.

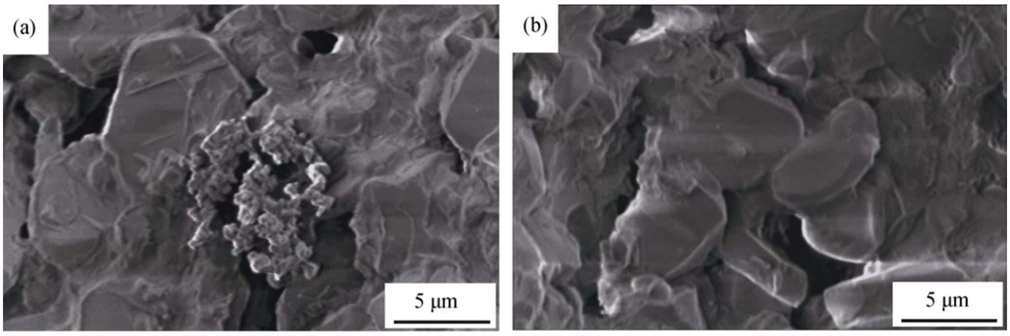

Fig. 3. SEM micrographs of Ni supported on α-Al_2O_3-based foams, reduced at 633 K for 90 min, obtained from: (a) the sample calcined at 773 K for 60 min and (b) the sample dried at 473 K for 60 min.

was completely covered with a chloride crust (Fig. 2(b)). The complete coverage of the foam is a result of the lower temperature applied during the drying procedure, which led to a slower evaporation of water from the aerosol. The chloride crust was mainly cracked, with inhomogeneous thickness. The presence of agglomerates in certain sites was noted. Similar to the oxidized sample, a main cause of the inhomogeneous chloride dispersion could be the foam cell morphology and its filter-like behavior. In addition, the cracks were formed because of the evaporation of water from the aerosol, in combination with $NiCl_2·6H_2O$ dehydration.

After the calcined sample was reduced at 633 K, SEM analysis clearly indicated the formation of large, sponge-like agglomerates (Fig. 3(a)). The residual agglomerates probably result from the greater stability of oxides phases compared with that of chloride phases. The obtained morphology is consistent with a lower degree of reduction of the oxide phase compared to that of the chloride phase supported on the foams (see Tables 1 and 2). In addition, the foam was completely covered with a Ni coating.

Interestingly, the reduction of the dried sample at 633 K resulted in an absence of agglomerates and cracks in the Ni coating (Fig. 3(b)). This coating morphology indicates that the chloride phase was reduced to a greater degree than the oxide phase. The latter explanation was confirmed by the greater degree of reduction obtained for the chloride compared with the oxide supported on the foams, as presented in Tables 1 and 2.

An explanation for the complete coverage of the foams with Ni coatings is a complex mechanism of mass transport that occurred during the reduction process when the diffusion mobility of Ni atoms became sufficiently high. The mass transport resulted in contact between Ni particles and contact surface growth. The contacts between Ni particles formed in sites not covered with the oxide and in cracked sites of the chloride crust. However, the mass transport mechanism was more pronounced during the chloride reduction. Hence, the hydrogen reduction of the catalyst synthesized from the chloride resulted in a relatively smooth Ni coating.

Table 1. Degrees of reduction of samples obtained from oxides and chlorides supported on the foams, reduced at 533 K for 90 min in static conditions

Sample	Reduction degree / %			
	Without additives	With additives		
		0.1wt% Pd	1wt% Cu	1wt% Fe
Oxides	12.8	20.0	15.2	13.5
Chlorides	23.7	98.2	74.7	67.5

Table 2. Degrees of reduction of samples obtained from oxides and chlorides supported on the foams, reduced at 633 K for 90 min in static conditions

Sample	Reduction degree / %			
	Without additives	With additives		
		0.1wt% Pd	1wt% Cu	1wt% Fe
Oxides	15.4	24.2	18.5	16.6
Chlorides	35.2	99.6	87.9	79.4

The synthesis of the Ni/Al_2O_3 catalyst from the oxide resulted in the formation of highly undesirable agglomerates. Such agglomeration can cause catalyst deactivation during their use because of abrasion in a gas stream and deposit formation. In addition, agglomeration hinders hydrogen reduction and decreases the catalytically active component's free surface area. However, the agglomerates and cracks were absent when the Ni/Al_2O_3 catalyst was prepared from the chloride precursor, which is extremely important for preserving the catalyst's activity, stability, and selectivity.

XRD spectra of the samples reduced from the oxide and chloride phases under static conditions at 633 K are presented in Fig. 4.

One of problems concerning Ni-based catalysts supported on γ-Al_2O_3 is the formation of $NiAl_2O_4$. This phase commonly occurs in catalysts prepared by impregnation. The presence of $NiAl_2O_4$ adversely affects catalytic activity by hindering reducibility and thus decreasing the amount of Ni available for catalytic reactions [6,10–11].

α-Al_2O_3 has been reported to minimize $NiAl_2O_4$ formation in Ni/Al_2O_3 systems [15]. The XRD analyses show that elemental Ni, α-Al_2O_3, and mullite were present after the oxide and chloride reduction processes (Figs. 4(a) and 4(b)). The α-Al_2O_3 and mullite phases belong to the foams. Residual oxide and chloride phases were not detected. In addition, the undesirable $NiAl_2O_4$ phase was not detected, even though the impregnation method was used.

3.2. Comparative analysis of Ni/Al_2O_3 and Ni–M/Al_2O_3 catalysts

Our further course of research included a comparative investigation of the degrees of reduction of Ni/Al_2O_3 and Ni–M/Al_2O_3 catalysts synthesized from oxides and chlorides. To enable the use of a lower reduction temperature, the experiments were conducted at 533 and 633 K. The samples were reduced under flowing H_2 (20 L/h) for 90 min in static conditions. The degrees of reduction of the oxides and chlorides supported on the foams are presented in Tables 1 and 2.

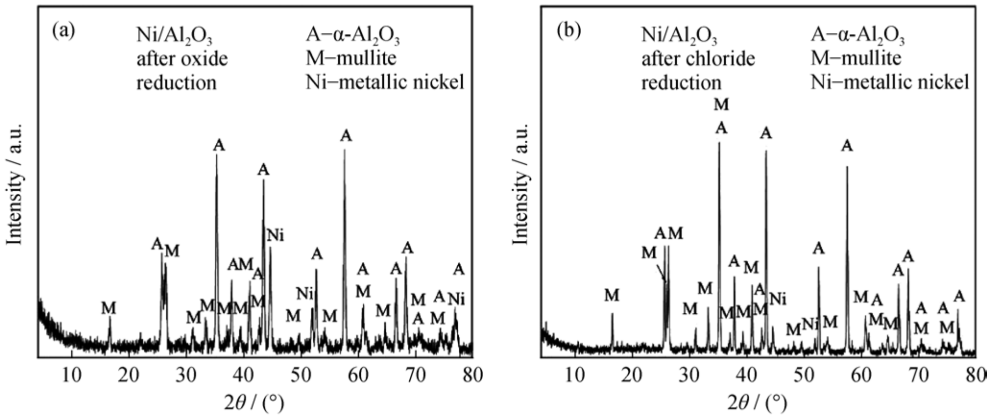

Fig. 4. XRD patterns of Ni supported on α-Al_2O_3-based foams after (a) oxide and (b) chloride reduction at 633 K for 90 min.

With respect to the Ni/Al_2O_3 catalysts, the degree of oxide reduction was approximately half the degree of chloride reduction at both investigated temperatures. Notably, the oxide reduction was slightly more efficient at 633 K than at 533 K. The obtained results can be explained by the stabilization of oxide phases during the calcination step. Furthermore, the stability of the oxide phase increases with an increase in calcination temperature.

With respect to the Ni–M/Al_2O_3 catalysts, all of the investigated additives increased the degree of reduction of the oxides and chlorides at both temperatures. As expected, the addition of Pd resulted in the greatest increase in reduction efficiency. The presence of Pd facilitated the reduction of the Ni species, most probably because of the hydrogen spillover effect. This phenomenon occurred on the Pd surface when H_2 molecules split into atomic hydrogen and quickly diffused into lattices of Ni species. In general, hydrogen spillover on metals and its positive influence on the properties of catalysts have been extensively investigated [27–30]. With respect to the additives, the degree of reduction increased in the order 1.0wt% Fe < 1.0wt% Cu < 0.1wt% Pd (Tables 1 and 2). Approximately 20.0% and 24.2% of the oxides were reduced at 533 and 633 K, respectively, in the case of catalysts that contained 0.1wt% Pd. We observed that the degrees of oxide reduction in the samples that contained additives were slightly higher at 633 than at 533 K. The reduction of chlorides in the presence of the additives was considerably more effective in all cases. With the addition of only 0.1wt% Pd, the extent of chloride reduction reached 98.2% and 99.6% at 533 and 633 K for 90 min, respectively. The results related to the reduction of chlorides in the presence of additives are consistent with those reported in our previous work [26]. The present research results indicate that the chlorides in the presence of the additives were reduced to a greater degree at 633 than at 533 K. However, in the presence of Pd addition, the difference in the degrees of reduction was minor and the reduction was nearly complete at 533 K. Therefore, we concluded that the lower reduction temperature (533 K) can be used for the catalyst synthesis. The developed process may be more favorable from technological and economical viewpoints.

4. Conclusions

A synthesis route for Ni-based catalysts supported on α-Al_2O_3-based foams was developed. In the preparation method, aerosolized solutions of metal chlorides were used to impregnate the foams. First, oxides and chlorides were formed on the foams by calcination (773 K) and drying (473 K), respectively. Afterward, low-temperature hydrogen reduction experiments were conducted at 533 and 633 K for 90 min under static conditions.

In the case of Ni/Al_2O_3 catalysts prepared from the oxides, the presence of undesirable agglomerates was noted. In the catalyst synthesized from chlorides, agglomerates and cracks in the Ni coating were absent. The degrees of reduction of samples that contained chlorides (23.7% and 35.2% at 533 and 633 K, respectively) were approximately twice those of samples that contained oxides (12.8% and 15.4% at 533 and 633 K, respectively).

With respect to the $Ni–M/Al_2O_3$ catalysts with added activity modifiers (M = Pd, Cu, Fe), the additives were observed to influence the degree of reduction; the low-temperature reduction efficiency of samples with and without additives was therefore compared. Modification with Pd resulted in the greatest influence on the extent of reduction among the investigated additives. However, in comparison with samples obtained by oxide reduction, all of the chloride samples were reduced to a substantially greater degree. With the addition of only 0.1wt% Pd, the degrees of reduction reached 98.2% and 99.6% after 90 min at 533 and 633 K, respectively. We concluded that a temperature of 533 K can be used to synthesize the catalysts on the basis of the nearly complete reduction process at that temperature. A lower reduction temperature was utilized, and the calcination step was avoided, which can contribute to the economic efficiency and technological simplification of the production process of these catalysts.

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