INFLUENCE OF THE ALUMINA ORIGIN ON THE REDUCIBILITY OF NiO CATALYST

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In order to determine the influence of the origin of alumina support on the reducibility of the $NiO-Al_2O_3$ catalyst four model systems were prepared, by impregnation of gibbsite, boehmite, γ-Al_2O_3 and α-Al_2O_3 with nickel nitrate solution. Prior to reduction (400^oC, hydrogen flow) the prepared model catalyst samples were calcined at 400^oC, 900^oC and 1000^oC for 24 hours. It was noticed that the sample prepared on α-Al_2O_3 can be easily reduced, thanks to weak interaction between the catalyst components. Samples prepared on gibbste, boehmite and γ-Al_2O_3, previously calcined at 400^oC are more difficult to reduce, due to stronger interaction between NiO and catalyst support. Samples calcined at 900^oC and 1000^oC can be reduced only after prolonged reduction time (eight hours), as evidenced by gravimetric method. However, this thermal effect was not strong enough to be observed by DTA and DSC. High resistance of these samples against reduction is explained by intensive nickel spinel, $NiAl_2O_4$, formation.

INTRODUCTION

Alumina supported nickel catalysts find broad application in a number of important catalytic processes, as steam reforming,[1] partial oxidation of methane,[2, 3] methanation of carbon oxides[4] and hydrogenation of unsaturated organics.[5] This catalytic system has perspective in methane dry reforming[6], in ozone decomposition[7] and also in catalytic ozonation of CO and VOCs[8]. Alumina supported nickel oxide can also be applied as gas and humidity sensor.[9, 10] This catalytic system is frequently subject of research, in terms of its morphology,[11, 12] structure,[13] texture[13] and catalytic activity.[1-8] The active component of the catalyst is nickel in metallic form, so the prepared catalysts require reduction of nickel precursor before application. Therefore, reduction of nickel oxide has attracted wide interest in the field of catalysis. Benton and Emmett in their pioneering study reveal their observations obtained by thermogravimetric analysis: *i)* the reduction of nickel oxide is auto-catalytic, proceeding mainly at the interface between the solid phases, *i.e.* NiO and Ni; *ii)* the reduction takes place less readily, when the preparation temperature is higher; *iii)* water vapor retards the reduction, especially at the start of reaction, and increases the induction period; *iv)* the induction (or incubation) period depends on pretreatment temperature and on the nature of the sample.[14] Reduction of nickel oxide is exothermic reaction.[15] The reduction mechanism of nickel oxide is different depending whether it is in the form of single crystal or powder,[16] and even a little amount of impurities can significantly influence the reduction kinetics.[17] The perception about the reduction mechanism of nickel oxide essencially remains the same even today.[18-20] Recent theoretical study (thermochemical approach) about the mechanism and kinetics of NiO reduction in hydrogen has confirmed the results of earlier observations.[21]

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Investigation of the reduction mechanism of the supported nickel oxide catalysts is more complex than the same when unsupported nickel oxide is concerned. The reducibility of nickel oxide could be influenced by: *i)* nickel loading of the catalyst;[22] *ii)* nature of the catalyst support;[22,23] and *iii)* type of gaseous reductant (e.g. natural gas versus hydrogen)[23]. The degree of reduction of nickel alumina supported catalysts generally increases with both reduction temperature and nickel content increase. Samples prepared by impregnation generally achieve a higher degree of reduction than those prepared by precipitation. Increasing of calcination temperature preceding reduction, significantly decreases the reducibility of nickel on alumina catalyst.[24]

The subject of this study was to investigate the influence of alumina support origin on the reducibility of NiO-Al_2O_3 catalyst. The samples were prepared by impregnation of gibbsite, $Al(OH)_3$, boehmite $AlO(OH)$, γ-Al_2O_3 and α-Al_2O_3. Such systems allow the study of the reducibility of nickel based alumina catalysts, depending on the structure, texture, stability and presence of crystal water in catalyst supports. The influence of the catalyst component interaction (CCI) on the reducibility of the catalyst was studied as a function of different calcination temperature.

RESULTS AND DISCUSSION

1. Structure and texture of the unreduced samples

Out of four investigated catalyst samples two of them are prepared using alumina precursor as supports (gibbsite and boehmite). Both lose crystal water during the heat treatment, and suffer a series of polymorphous transformation. The two other catalyst samples are prepared using previously synthesized alumina supports (γ-Al_2O_3 and

α-Al_2O_3). They differ in thermal stability: γ-Al_2O_3 is subjected to polymorphous transformations during the heat treatment, while α-Al_2O_3 represents thermodynamically the most stable form of alumina. According to Linsen[25] gibbsite transformation depends on initial temperature of heat treatment: at slightly elevated temperature the following transformation occurs: gibbsite $\rightarrow$ χ (250°C) $\rightarrow$ κ (900°C) $\rightarrow$ α (1200°C), while when the heat treatment is initiated at lower temperature (180°C), gibbsite transforms to boehmite, following its transformation to γ-Al_2O_3 (at 450°C). In contrast, gelatinous boehmite (corresponds to pseudo boehmite) decomposes at about 300°C into γ-Al_2O_3. This thermodynamically unstable γ-Al_2O_3 suffers further transformations as follows: γ (900°C) $\rightarrow$ δ (1000°C) $\rightarrow$ (θ + α) (1200°C) $\rightarrow$ α-Al_2O_3.[25]

Results of DTA of the synthesized nickel hydroxide (or hydrated oxides, which is the precursor of nickel oxide), performed at heating rate of 10°C/min in air, indicate appearance of two endothermic peaks: at 105°C (release of surface water) and at 293°C (release of water from the hydroxide). It is worth noting that at heating rate of 5°C/min this second peak split in two peaks, the first and smaller one appearing at 245°C and the second one at 275°C. According to reference[26] the transformation of nickel hydroxide into nickel oxide in the well crystalline sample takes place via a two-phase mixture, whereas in a poorly ordered sample it follows a single phase mechanism. This indicates that the decomposition mechanism mainly depends on the preparation condition of the sample.

In Table 1 phase composition of nickel oxide and four thermally treated pure supports are presented. The data reveal that gibbsite, boehmite and γ-Al_2O_3 thermally treated in air results in the same products, however, the fractions of different crystalline form of aluminas differ from sample to sample. That is clear evidence on different alumina precursors having different transformation kinetics.

Table 1

Phase composition of the NiO and the four supports treated at different temperatures for 24 hours in air

Sample	400°C	900°C	1000°C
NiO precursor	NiO	NiO	NiO
Gibbsite	χ-Al_2O_3	γ-Al_2O_3*; θ-Al_2O_3	θ-Al_2O_3
Boehmite	γ-Al_2O_3	θ-Al_2O_3	θ-Al_2O_3; α-Al_2O_3*
γ-Al_2O_3	γ-Al_2O_3	γ-Al_2O_3*; θ-Al_2O_3	θ-Al_2O_3
α-Al_2O_3	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3

* traces

Table 2

Textural properties of calcined NiO and four supports before and after impregnation
(calcined at 350°C for 6 hours, following 1 hour at 400°C)

Sample	Pore radii, nm	BET surf., m^2/g	Sample	Pore radii, nm	BET surf., m^2/g
NiO	**45**	**55.8**		**45**	**55.8**
Gibbsite	400	15.9	NiO-Gibbsite	17, 185	171.2
Boehmite	2500	234.6	NiO-Boehmite	80	178.9
γ-Al$_2$O$_3$	350	227.6	NiO-γ-Al$_2$O$_3$	12, 120	215.8
α-Al$_2$O$_3$	20, 2500	5.8	NiO-α-Al$_2$O$_3$	14, 195	4.3

The phase composition of calcined catalyst samples (not shown) differ from the previous supports heated at the same temperature (400°C) only in additional presence of NiO and in appearance of nickel spinel phase, NiAl$_2$O$_4$, in the samples thermally treated at 900°C and 1000°C.

The textural properties of nickel oxide and four supports before and after impregnation and calcinations are listed in Table 2. Very high value of the main pore sizes and high specific surface areas of the supports provide a basis to presume, that in current conditions of pore size analysis, the smallest pores were not registered. Namely, mercury under applied range of pressures did not enter the pores, and that is the most important prerequisite for pore size determination with mercury penetration device. Impregnated and calcined samples, except the boehmite based sample, have bimodal pore structure. Large increases in specific surface area of the gibbsite based sample can be explained by thermal decomposition of this trihydroxide during its calcination, see Table 2.

2. The reduction of the calcined samples

According to gravimetric data after eight-hour reduction, in hydrogen flow (12 L / h) at 400°C, practically the entire amount of nickel is reduced, see Table 3. This means that in samples previously calcined at 900°C and 1000°C not only the free nickel oxide was reduced, but also the nickel bounded in the form of nickel spinel, NiAl$_2$O$_4$. The samples exposed to reducing atmosphere of hydrogen for two hours are only partially reduced. This is especially true for the samples that were previously calcined at higher temperatures. Differences in the degree of reduction were more pronounced in the samples calcined at 900°C and 1000°C. Influence of the origin of the catalyst support on the reducibility is the most highlighted in the samples that were exposed to hydrogen atmosphere for one hour. Since the main task of

this study was to determine the impact of the support origin on the reducibility of the prepared samples, further investigations were performed only on the samples that were reduced during 60 minutes.

Independently of calcination temperature the fraction of the reduced nickel is significantly lager in the sample which was prepared on α-Al$_2$O$_3$. The fact clearly indicates the weakest CCI in this sample. Accordingly, samples previously calcined at 900°C are reduced easier than those formerly treated at 1000°C. Samples prepared on gibbsite and boehmite were less reducible than those prepared on γ-Al$_2$O$_3$ and α-Al$_2$O$_3$. Crystal lattice water, which is present in these samples, promotes nickel spinel formation during the calcination step, and this one is less reducible relative to the free nickel oxide. Lower temperature of calcination prior to reduction significantly increases the reducibility of samples. The samples that were exposed to hydrogen atmosphere during 480 min were reduced completely, regardless of their origin and the temperature of prior calcination.

The percentage of reduced nickel was also determined by XRD. The area of the XRD signal from the plane of nickel (200) in NiO-α-Al$_2$O$_3$ sample, previously calcined at 400°C and then reduced in hydrogen flow for 60 minutes, arbitrarily was taken as 100% of nickel reduction. Other values of reduced nickel in different samples were calculated relatively to the area of this XRD signal. It can be concluded that reducibility data based on gravimetric (see Table 3) and XRD diffraction (see Table 4) methods coincide.

The results of the thermogravimetric and XRD analysis show that the free nickel oxide was completely reduced after thermal treatment of the NiO sample at 400 $^{\circ}$C, in hydrogen flow 12 L / h during 60 minutes. At similar conditions the reduction of supported nickel oxide samples is incomplete, reduction fraction differing, however, depending on applied calcination temperature. There is decrease on fraction of reduced NiO following higher calcination temperature regardless

on nature of applied support. The fraction of the reduced NiO, follows the subsequent order in calcination temperatures: 400 ^{o}C >900 ^{o}C >1000 ^{o}C, *i.e.* as lower is the temperature of calcination as higher is the fraction of reduced NiO. Similar behavior show the previously calcined (500°C, 600°C, and 700°C) NiO samples supported on κ-Al$_2$O$_3$.[27] Regardless of calcinations temperature the highest fraction of reduced nickel was obtained using α-Al$_2$O$_3$ and γ-Al$_2$O$_3$ supports, and the lowest in the samples that were prepared on boehmite and gibbsite. The percentage of reduced NiO follows the subsequent order in terms of used supports: α-Al$_2$O$_3$> γ-Al$_2$O$_3$ > boehmite ≥ gibbsite. Low reducibility of NiO supported on boehmite and gibbsite can be interpreted in terms of presence of crystalline water in these samples. Crystalline water in boehmite and gibbsite can slow the reduction of nickel oxide,[14] and in the same time can contribute to nickel spinel formation, NiAl$_2$O$_4$, compound which is difficult to reduce.[6,28]

Table 3

Percent of reduced NiO after 60, 120 and 480 min of heat treatment at 400°C in hydrogen flow 12 L/h, according to gravimetrical analysis. The samples prior to reduction were heat treated at 400°C, 900°C and 1000°C for 24 hours

Sample	Percent of reduced NiO after		
	480 min	120 min	60 min
NiO	100.0	100.0	100.0
G-400	100.0	84.1	75.7
B-400	100.0	95.1	87.8
γ-400	100.0	99.8	85.1
α-400	100.0	100.0	93.9
G-900	100.0	85.8	70.5
B-900	100.0	78.1	73.1
γ-900	100.0	89.6	83.2
α-900	100.0	94.1	87.5
G-1000	100.0	89.7	60.6
B-1000	100.0	71.6	42.6
γ-1000	100.0	82.2	66.1
α-1000	100.0	88.4	75.4

Table 4

Percent of reduced NiO after 60 min of heat treatment at 400°C in hydrogen flow 12 L/h, according to XRD analysis

Sample	Area of Ni(200) signal, in arbitrary units, at $2\theta = 51.8^{o}$	Percent of reduced NiO
NiO	80.0	100.0
G-400	57.0	71.3
B-400	55.0	68.7
γ-400	63.1	78.8
α-400	80.0	100.0
G-900	52.5	65.6
B-900	50.8	63.5
γ-900	59.4	74.2
α-900	75.0	93.7
G-1000	45.7	57.1
B-1000	20.0	25.0
γ-1000	54.4	67.9
α-1000	77.5	96.8

3. DTA and DSC analysis

The DTA curves obtained in hydrogen flow of the samples previously calcined at 400°C, are shown in Fig. 1. The thermal effects shown as minimums in Fig. 1 represent exothermic heat effects, due to the fact that the calibration of the used DTA device "Stanton" was opposite to the convention.

Fig. 1 – DTA curves obtained in hydrogen flow of the samples previously calcined samples at 400°C for 24 hours.

The temperature of the reduction of free nickel oxide samples by the applied hydrogen flow is 240°C. This temperature is lower than the reduction temperatures of supported samples. The start temperature of the reduction of gibbsite (259°C) and α-Al$_2$O$_3$ (284°C) is lower than the start temperature of reduction of boehmite (301°C) and γ-Al$_2$O$_3$ (307°C) which could indicate the presence of the free nickel oxide in these samples. These samples have low specific surface area (see Table 2), and a significant amount of nickel oxide was free, without major interaction with catalyst support. During the impregnation of the active component over boehmite and γ-Al$_2$O$_3$, both having large specific surface area, an easy and quick absorption was observed. In these systems nickel ions were distributed not only on the surface but also in catalyst bulk. Similar results were obtained with this samples reduced in carbon monoxide flow. The reducibility of the samples in carbon monoxide flow can be defined in sequence:

free NiO>NiO-α-Al$_2$O$_3$>NiO-gibbsite>NiO-γ-Al$_2$O$_3$>NiO-boehmite. Lower reduction temperature of the free nickel oxide (205°C) than the reduction temperature of α-alumina supported nickel oxide (263.7°C) testifies on achieved CCI even in the catalyst prepared on a very stable support, as α-Al$_2$O$_3$, see Fig. 2.

Both DTA (in hydrogen flow) and DSC analysis (in carbon monoxide flow), offered no evidence on reduction of the samples previously calcined at 900°C and 1000°C. Only exception was the sample prepared on α-Al$_2$O$_3$ performing an elevated reduction in carbon monoxide (from 263.7°C onto 294.5°C in sample previously calcined at 900°C, and onto 295.0°C in sample previously calcined at 1000°C). In samples prepared on gibbsite, boehmite and γ-Al$_2$O$_3$, calcined at 900°C and 1000°C, the formed stable nickel spinel, NiAl$_2$O$_4$, could not be reduced in conditions of thermal analysis.

Fig. 2 – DSC curves of the samples in carbon monoxide flow, previously calcined samples at 400°C for 24 hours.

EXPERIMENTAL

Alumina (γ-Al$_2$O$_3$ and α-Al$_2$O$_3$) or their precursors, (gibbsite and boehmite) were synthesized in our Laboratory according to Linsen.[25] The active component of the catalyst was introduced by impregnation of the support (fraction 100-125 μm), or their precursor (gibbsite and boehmite), by metal salt Ni(NO$_3$)$_2$·6H$_2$O, diluted in distilled water. The molar ratio of dry metal oxides was NiO:Al$_2$O$_3$ = 1:1 (42.28 % NiO *i.e.* 33.22 % Ni). During the impregnation boehmite and γ-Al$_2$O$_3$ absorb the nickel nitrate solution easily and quickly, which is not the case with gibbsite and α-Al$_2$O$_3$. Therefore, in the last two cases the impregnation was carried out in several stages (interrupted by drying between two impregnation steps).

The impregnated sample precursors were dried at 105°C overnight, calcined at 350°C for 6 hours, following additional 1 hour at 400°C. After this treatment the release of the yellow nitric oxides was not noticeable. Further thermal treatment of the previous systems was carried out in air at 400°C, 900°C and 1000°C during 24 hours. The reduction of the calcined

samples was carried out in a quartz tube furnace, in hydrogen flow (12 L/h), at 400 °C for 60, 120 and 480 minutes. The reduced samples were stored in appropriate test tubes under nitrogen atmosphere.

The nickel oxide precursor was prepared by coprecipitation of nickel nitrate hexahydrate solution with 20 % NaOH at pH= 9.5 and ambient temperature. The obtained precipitate was matured for 24 hours, subsequently vacuum filtered and washed until free of nitrate ions. The NiO precursor was dried at 105°C overnight, calcined at 350°C for 6 hours, and after that at 400°C for 1 hour. Further thermal treatment and reduction procedure of the obtained free NiO sample were equivalent with the impregnated samples.

Different methods were applied for characterization of the samples. Thermal investigation of the unreduced calcined samples were carried out in a DSC equipment, using Du Pont DSC 910 cell, in temperature interval between ambient temperature and 400°C in carbon monoxide flow (25 mL/min) at heating rate 10°C/min. The same investigation, in similar conditions in hydrogen flow, was carried out in DTA

equipment, produced by Stanton-Redcroft, Differential Thermal Analyzer, Model No. DTA 673 (ambient to 1000°C). The application of this equipment was necessary in a precautionary reason, to avoid a possible explosion, which could be happen in case of the formation an explosive gas mixture of hydrogen and air, which could be easily destroy the delicate DSC cell. Crystalline phase composition was measured by XRD using a Philips PW 1050 with CuK$_\alpha$ characteristic line. During the XRD studies of the reduced samples the samples were protected with amorphous transparent tape. BET surface area, S, was measured by Low Temperature Nitrogen Adsorption (LTNA) using a Sorptometer 212D Perkin-Elmer-Shell. The most frequent pore diameters by mercury penetration porosimeter (Carlo Erba, Model 1520) were determined. The pressure 1.10^2-$1.5.10^5$ kPa was applied, which correspond to the radii of pores between 5-7500 nm.

CONCLUSIONS

The samples prepared on gibbsite and boehmite are less reducible than the samples prepared on γ-Al$_2$O$_3$ and α-Al$_2$O$_3$. Crystal lattice water in these samples interferes with the reduction of nickel oxide, and promotes nickel spinel formation, NiAl$_2$O$_4$ which is less reducible than the free nickel oxide. The fraction of reduced NiO in prepared samples follows order: α-Al$_2$O$_3$> γ-Al$_2$O$_3$ > boehmite ≥ gibbsite in terms of used supports. Lower temperature of calcination prior to reduction significantly increases the reducibility of samples. Regardless of calcination temperature the percentage of the reduced nickel is significantly lager in the sample which was prepared on α-Al$_2$O$_3$. This fact clearly indicates that in this sample the degree of CCI is the weakest. Lower reduction temperature of the free nickel oxide (205°C) than the reduction temperature of α-alumina supported nickel oxide catalyst (263.7°C) testifies on achieved CCI even in the catalyst prepared on the most stable α-alumina support. Reducibility data obtained by gravimetric method and by method of XRD show very similar tendency.

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