Activation of Ni/Al_2O_3 catalysts through modification of the Al_2O_3 support

Lars Peter Lindfors[1]
Neste Oy, Technology Centre, PO Box 310, FIN-06101 Borgå, Finland

and

Stefan Smeds
Laboratory of Industrial Chemistry, Åbo Akademi, FIN-20500 Åbo, Finland

Received 18 March 1994; accepted 8 July 1994

The effect of alumina pretreatment on the performance of alumina supported nickel catalysts was demonstrated in gas phase hydrogenation of toluene to methylcyclohexane. The state of the alumina was changed from pure γ to pure θ phase through various heat treatments in air. The catalysts were prepared from vapor phase by saturating the accessible binding sites on the pretreated alumina with the nickel precursor. The highest number of active sites for hydrogenation was observed for catalysts prepared on alumina having an incomplete phase transition and a θ/γ alumina phase ratio between 0.5 and 10. Results from temperature programmed desorption (TPD) studies revealed that a maximum in weakly chemisorbed hydrogen as well as in total amount of desorbed hydrogen was found for the same catalysts. By hydrogen chemisorption studies the total hydrogen uptake was found to correlate with the observed hydrogenation maximum. It is suggested that both the chemical and physical properties of the alumina influence the activity. An optimal metal–support interaction and structural defects on the alumina due to the phase transition can explain the observed maximum in the number of active sites and in hydrogen uptake.

Keywords: Ni/Al_2O_3 catalysts; γ- and θ-alumina; hydrogenation activity/TOF; TPD of hydrogen; H_2 chemisorption

1. Introduction

In industrial catalytic processes such as hydrogenation of hydrocarbons, hydrocracking, steam reforming and methanation, catalysts containing active components deposited on metal oxide supports are extensively used. In the development of such catalysts, the selection and modification of the oxidic support is very impor-

---

[1] To whom correspondence should be addressed.

tant. It has been known within the catalysis society for quite some time that the catalytic activity cannot be explained solely by the active component. Metal–support interactions, such as the strong metal–support interaction (SMSI), have been widely discussed [1].

Due to many reasons the support plays a primary role in the performance of a catalyst: the interaction between active species and supports can be widely varied thus influencing e.g. the dispersion, reducibility, activity and resistance toward agglomeration of active species during both catalyst preparation and reaction. The interaction can be strongly affected by varying the pretreatment of the support, influencing its acidity and ability to form bonds with precursors of the active components, as well as the structure and physical properties. A selection of proper preparation conditions results in catalysts having well dispersed active species giving a high turnover frequency.

Narayanan and Sreekanth studied the influence of various metal oxide supports on the hydrogenation activity of nickel [2]. Their conclusion was that the reducibility and dispersion of nickel depend on the structural and textural properties of the support. Narayanan and Uma studied the effect of the calcination temperature of alumina on the dispersion, reduction and hydrogenation of alumina supported nickel catalysts [3]. They found that a calcination of the γ-alumina between 600 and 800°C, before loading the nickel, reduced the interaction between nickel species and alumina. As a consequence, the area of metal available for hydrogen adsorption and hydrogenation increased. Hu et al. [4] investigated how the reducibility of alumina supported nickel catalysts was affected by thermal treatment. They demonstrated that both the preparation and pretreatment conditions have a strong effect on the reducibility of nickel and on the ability of the catalysts to chemisorb reactants.

Chen et al. studied the effect of different alumina supports on the properties of supported nickel catalysts [5]. They concluded that the metal dispersion and the maximum temperature for reduction significantly depend on the source of the alumina support material. Guo et al. studied the activation of a silica supported nickel catalyst through surface modification of the support [6]. They found that the calcination of the support influenced the deposition of nickel precursors; a higher degree of precursor dispersion was achieved on calcined, dehydrated silica supports, resulting in an increase in nickel dispersion after reduction. In a patent filed by Unilever NV, novel nickel catalysts supported on transition alumina, were presented [7]. A commercially available γ-alumina was calcined at 1050°C, yielding predominantly θ-alumina. Nickel catalysts prepared on the modified alumina were found to have a high activity, possibly due to a very fine dispersion of the active phase and a decreased formation of nickel aluminate.

Jacobs et al. studied the effect of alumina pretreatment on the activity and surface composition of alumina supported nickel catalyst [8]. A correlation between the hydrogenation activity and the θ/γ alumina phase ratio was observed; with a ratio increasing from 0 to 0.3, both the activity and the amount of nickel on the surface of the catalyst increased.

The purpose of this work was to study the effect of Al_2O_3 pretreatment, resulting in alumina ranging from pure γ over various θ/γ phase ratios to pure θ phase, on the activity of Ni/Al_2O_3 catalysts. The test reaction was gas phase hydrogenation of toluene to methylcyclohexane, carried out in a fixed bed reactor working at differential conditions. XRD, XRF, H_2 chemisorption, temperature programmed desorption (TPD) and N_2 adsorption/condensation were used in the characterization of the alumina support and the catalysts.

2. Experimental

The alumina used as support (AKZO 000-1.5E) was crushed and sieved to a size of 0.15–0.35 mm. Different samples were heated in air at 200, 800, 875, 925 and 950°C at a heating rate of 120°C/h, whereafter they were kept at the maximum temperature for 6 h. Four Ni/Al_2O_3 catalysts containing $\sim$ 10 wt% Ni were prepared on the alumina pretreated at the respective temperatures (Ni800–Ni950) using atomic layer epitaxy (ALE), a novel vapor phase technique discussed elsewhere [9–12]. The catalysts were prepared in their oxidic form in sequences of reaction cycles consisting of chemisorbing nickel acetylacetonate to saturation of the accessible binding sites followed by removal of ligand residues with air treatment and rinsing with nitrogen [11].

The reproducibility in catalyst preparation was determined from five samples for the catalyst processing consisting of two and four reaction cycles. The nickel content was determined to be 5.8 ± 0.7 and 10.2 ± 1.1 wt%, respectively and nickel was shown to be evenly distributed in all catalysts as measured by X-ray mapping (SEM-EDS). H_2 chemisorption revealed that nickel was highly dispersed in all catalysts. In other words, no significant differences could be observed between catalysts prepared using the same processing parameters.

The pure alumina and the prepared catalysts were characterized using various techniques. The specific surface area, pore volume and average pore radius were determined from nitrogen adsorption and condensation using a Micromeritics ASAP 2400 instrument. The alumina phases, along with possible crystalline Ni-species, were analyzed by XRD using a Siemens Diffrac 500/X-ray source Cu K_α. The alumina phase ratios were determined semi-quantitatively. The reference samples consisted of various mixtures of the alumina treated at 200°C (pure γ) and at 950°C (pure θ). The bulk nickel content was studied by means of XRF using a Siemens SRS 303 Fluorescens spectrometer/X-ray source Rh. The hydrogen uptake and Ni-dispersion were studied using H_2-chemisorption at 25°C (Sorptomatic 1900, Carlo Erba Instruments), whereas the number and strength of the hydrogen binding sites on the catalysts were determined using TPD of hydrogen (QTMD, Carlo Erba Instruments).

3. Experimental procedure

3.1. CATALYST TESTING

The studied catalysts contained comparable amounts of nickel and their performance in toluene hydrogenation was evaluated in a fixed bed reactor in an experimental set-up described elsewhere [13]. The catalysts were activated in flowing hydrogen in situ at 500°C for 4 h and tested at differential conditions, at conversion levels below 5%.

The reactor was operated at atmospheric pressure and 175°C at conditions where thermodynamics and mass transfer did not limit the reaction. The experimental data was obtained after 30 min, i.e. the time required for achieving steady-state conditions, confirmed by studying the exit gas stream at various reaction times (from 15 min to 60 min).

The product flow was analyzed on-line using a gas chromatograph (Hewlett-Packard 5890 A) equipped with a 40 m long capillary column (Silica / J&W Scientific, Inc.) and an FI-detector. Methylcyclohexane along with traces of methylcyclohexenes were the only products detected. The reproducibility of the measurements was checked by making duplicate experiments for each catalyst. The average deviation in rate data was typically 5% or less.

3.2. HYDROGEN CHEMISORPTION

The catalysts were reduced at 500°C in flowing hydrogen (200 ml/min) during 2 h. Prior to the chemisorption experiments the reduced catalyst was degassed in a sample burette (Rotaflow) at 500°C. After 1 h of degassing the sample burette was cooled down to the adsorption temperature of 25°C (200°C/h). The hydrogen adsorption isotherms were obtained by measuring the equilibrium pressure as a function of the amount of H_2 introduced.

3.3. TPD OF HYDROGEN

The TPD experiments were performed in vacuo in the same burette that was used in the chemisorption experiments. After reduction, the sample burette was cooled to room temperature (200°C/min) under continuous hydrogen flow (200 ml/min). The sample was exposed to the hydrogen flow for 1 h at room temperature, after which the hydrogen chemisorption was considered to be complete. The burette was placed in a heater coupled to a quadrupole mass spectrometer (QTMD, Carlo Erba Instruments) and a vacuum pump (Elettrorava Turbo Controller). The sample was evacuated to a pressure of 10^{-5} mbar for 45 min in order to remove physisorbed hydrogen. Six mass numbers were monitored simultaneously during the TPD experiment, the heating rate being 15°C/min. The main desorption product was always hydrogen (H_2). Traces of water were also detected.

4. Results and discussion

In table 1 the characteristics of the heat treated aluminas are shown. The specific surface area, s, decreases with increasing calcination temperature, whereas the average pore diameter, d_p, increases. The pore volume, v_p, is not strongly influenced in contrast to the θ/γ phase ratio, measured via XRD, which naturally increases strongly with increasing calcination temperature.

In table 2 the characteristics of the catalysts are presented. When tables 1 and 2 are compared, it can be seen that the decrease in surface area and average pore diameter due to catalyst preparation are ~ 10% and ~ 5%, respectively. In other words, the influence of nickel deposition does not significantly influence the physical properties, indicating that nickel is not present in larger clusters. This assumption is supported by the XRD results shown in table 2; the catalysts were found to be XRD-amorphous with respect to nickel species, indicating a high dispersion and an average nickel particle size of less than 30 Å.

Fig. 1 illustrates TPD of hydrogen for the catalysts Ni800–Ni950, prepared by using alumina pretreated at 800–950°C. When fig. 1 is compared with table 3, it can be seen that the amount of desorbed hydrogen at temperatures corresponding to actual reaction conditions, i.e. at $T < 600$ K, is highest for the catalysts showing the highest overall activity (table 3).

The pretreatment of the alumina has an evident effect on the activity of the catalysts, as a correlation between the hydrogenation activity, hydrogen uptake and θ/γ-alumina phase ratio was observed. Table 3 shows that the amount of desorbed hydrogen reaches its maximum and that the nickel particle size, calculated based on hydrogen chemisorption, is smallest for the intermediate aluminas, having θ/γ phase ratios between 0.5 and 10. The TPD area corresponds to the area under the TPD curves shown in fig. 1, numerically integrated between ambient temperature and 600 K. In other words, the larger the area, the higher the amount of adsorbed hydrogen availabe during hydrogenation. The calculated particle size (22–28 Å, using a shape factor of 4, corresponding to cylindrical particles) is in good agreement with the lack of crystalline Ni-species, as analyzed via XRD. The total hydrogen uptake at 100 mbar and 25°C, as determined by H_2-chemisorption and the correlating Ni-particle size are in good agreement with the TPD and activity results for all samples.

Table 1
Characteristics of alumina heat treated at 200–950°C

Alumina	s (m^2/g)	v_p (cm^3/g)	d_p (Å)	θ/γ (XRD)
Al200	190	0.49	100	<0.05
Al800	150	0.47	125	~ 0.3
Al875	140	0.47	135	~ 0.5
Al925	125	0.46	150	~ 10
Al950	120	0.45	150	>20

Table 2
Characteristics of the prepared Ni/Al_2O_3 catalysts

Catalyst	Ni (wt%) XRF	s (m^2/g)	v_p (cm^3/g)	d_p (Å)	Ni-crystals (Å) XRD
Ni800	10.1	135	0.39	115	amorphous
Ni875	9.5	130	0.41	125	amorphous
Ni925	9.3	110	0.39	145	amorphous
Ni950	8.6	110	0.40	145	amorphous

Fig. 2 shows the turnover frequency for toluene per exposed nickel atom and hour along with the amount of desorbed hydrogen below 600 K and the total hydrogen uptake in H_2 chemisorption, as a function of alumina phase ratios for the Ni/Al_2O_3 catalysts (table 3).

It seems that the number of accessible Ni-atoms for hydrogenation increases due to the phase transition of alumina. As the phase transition occurs, the strength and number of binding sites changes. Probably the interaction between active Ni-species and support reaches an optimum at θ/γ ratios between 0.5 and 10. Another contribution to the rate maximum can be due to favorable structural properties, a result of defects on the alumina surface as the phase transition occurs. In a previous study, the activity of similar Ni/Al_2O_3 catalysts prepared via ALE was found to increase as the ratio of θ/γ-alumina increased from 0 to ~ 0.3 [8]. The enhanced

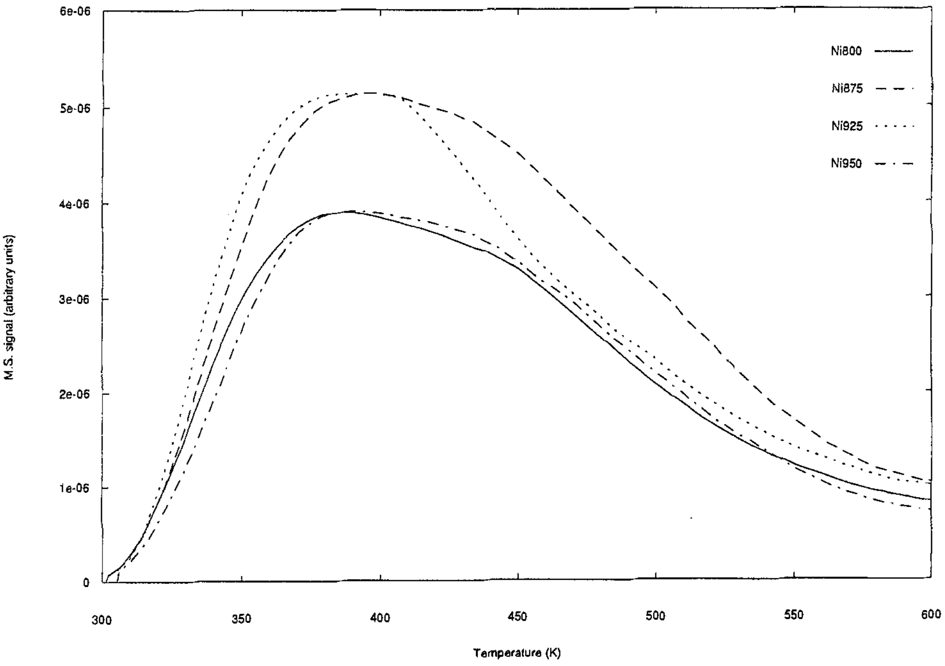

Fig. 1. TPD of H_2 for catalysts Ni800–Ni950.

Table 3
Catalysts characteristics

Catalyst	H_2 uptake[a] (cm^3/g_{Ni})	Ni-particle size[b] (Å)	TPD area (a.u.)	Activity ($g_{MECH}/g_{Ni}\,h$)	TOF[c]
Ni800	45	28.5	360	140	358
Ni875	59	22.0	480	185	359
Ni925	55	23.5	435	165	344
Ni950	51	25.5	350	115	259

[a] Total H_2-chemisorption at 25°C and 100 Torr.

[b] Ni-particle size calculated according to $d_p = 4/\rho_{Ni}/A_{Ni}$.

[c] Turnover frequency of toluene to methylcyclohexane per exposed nickel atom and hour.

activity correlated with an increase in nickel atoms observed on the catalyst surface by means of low-energy ion scattering (LEIS), probing the outermost atomic layer.

As the results of the separate studies are in good agreement, we propose that the observed maximum in hydrogenation activity and hydrogen uptake is due to favorable strength and number of the binding sites on alumina. This results in well dispersed reducible nickel species, which are able to interact with reactants during reaction. For catalysts prepared on pure γ-alumina the distribution of the strength of the binding sites is broader. Some of the bonds are so strong that reducibility and activity of the particular Ni-species is affected. On the other hand, when pure θ-alumina is used as support, the number of binding sites decreases, thus increasing the probability of nickel growth in clusters, decreasing the utilization of nickel. As can be seen from fig. 2 and table 3, the turnover frequency remains quite constant during the heat treatment up to 925°C, i.e. going from a θ/γ alumina phase ratio of

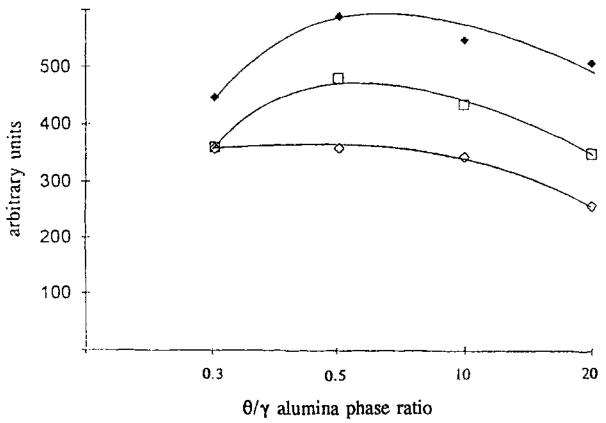

Fig. 2. TOF for toluene per exposed nickel atom and hour (◇), TPD areas of H_2 desorbed below 600 K (a.u.) (□) and H_2 uptake ($cm^2/g_{Ni} \times 10$) (◆) for catalysts Ni800, Ni875, Ni925 and Ni950, versus the θ/γ phase ratio.

0.3 to 10. However, both the ability of the catalyst to chemisorb hydrogen and the overall hydrogenation activity increase up to a θ/γ ratio between 0.5 and 10, whereafter they decrease. These observations indicate that the average turnover frequency, i.e. the site activity, is practically constant in the alumina phase ratio interval from 0.3 to 10. However, the number of active sites reaches a maximum as the disorder on the alumina surface is "optimal".

5. Conclusions

A maximum in catalyst activity was observed for Ni/Al_2O_3 catalysts prepared on alumina having an incomplete phase transition corresponding to θ/γ phase ratios between 0.5 and 10. The observed rate maximum can be due to the existence of an optimum in number and strength of binding sites on the alumina. The bonding properties are crucial for the interaction between nickel and alumina, thus influencing the size and growth of nickel clusters (during preparation and reaction) as well as the reducibility and the number of active sites. The turnover frequency was found to remain quite constant, whereas the number of nickel species accessible to reactants was observed to increase, with increasing disorder on the alumina. It seems plausible that the transition defects, a result of the phase transition, create a larger number of favorable bonding sites for nickel on alumina. This leads to a higher number of active nickel species, as the increasing number of active nickel corresponds to the observed activity maximum. However, the average site activity might not change due to the phase transition.

Acknowledgement

Our sincere thanks go to Ms. U. Lehtovirta, Dr. M. Lindblad, Mr. S. Hornytzkyj and Dr. J. Vilhunen for their contribution in the preparation and characterization of the catalysts.

References

[1] M. Boudart and G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions* (Princeton Univ. Press, Princeton, 1984) pp. 201–211.
[2] S. Narayanan and G. Sreekanth, J. Chem. Soc. Faraday Trans. I 85 (1989) 3785.
[3] S. Narayanan and K. Uma, J. Chem. Soc. Faraday Trans I 81 (1985) 2733.
[4] J. Hu and J.A. Schwarz, Appl. Catal. 51 (1989) 223.
[5] S.L. Chen, H.L. Zhang, J. Hu, C. Contescu and J.A. Schwarz, Appl. Catal 73 (1991) 289.
[6] S.L. Guo, M. Arai and Y. Nishiyama, Appl. Catal. 65 (1990) 31.
[7] W.P. van Beek, W. Den Hoed, W.A. van Leeuwen, E.K. Poels and C. Visser, Unilever NV, EP 0 290 100 B1 (1990).

[8] J.-P. Jacobs, L.P. Lindfors, J.G.H. Reintjes, O. Jylhä and H.H. Brongersma, Catal. Lett. 25 (1994) 315.
[9] T. Suntola, Mater. Sci. Rep. 4 (1989) 261.
[10] M. Lindblad and L.P. Lindfors, *Proc. 10th Int. Congr. on Catalysis*, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadémiai Kiadó, Budapest, 1993) p. 1763.
[11] M. Lindblad, L.P. Lindfors and T. Suntola, Catal. Lett. 27 (1994) 323.
[12] E.-L. Lakomaa, Appl. Surf. Sci. 75 (1994) 185.
[13] L.P. Lindfors, T. Salmi and S. Smeds, Chem. Eng. Sci. 48 (1993) 3813.