Catalysis Letters 27 (1994) 323–336

Preparation of Ni/Al_2O_3 catalysts from vapor phase by atomic layer epitaxy

Marina Lindblad [a], Lars Peter Lindfors [b] and Tuomo Suntola [a]

[a] *Microchemistry Ltd., PO Box 45, SF-02151 Espoo, Finland*
[b] *Neste Oy, Technology Centre, PO Box 310, SF-06101 Porvoo, Finland*

Received 29 October 1993; accepted 31 May 1994

Ni/Al_2O_3 catalysts were prepared by saturating gas–solid reactions as an atomic layer epitaxy (ALE) process. Vaporized $Ni(acac)_2$ was chemisorbed on a porous alumina support, and the produced surface complex was then air treated to remove the ligand residues. The nickel content could be precisely controlled by repeating this reactor cycle. On alumina preheated at 800°C, the nickel content varied from 3 to 21 wt%, when the number of reaction cycles was increased from one to ten. The performance of the Ni-catalysts was evaluated in the gas-phase hydrogenation of toluene. The preheat temperature of alumina influenced the activity of the catalyst, and a maximum in the activity was observed for catalysts prepared from alumina preheated at 875°C. Catalysts prepared by four reaction cycles, containing about 10 wt% nickel, gave the highest utilization of nickel.

Keywords: Ni/Al_2O_3 catalysts; surface saturation; chemisorption; ALE; hydrogenation of toluene

1. Introduction

Typically, heterogeneous catalysts consist of active metal components supported on porous high surface area materials. Various techniques are available for the deposition of the active components. The general development of these techniques is toward more selective catalysts with well-defined active species. The atomic layer epitaxy (ALE) technique [1] is a novel approach in this direction.

The ALE technique was originally developed for the production of thin film materials for electroluminescent applications [2]. Recently, ALE has also been applied to the modification of porous materials, in the preparation of heterogeneous catalysts [3–5]. A better control of the build-up of surface structures is achieved by the sequential introduction of the active components (and other surface-modifying agents) in saturating gas–solid reactions. Uncontrolled deposition through condensation of the reactants of their decomposition products is prevented by the choice of reaction temperature. The prediction of a specific surface structure is difficult because of the heterogeneity of the surface structure of the support material. Due to the utilization of surface saturation by chemisorption, ALE exhibits a self-controlling feature, which allows a homogeneous distribution of the active species throughout the porous support. In the present work ALE was adopted in the preparation of Ni/Al_2O_3 catalysts from the vapor phase.

Conventionally, Ni-catalysts are prepared from solution by impregnation or coprecipitation. Nickel deposited from the vapor phase both on alumina and active carbon has been reported by Uemura et al. [6] and Omata et al. [7], respectively. Uemura vaporized $NiCl_2$ at 800°C and allowed it to interact with alumina at 740–800°C. $NiCl_2$ condensates on alumina and the nickel content depends on the reaction time. Omata prepared the vaporous reactant, $Ni(CO)_4$, in situ at 250°C and 11 atm, from nickel oxide and carbon monoxide. After the deposition of $Ni(CO)_4$ on active carbon at 50 or 180°C, the nickel surface species were decomposed at 250°C in nitrogen. In both cases the reported particle sizes of nickel were of the order of 500 nm.

The Ni/Al_2O_3 catalysts were prepared by growing oxidized nickel species on alumina by sequential reactions with vaporized $Ni(acac)_2$ and air. Unlike conventional preparation methods, in ALE, the nickel loading obtained during each $Ni(acac)_2$ sequence is controlled by the surface itself, not by the dose of $Ni(acac)_2$. In this study the distribution of nickel on alumina and the interaction between $Ni(acac)_2$ and alumina were evaluated. The activities of these catalysts were tested in the gas-phase hydrogenation of toluene. The highest ratio of active nickel to the total amount of nickel as a function of nickel content was sought. Preheating of alumina alters the chemical nature of the surface end, hence, the interaction between the metal compound and alumina. Thus, the preheat temperature of alumina was taken as a parameter in the optimization of the activity of the catalyst.

2. Experimental

2.1. PREPARATION OF Ni/Al_2O_3

The support material used was γ-Al_2O_3 (AKZO Alumina 000-1.5E) crushed and sieved to a particle size of 0.15–0.35 mm. The specific surface area (SA), the pore volume (PV) and the average pore diameter (d_p) of alumina preheated at temperatures between 200 and 950°C are given in table 1. The preheating regulates the type and number of adsorption sites on alumina [8]. When the preheat temperature exceeds 600°C, alumina is transformed from a pure γ-phase to a mixture of γ- and θ-phases, altering the chemical nature of alumina. The θ/γ-ratios are also shown in table 1. The preheat temperature should be greater than or equal to the reaction temperature to avoid the release of water from the support during the reaction steps. Nickel acetylacetonate, $Ni(acac)_2$ (Merck, >98%), was used as reactant without further purification.

Table 1
Characteristics of alumina preheated at various temperatures

Sample	Preheating		SA (m^2/g)	PV (cm^3)	d_p (Å)	θ/γ-ratio
	(°C)	(h)				
Al-200	200	6–16	190	0.50	100	<0.05
Al-600	600	6	180	0.50	110	<0.05
Al-800/1	800	1	155	0.50	120	~0.25
Al-800/6	800	6	150	0.45	120	~0.30
Al-875	875	6	140	0.45	130	~0.50
Al-925	925	1	125	0.45	150	~10
Al-950	950	6	120	0.45	150	>20

The catalysts were prepared in a modified MC 120 flow-type reactor (Microchemistry Ltd.) (fig. 1). The gaseous reactants were passed through a stationary bed of alumina. The reactions were carried out at a pressure of 3–10 kPa in nitrogen atmosphere.

In the preparation of Ni/Al_2O_3 catalysts by ALE, alumina was preheated followed by sequential reactions with $Ni(acac)_2$ and ambient air (fig. 2). The preheating was carried out in a muffle furnace under atmospheric pressure at 200–950°C for 6–16 h and, in addition, in the ALE reactor at 200–450°C for 3 h to remove water adsorbed during the transfer. The solid $Ni(acac)_2$ reactant was vaporized at 200°C. The temperature and length of the $Ni(acac)_2$ sequence was 200°C and 3–4 h, respectively. The air sequence was initiated at 200°C and continued at 400°C for a total of 4–5 h to remove the ligand residues from the samples. This procedure reduced the carbon content below detection limit (<0.1 wt%). Each reaction sequence was completed with a nitrogen purge at the reaction temperature

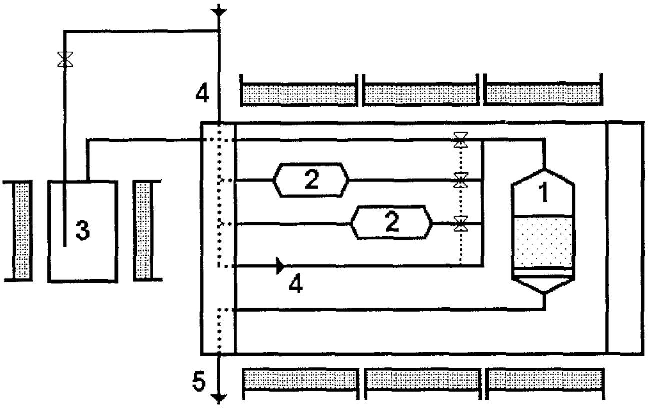

Fig. 1. Schematic picture of the ALE reactor (1 = reaction chamber, 2 = solid reactant, 3 = liquid/gas reactant, 4 = carrier gas, and 5 = to pump).

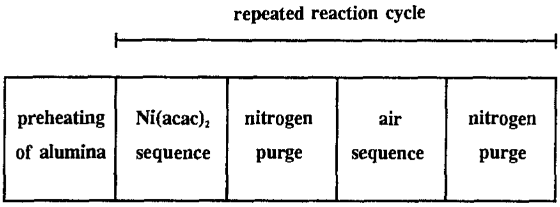

Fig. 2. ALE procedure in the preparation of Ni/Al_2O_3-catalysts by repeated reaction cycles of Ni(acac)$_2$ and air sequences.

concerned. Before the next reaction cycle, the reaction temperature was stabilized at 200°C. The nickel content was varied by increasing the number of reaction cycles from one to ten.

For a reactant to be beneficial in an ALE process, it must have sufficient volatility and stability at the reaction temperature. The vaporization (200°C) and decomposition ($\sim$ 230°C) temperatures of Ni(acac)$_2$ restricted the reaction temperature to about 200°C.

2.2. ANALYTICAL METHODS

Nickel was determined by wavelength dispersive X-ray fluorescence (XRF) using a Siemens SRS 303 Fluorescens spectrometer (X-ray source Rh). Carbon was determined with a LECO CR12 carbon analyzer. The crystallite size of the nickel species and the θ/γ-phase ratio of alumina were studied by X-ray diffraction (XRD) using a Siemens Diffrac 500 diffractometer (with a Cu anode X-ray tube). The penetration of nickel into the pores of the particles was investigated by SEM using a Jeol JSM 840A scanning electron microscope fitted with a PGT IMIX III energy dispersive X-ray and image analyzer. Cleaved surfaces were exposed by cutting catalyst particles embedded in epoxy resin with a diamond knife. The specific surface area (BET), pore volume and average pore diameter were determined by means of nitrogen adsorption and condensation using a Micromeritics Rapid Surface Area Analyzer 2200. The binding of Ni(acac)$_2$ to alumina was studied with a Fourier transform infrared spectrometer (FTIR) equipped with a diffuse reflectance accessory (Galaxy Series 6020). The accessory was installed in a glove-box, into which the samples were inertly transferred. The spectra were presented in a diffuse transmittance format.

2.3. ACTIVITY TESTS (TOLUENE HYDROGENATION)

Prior to testing, the catalysts were reduced in situ with flowing hydrogen (0.5 mol/h) at 1 atm and 500°C. The toluene hydrogenation experiments were carried out at 1 atm and 175°C in a laboratory scale fixed bed tubular reactor. With the molar ratio of hydrogen and toluene equal to three, the reaction conditions corresponded to a thermodynamical hydrogenation conversion equilibrium above 95%. The activities of the catalysts were compared at a constant conversion level of 20%, achieved by using 0.15–0.2 g of Ni-catalyst. The catalyst was mixed with 6 g of inert diluent, SiC, and placed in the middle of the reactor with a thermocouple. The products were analyzed on-line using a gas chromatograph (Hewlett-Packard 5890 A) equipped with a capillary column (40 m, Silica, J&W Scientific) and a flame ionization detector. Methylcyclohexane (MECH) and unreacted toluene (T) along with traces of methylcyclohexene were detected in the product stream.

3. Results and discussion

3.1. ALE IN THE PREPARATION OF Ni/Al_2O_3

The active component, $Ni(acac)_2$, was chemisorbed from the vapor phase onto the support. In each ALE sequence, the surface reaction is allowed to proceed to saturation. Surface saturation is ensured by using an excess of reactant. The metal loading is then determined by the ability of the surface to chemisorb the reactant, not by the dosing of the reactant. The effect of the dose of $Ni(acac)_2$ on the nickel content is shown in fig. 3. Saturation of bonding sites proceeds from the top of the alumina bed toward the bottom with increasing dose, i.e. in the direction of the reactant flow (see fig. 1). A dose exceeding that needed for surface saturation will

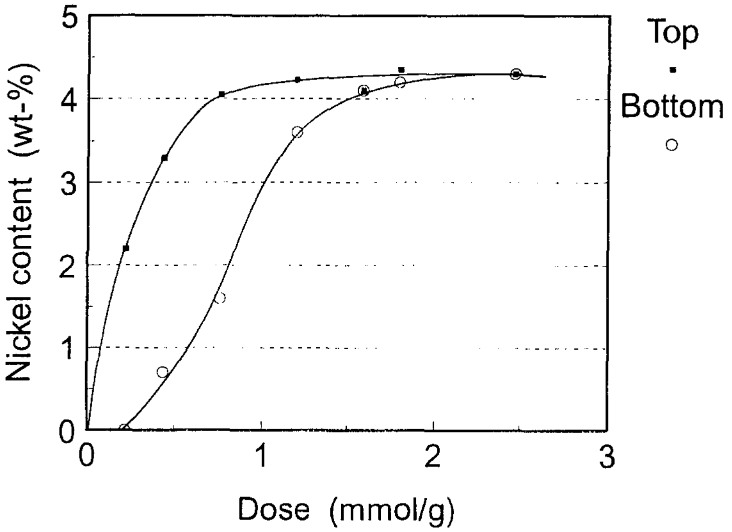

Fig. 3. Nickel content (wt%) in samples taken from the top and the bottom part of the alumina bed as a function of reactant dose (mmol/g). Ni/Al_2O_3 samples were prepared by a single $Ni(acac)_2$ sequence on alumina preheated at 200°C.

not alter the nickel content. The excess of reactants remains in the vapor phase and is removed from the reactor in the nitrogen flow.

The saturation level obtained in a reaction sequence depends on the number of the bonding sites, the size and chemical form of the reactant molecule and the reaction temperature [4]. The reproducibility of ALE in obtaining a desired saturation level in the preparation of Ni/Al_2O_3 catalysts by a single Ni(acac)$_2$ sequence (on 200°C alumina) was determined from five samples. The mean value and the standard deviation of the nickel content was 4.4 ± 0.4 wt%, which is within the analytical accuracy.

Various means can be used for the regulation of the metal content in catalysts prepared from a single reaction sequence of the active component [4,5,9]. To further increase the metal content, cycles of reactions can be carried out where sequences of the active component and ligand-removing agents are alternated. This latter procedure was adopted for the preparation of Ni-catalysts with different nickel contents. An air sequence was used to remove the ligand residues and to oxidize the nickel species. The sequential introduction of the different reactants prevents gas phase reactions between the reactants and condensation of reaction products. In fig. 4 the obtained nickel content is shown as a function of the number of reaction cycles. The reproducibility in carrying out two and four reaction cycles (on 800°C alumina) was determined from five samples giving 5.8 ± 0.7 and 10.2 ± 1.1 wt% of nickel, respectively.

In the preparation of Ni-catalysts by repeated Ni(acac)$_2$ and air sequences, the surface exposed to the gaseous reactant is different after each reaction sequence. Only the first Ni(acac)$_2$ sequence is carried out on pure alumina, and here, the pre-

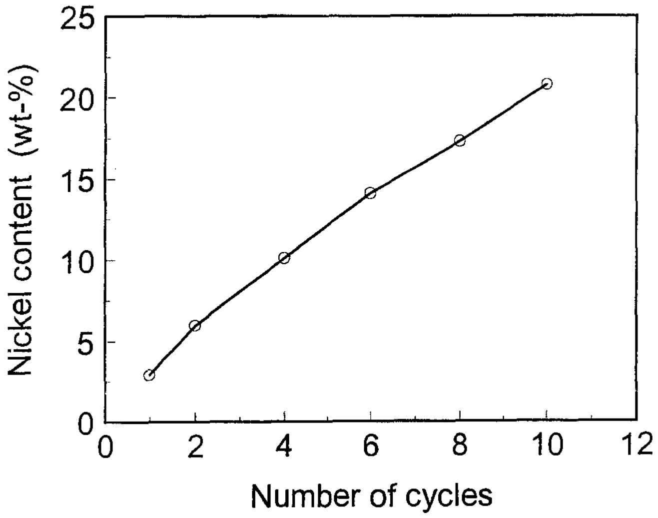

Fig. 4. Nickel content (wt%) in Ni/Al_2O_3 catalysts as a function of reaction cycles. Preheat temperature of alumina was 800°C.

heating of alumina has its main influence on the saturation level obtained. For the following $Ni(acac)_2$ sequences, the available surface sites are those of uncovered alumina and those related to the oxidic nickel species created in the preceding reaction cycles. $Ni(acac)_2$ will always choose the most (energetically and sterically) favorable sites when reacting with the surface. The growth mechanism of the oxide nickel species was studied by low energy ion scattering (LEIS) and X-ray photoelectron spectroscopy (XPS) [10]. The study does not conclude on the type of surface sites used during each reaction cycle, but it suggests that $Ni(acac)_2$ can use surface sites present on both nickel oxide species and bare alumina.

3.2. DISTRIBUTION OF NICKEL ON ALUMINA

Surface saturating reactions give homogeneous distributions of the active components as the surface itself controls the amount of metal species bound. This was verified by determining the distribution of nickel on alumina for the fresh Ni/Al_2O_3 catalysts in the oxidic form. The distribution was studied by considering the diffusion of $Ni(acac)_2$ both in the alumina bed and within the pores of the alumina particles. As shown in fig. 3, a homogeneous distribution of nickel in the alumina bed was achieved when a dose that ensures surface saturation was used. According to the SEM-EDS picture (fig. 5), nickel was evenly distributed throughout the porous alumina particles.

In table 2 the specific surface area (SA), the pore volume (PV) and the average pore diameter (d_p) are shown for Ni/Al_2O_3 samples with increasing nickel content. The physical properties of the 800°C alumina used in the samples are shown for comparison. A trend toward smaller surface areas, pore volumes and pore diameters was seen with increasing nickel content, however, no significant blocking of the pores was detected. Thus, the formation of large nickel oxide particles can be excluded. This conclusion was also supported by the dispersion of nickel in 10 wt% Ni/Al_2O_3 prepared by four reaction cycles. A dispersion of 23% was determined for this sample by H_2-chemisorption [11].

The crystallite sizes of the nickel species (CS_{NiO}) were determined by XRD (table 2). The nickel surface species were XRD amorphous for nickel contents below 15 wt%, at higher contents small NiO crystallites were observed. These were not agglomerated into larger particles as pointed out above.

3.3. INTERACTION OF $Ni(acac)_2$ WITH ALUMINA

The stability of the supported nickel against agglomeration depends on the interaction between $Ni(acac)_2$ and pure alumina. The reproducibility of different saturation levels and the homogeneous distribution of nickel excluded the possibility of uncontrolled decomposition and condensation of $Ni(acac)_2$. The binding of $Ni(acac)_2$ to alumina (in the first reaction sequence) was studied by determining the carbon/nickel ratio of the Ni/Al_2O_3 samples and with FTIR spectroscopy.

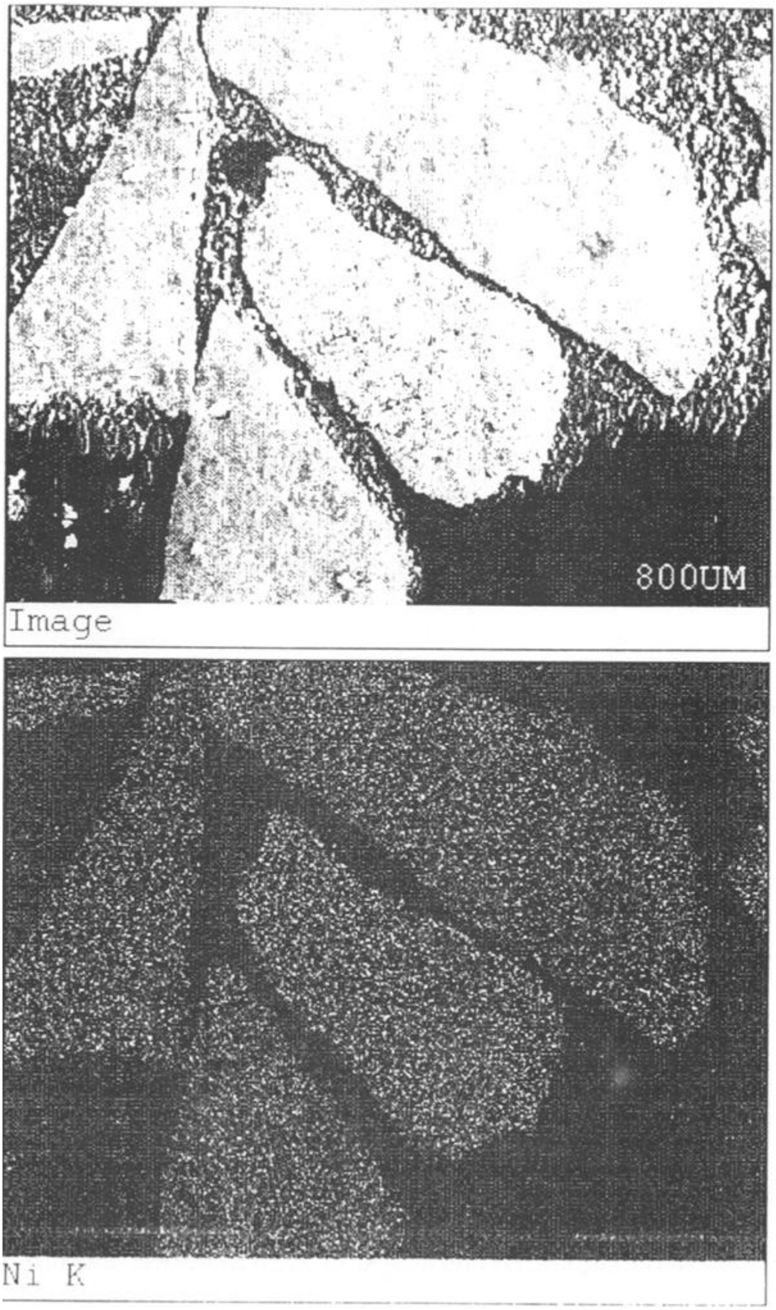

Fig. 5. SEM-EDS picture of Ni/Al$_2$O$_3$-catalyst.

Table 2
Characteristics of Ni-catalysts (marked as Ni-x, where x equals the number of reaction sequences)

Catalyst	Ni (wt%)	SA (m^2/g)	PV (cm^3)	d_p (Å)	CS_{NiO} (Å)
Al_2O_3/800°C	–	150	0.45	120	–
Ni-1	3	–	–	–	–
Ni-2	6	145	0.45	120	–
Ni-4	10	135	0.40	120	<20
Ni-6	14	135	0.35	110	<20
Ni-8	17	130	0.35	110	~20
Ni-10	21	125	0.30	100	~20

The C/Ni ratio of the Ni/Al_2O_3 samples can aid in the evaluation of the type of interaction. For associative and dissociative adsorption, the ratio equals that of the original reagent, whereas lower ratios can be due to ligand substitutions. For Ni/Al_2O_3 samples with alumina preheated at 200 and 800°C, the C/Ni ratios were about 5 and 8, respectively. As each acetylacetonate ligand contains 5 carbon atoms, the C/Ni ratio of 5 suggests that an exchange reaction takes place between Ni(acac)$_2$ and a OH group of alumina, releasing one ligand as acetylacetone (acacH) and retaining the other ligand on the nickel atom,

$$\text{Al–OH} + \text{Ni(acac)}_2 \rightarrow \text{Al–O–Ni(acac)} + \text{acacH}\uparrow . \qquad (1)$$

The increasing probability of ligand substitution with decreasing thermal stability of metal acetylacetonates was discussed by Kenvin et al. [12]. Because the reaction temperature of 200°C for Ni(acac)$_2$ was near its decomposition temperature of about 230°C, the reaction conditions were such that the loss of a ligand was more favored compared with associative adsorption. According to van Veen et al. [13] transition-metal acetylacetonates and acetylacetone in solution can react dissociatively on Lewis sites of alumina. In these reactions ligands are directly bound to alumina. As the number of Lewis sites on alumina increases with increasing preheat temperature, these additional reactions can be responsible for the higher ratio of 8 also observed.

The nature of the remaining ligand was studied by looking at the CH vibration bands appearing in the region of 3200–2800 cm^{-1} and the characteristic bands due to the CC and CO bonds in the conjugated chelate ring appearing in the region of 1600–1500 cm^{-1}. In fig. 6 the FTIR spectrum of a Ni/Al_2O_3 sample is compared with those of Ni(acac)$_2$ and the corresponding pure alumina preheated at 800°C. The CH vibration bands of the nickel surface species appeared at the corresponding wavenumbers as those of Ni(acac)$_2$. The differences in the relative intensities of the bands can be ascribed to the presence of the enol form, in addition to the keto form, of Ni(acac)$_2$ (or acacH) in the commercial reagent, as evidenced by the OH band at 3640 cm^{-1}. Acetylacetonate ring-opening through enol formation can then be disregarded for the surface nickel species. Ni(acac)$_2$ has two characteristic vibration bands at 1590 and 1515 cm^{-1}, due to the conjugated CC and CO bonds in the

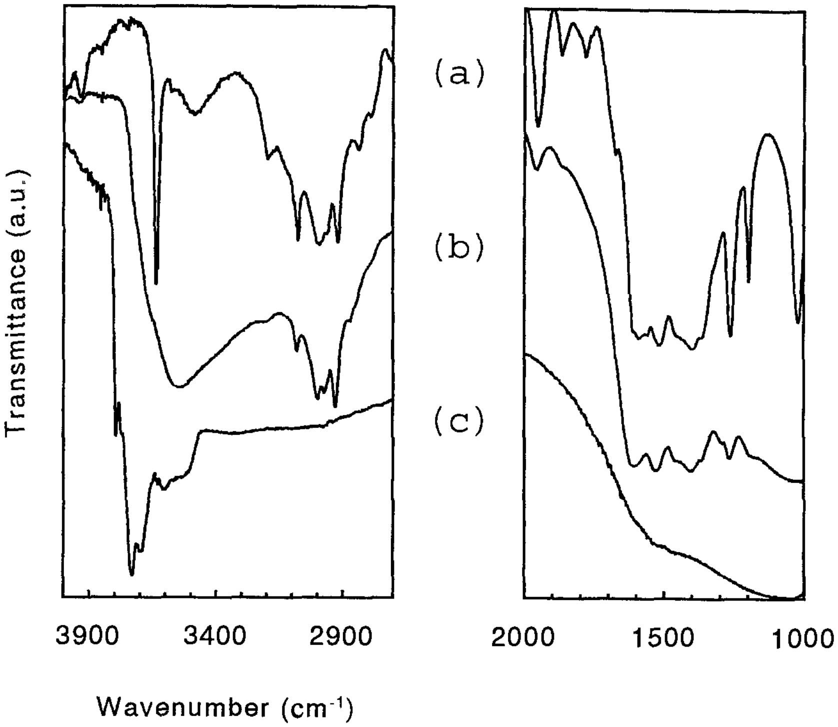

Fig. 6. FTIR spectra of (a) $Ni(acac)_2$, (b) 2.4 wt% Ni/Al_2O_3 prepared in a single $Ni(acac)_2$ sequence and (c) 800°C alumina.

ring [14]. In the spectrum of supported $Ni(acac)_2$ these bands have been shifted toward higher wavenumbers and appear at 1615 and 1535 cm^{-1}, respectively. From the similarity of the bands of $Ni(acac)_2$ and the nickel species on alumina, it was concluded that the surface nickel species retain acetylacetonate ligands with the ring structure intact. Even though pure alumina absorbs at 1600–1500 cm^{-1}, it has no vibration bands in that region that would affect the interpretation.

The amount of nickel bound to pure alumina in the first $Ni(acac)_2$ sequence was shown to be mainly restricted by the size of the supported nickel species. The saturation level of nickel decreased from an average value of 4.4 to 2.9 wt%, when the preheat temperature of alumina was varied between 200 and 800°C. The corresponding surface densities of the nickel species were 2.4 and 2.0 Ni atoms/nm^2, respectively, when taking into account the decrease in the surface area of alumina from 190 to 150 m^2/g with increasing preheat temperature. The size of the supported nickel species, retaining one acetylacetonate ligand, was estimated to be 0.45 nm^2. This gave a theoretical density of 2.2 Ni atoms/nm^2, very close to the experimental values.

As the supported nickel species chemisorbed during the first $Ni(acac)_2$ sequence retain one acetylacetonate ligand and the size of these species mainly influenced the saturation level, it was proposed that these surface species are atomically dispersed (shown schematically in fig. 7).

By comparing the FTIR spectra of pure alumina and a Ni/Al_2O_3 catalyst in the OH region, it was concluded that the adsorption of Ni(acac)$_2$ interferes with the OH groups of alumina. The disappearance of isolated OH groups can be due to exchange reactions with Ni(acac)$_2$ but, as well, due to a shift toward lower wavenumbers as a result of hydrogen bonding with the acetylacetonate ligands. The proposed interaction mainly through ligand substitution favors a decreased number of OH groups. Nevertheless, further evidence is needed to make a definite conclusion about the role of the OH groups as bonding sites.

3.4. ACTIVITY IN TOLUENE HYDROGENATION

The activity of the Ni/Al_2O_3 catalysts was optimized regarding the preheat temperature of alumina and the nickel content of the catalysts. The catalytic activity was measured for the gas-phase hydrogenation of toluene. The test reaction has also been studied in more detail for a Ni/Al_2O_3 catalyst prepared from the vapor phase: the reaction kinetics was modelled in a differential reactor [15], and the adsorption characteristics of hydrogen were evaluated by H_2-chemisorption and TPD measurements [11].

The number of nickel sites active in the hydrogenation reaction was studied as a function of the nickel content of the catalysts. In fig. 8 the activities for the series of Ni-catalysts containing between 3 and 21 wt% nickel (table 2) are shown. The monoatomically dispersed nickel species bound during the first reaction cycle (<5 wt% Ni) were catalytically inactive. There was a maximum in the utilization of nickel corresponding to a nickel content of about 10 wt%. Here, the ratio between active nickel (in contact with reactants) and the total amount of nickel obtained its highest value. According to preliminary H_2-chemisorption measurements the calculated dispersion values followed the same trend as the activities in the hydrogenation of toluene. The activity has been discussed in relation to a proposed growth mechanism of nickel [10].

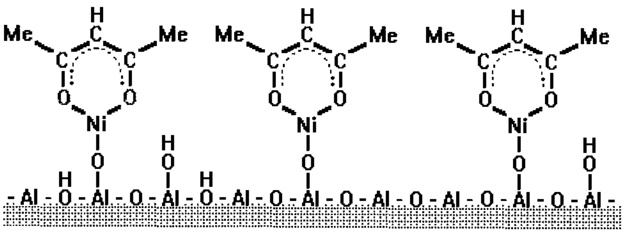

Fig. 7. A schematic representation of the surface saturation of Ni(acac)-species on alumina.

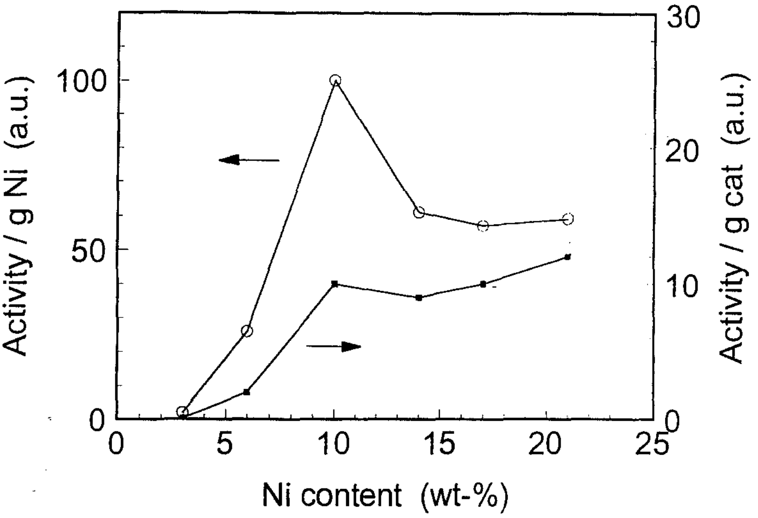

Fig. 8. Activity (in a.u.) per gram catalyst (/g cat) and per gram nickel (/g Ni) of Ni/Al_2O_3-catalysts as a function of nickel content.

The influence of the preheating of alumina on the activity was studied for Ni-catalysts prepared by four reaction cycles and containing about 10 wt% nickel. The addition of nickel decreased the surface area and the pore volume by 10–20% and the pore diameter by less than 10% compared with that of the corresponding pure alumina samples (table 1). During the preheating of alumina physically adsorbed water is desorbed and a certain degree of dehydroxylation is attained. In addition, at higher temperatures (>600°C) the alumina gradually changes from γ- to θ-phase. In table 3 the activity per gram nickel (in a.u.) is given as a function of the preheating of alumina expressed by the θ/γ-ratio. A maximum in the activity was observed for the catalyst with alumina preheated at 875°C having a θ/γ-ratio of about 0.5.

Narayanan and Uma have studied the effect of the preheat temperature of alumina and the nickel content of the catalyst on the metal–support interaction [16].

Table 3
Activity of Ni/Al_2O_3 catalysts in hydrogenation of toluene as a function of the preheat temperature of alumina (expressed by the θ/γ-ratio)

Catalyst	Ni-content (wt%)	θ/γ-ratio	Activity/g Ni (a.u.)
Ni-4a	13	<0.05	30
Ni-4b	11	<0.05	40
Ni-4c	12	~ 0.25	50
Ni-4d	10	~ 0.30	80
Ni-4e	10	~ 0.50	100
Ni-4f	9	~ 10	90
Ni-4g	9	>20	60

The Ni/Al_2O_3-catalysts were prepared by pore-volume impregnation of the support with a solution of nickel nitrate, and the activity was tested in benzene hydrogenation. Results in line with those reported in this study were obtained, i.e. a maximum in the activity was observed for both the preheat temperature of alumina (~ 800°C) and the nickel content (10–20 wt%). They ascribed the increase in the activity to a reduced interaction between the metal and the support. This favors the reduction of the supported nickel oxide species and increases the area of metal available for reactions.

4. Conclusions

It has been shown that oxidic nickel species can be grown on alumina by saturating gas–solid reactions. The surface-controlled preparation of Ni/Al_2O_3 by sequential reactions with vaporized $Ni(acac)_2$ and air was shown to give homogeneous and reproducible nickel contents. The ALE conditions were fulfilled, i.e. $Ni(acac)_2$ was chemisorbed to surface saturation in each $Ni(acac)_2$ sequence. The nickel content could then be controlled by the number of reaction cycles.

A model for the interaction of $Ni(acac)_2$ with alumina is proposed in which the main reaction is an exchange reaction with OH groups on alumina. The supported nickel species retains one acetylacetonate ligand, and the size of this surface complex determines the amount of nickel bound to alumina.

The best performance in the hydrogenation of toluene was obtained for the Ni-catalyst prepared from alumina preheated at 875°C and containing about 10 wt% nickel. The optimized catalyst exhibited a catalytical activity comparable to that of commercial Ni-catalysts having a good nickel dispersion at nickel loadings lower than 20 wt%.

Acknowledgement

The authors thank Mirja Rissanen (Microchemistry Ltd.) for the ALE processing and the Analytical Department of Neste Oy for the characterization. The Department of Chemistry, University of Joensuu, kindly allowed us to use their FTIR equipment. The valuable discussions with Dr. Outi Krause (Neste Oy) are gratefully acknowledged.

References

[1] T. Suntola, Mater. Sci. Rep. 4 (1989) 261.
[2] T. Suntola and J. Antson, US Patent No. 4058430 (1977).
[3] T. Suntola, E.-L. Lakomaa, H. Knuuttila, P. Knuuttila, O. Krause and S. Lindfors, FI 84562.

[4] T. Suntola et al., FI 87892 (1993).
[5] E.-L. Lakomaa, Appl. Surf. Sci., in press.
[6] S. Uemura et al., J. Chem. Eng. Japan 22 (1989) 48.
[7] K. Omata, H. Mazaki, H. Yagita and K. Fujimoto, Catal. Lett. 4 (1990) 123.
[8] H. Knözinger and P. Ratnasamyk, Catal. Rev. -Sci. Eng. 17 (1978) 31.
[9] M. Lindblad and L.P. Lindfors, in: *New Frontiers in Catalysis*, Proc. 10th Int. Congr. on Catalysis, part B, eds. L. Guczi, F. Solymosi and P. Tétényi (Adadémiai Kiadó, Budapest, 1993) p. 1763.
[10] J.-P. Jacobs, J.G.H. Reintjes, H.H. Brongersma, L.P. Lindfors and O. Jylhä, Catal. Lett. 25 (1994) 315.
[11] S. Smeds, T. Salmi, L.P. Lindfors and O. Krause, Appl. Catal., submitted.
[12] J.C. Kenvin, M.G. White and M.B. Mitchell, Langmuir 7 (1991) 1198.
[13] J.A.R. van Veen, G. Jonkers and W.H. Hesselink, J. Chem. Soc. Faraday Trans. I 85 (1989) 389.
[14] J.P. Dismukes, L.H. Jones and J.C. Bailar Jr., J. Phys. Chem. 65 (1961) 792.
[15] L.P. Lindfors and T. Salmi, Ind. Eng. Chem. Res. 32 (1993) 34.
[16] S. Narayanan and K. Uma, J. Chem. Soc. Faraday Trans. I 81 (1985) 2733.