

## THE QUANTITY OF REDUCED NICKEL IN SYNTHETIC TAKOVITE: EFFECTS OF PREPARATION CONDITIONS AND CALCINATION TEMPERATURE\*

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**Abstract**—Takovite,  $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 5\text{H}_2\text{O}$ , with molar Ni/Al ratios of 2.5 and 3 is prepared by precipitation at pH levels of 7 and 10, periods of reaction of 3 and 20 hr, and calcination temperatures varying between 120° and 853°C. The quantity of reduced Ni is determined as a function of the calcination temperature, and the solid phases remaining after reduction are determined with XRD. The Ni/Al ratio, pH of precipitation, and calcination temperature are important preparation conditions. A precursor of a Ni/Al ratio of 2.5 precipitated at a pH-level of 10 exhibits on reduction metallic Ni particles of about 15 nm irrespective of the drying or calcination temperature. After reduction, a considerable amount of  $\text{NaAlO}_2$  is present. Metallic Ni particles of 6 nm are present in a reduced precursor of Ni/Al ratio of 2.5 precipitated at a pH-level of 7. The size of the Ni particles present in a reduced precursor of Ni/Al ratio of 3 precipitated at a pH-level of 10 rises from 4–8 nm to 16 nm after calcination at temperatures increasing from 120° to 853°C. The last precursor contains much less sodium, and shows after reduction a disordered NiO phase containing some alumina. Especially, the takovite with the molar Ni/Al ratio of 2.5, thoroughly washed to remove Na, and calcined at  $T \leq 260^\circ\text{C}$  before reduction of Ni provides a promising catalyst for the production of hydrogen-carbon monoxide flows out of methane and steam.

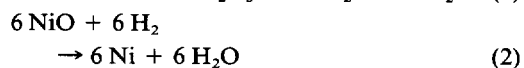
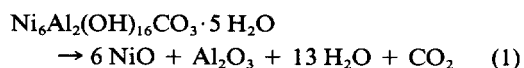
**Key Words**—Calcination, Nickel particle size, Takovite, Temperature programmed reduction.

### INTRODUCTION

Thermostable nickel-on-alumina catalysts with high loadings of Ni are useful as liquid-phase hydrogenation catalysts, currently used for carbon monoxide-hydrogen gas flows by steam reforming of methane and naphthas. Recently, Kruissink and Van Reijen (1981) investigated the use of reduced nickelhydroxide/aluminumhydroxide coprecipitates for the reaction of  $\text{H}_2/\text{CO}$  flows to methane. Since steam is produced at high temperatures with methanation, sinter-stable alumina is preferred as support. Silica may react with steam at high temperatures to form volatile species.

Ni–Al coprecipitates, reacting to form the mineral takovite, can be prepared from Ni and Al salts with molar Ni/Al ratios between 1 and 5.6 for fresh precipitates (and between 2 and 3 with hydrothermally aged samples (de Korte *et al.*, 1985). Takovite belonging to the group of Feitknecht clays, contains mixed positively charged Ni and Al double hydroxide layers, separated by layers of carbonate and structural water. The morphology of the clays consists of rod shaped sponge-like clusters with dimensions of  $100 \times 200$  nm. Sur-

prisingly, the external morphology is not changed with calcination of the takovite to the corresponding oxides and even after reduction of the NiO present after calcination to Ni (Doesburg *et al.*, 1983). The calcination of takovite (with Ni/Al = 3), and the reduction to the Ni-on-alumina catalyst involves the following steps:



Similar reaction steps can be written for  $\text{Ni}_{5.7}\text{Al}_{2.3}(\text{OH})_{16}(\text{CO}_3)_{1.15} \cdot 4.55\text{H}_2\text{O}$  with the molar Ni/Al ratio of 2.5. In Eqs. 1, and 2, it is assumed that the Ni present in takovite is completely calcined to the NiO and that the resulting NiO is completely reduced to metallic Ni. However, calcination actually leads to other oxide phases. Oxide phases mentioned in the literature are a DOSI (disordered oxide spinel intermediate) phase, which is composed of NiO containing some Al ions with a characteristic XRD reflection at 1.464 Å, and a NCA (Ni containing alumina) phase, which is a very poorly ordered Ni deficient spinel  $\text{Ni}_{1.6}\text{Al}_{2+2\delta/3}\text{O}_4$  phase with a characteristic reflection at 1.415 Å. The DOSI XRD reflection is situated between

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the d(110) of NiO at 1.476 Å (JCPDS, 22-1189) and the d(440) of NiAl<sub>2</sub>O<sub>4</sub> at 1.423 Å (JCPDS, 10-0339). The NCA reflection is situated between the d(440) of NiAl<sub>2</sub>O<sub>4</sub> at 1.423 Å and the d(440) of Al<sub>2</sub>O<sub>3</sub> at 1.400 Å (JCPDS, 29-0063).

In the spinel structure (NiAl<sub>2</sub>O<sub>4</sub>) the oxygen ions are arranged in a ccp structure. One-half of the octahedral sites is occupied by Al ions, and the other half is vacant. Ni ions fill 12.5% of the tetrahedral sites and 87.5% is empty.

De Korte *et al.* (1985) usually observed three maxima at 450°, 550°, and 750°C in the temperature programmed reduction (TPR) profiles of takovite with a Ni/Al ratio of two during calcination at 900°C. The first reduction peak displaying an activation energy of 130 kJ/mole is attributed to NiO dispersed on a supporting phase. The second peak, with an activation energy of 150 kJ/mole, is due to reduction of the DOSI phase. And the third peak with an activation energy of 320 kJ/mole, is due to reduction of the NCA phase. The rate-determining step in the reduction of the NiO or DOSI phase is probably the formation of Ni-nuclei in the individual takovite crystals. The rate determining step in the reduction of the NCA phase is assumed to be cation diffusion.

Calcination is an important procedure in the preparation of the catalysts. With high calcination temperatures, it is observed that the maximum in the reduction of NiO to Ni is shifted to higher temperatures (de Korte *et al.*, 1985). Less attention has been paid to the effect of the calcination temperature on the fraction of Ni present in the catalyst being reduced to metallic Ni. When the takovites are prepared from solutions of Na<sub>2</sub>CO<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub>, the anions taken up into the interlayer depend on the pH of the solution. At a pH of 7 more nitrate will be taken up, while after precipitation at a pH of 10 carbonate ions will be present in this interlayer, which could affect the size of the nickel particles after calcination and reduction and the amount reducible nickel.

The nickel-on-alumina catalysts resulting from a thermal pretreatment are especially important for the production of hydrogen-carbon monoxide flows out of methane and steam. With nickel catalysts, prevention of growth of carbon fibrils causing plugging of the reactor tubes is one of the main items. The catalysts produced from takovite need the presence of small Ni particles with diameters smaller than 8 nm well attached to the alumina support, which is prerequisite to prevent growth of carbon fibrils. Since even a small fraction of larger Ni particles can lead to a considerable formation of carbon fibrils, it is essential that no larger Ni particles are present in the catalyst. Production of Ni catalysts from takovite, in which the nickel is uniformly present within a chemical compound, completely prevents the presence of larger supported Ni particles. According to the present state of the art, low

Table 1. Preparation conditions of the takovite minerals.

Sample	Ni/Al	T (°C)	Time (hr)	pH	d(003) Å XRD
1	2.5	50	3	10	7.72
2	3	50	3	10	7.82
3	3	20	3	10	7.82
4	3	20	20	10	7.74
5	2.5	50	3	7	7.69

loadings of 0.5–1 wt. % of nickel-on-alumina catalysts are produced by impregnation and drying of preshaped alumina supports or by coprecipitation of nickel and alumina. These conventional procedures do not prevent formation of larger Ni particles that are liable to promote growth of filamentary carbon.

With supported catalysts, in which an active component has been applied on a thermostable support, the mechanical strength of the catalyst bodies is of decisive importance. Disintegration of the catalyst bodies during loading into the reactor, thermal pretreatment or use leads to technically unacceptable pressure drops. The production of mechanical strong bodies of takovite from the cake resulting from filtering, washing, and drying of takovite will be investigated in this paper. For this aim takovites of different molar Ni/Al ratios of 2.5 and 3 are prepared.

## EXPERIMENTAL METHODS

To investigate the effect of the Ni/Al ratios on the behavior of the catalyst precursors during thermal treatment, nickel-on-alumina precursors exhibiting the takovite structure are prepared at Ni/Al ratios of 2.5 and 3. To study the effect of anions in the interlayer on the behavior of the catalyst precursor during calcination, takovite is precipitated at pH levels of 7 and 10. The temperature of the liquid during precipitation and the period of time involved in the precipitation can affect the crystallinity of the takovite and, hence, the reactions during calcination. To assess the effect of the crystallinity, precipitations of takovite are carried out at 20° and 50°C with precipitation times of 3 and 20 hr. Na ions remaining in the takovite precursors are difficult to remove by washing. A sample containing an appreciable amount of Na as observed by a considerable amount of NaAlO<sub>2</sub> after reduction is studied too.

### Synthesis

The preparation conditions of the different samples are listed in Table 1. Five takovite samples are prepared with Ni/Al molar ratios of 2.5 and 3, pH-levels of 7 and 10, synthesis time of 3 hr with one sample of 20 hr, and temperatures of 20° and 50°C.

A solution containing 0.2 M Al is prepared by dissolving 18.7 g (0.05 mole) Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 250 ml H<sub>2</sub>O. Subsequently, 36.3 or 43.6 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O is

added to establish molar ratios Ni/Al of 2.5 or 3. A second solution containing 0.26 M  $\text{CO}_3^{2-}$  is prepared by dissolving 36.25 g  $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$  in 1 liter water, contained in a 3.5 liter double walled precipitation vessel kept at 20° or 50°C with a thermostat bath. The amount of carbonate is ten times higher than the stoichiometrically required quantity.

The entire Ni- and Al-containing solution is added at a rate of 1.4 ml/min to the carbonate solution over 3 hr, except for Sample 4 in which the solution is added over 20 hr. The pH is kept at a constant level of  $10 \pm 0.01$  or  $7 \pm 0.01$  by computer-controlled addition of 3 M NaOH. After completion of the addition of the Ni–Al solution, the suspensions are centrifuged at 3000 rpm for 5 min, and the precipitates are dried at 120°C (Samples 1A–5A).

#### Sample codes

Sample 1 is divided in 6 fractions, of which 1A is only dried at 120°C, and 1B to 1F are calcined at 260°, 399°, 493°, 585°, and 850°C, respectively, for 1 hr in an Ar flow of 63 ml/min. Samples 2A to 2F are kept for 1 hr in Ar at 120°, 260°, 395°, 499°, 586°, and 853°C under identical conditions. Finally, Samples 3A, 4A, and 5A are dried at 120°C for XRD and TGA investigations, and 3B, 4B, and 5B are calcined at 260°C for 1 hr in Ar before TPR experiments are carried out.

#### TPR

Amounts of 0.5 g of the sieve fraction between 0.7 and 2 mm of the takovite Sample 1A–1F, 2A–2F, 3B, 4B, and 5B are placed in a vertical quartz reactor tube with 8.4 mm diameter, forming a catalyst bed with a height of 1.8 cm and volume of 1 ml. The  $\text{H}_2$  consumption is measured from 20° to 850°C from an upstream 10% $\text{H}_2$ /90% Ar flow at a flow rate of 70 ml/min. The space velocity of the plug-flow, which is the division of the flow rate (ml/hr) by the volume of the catalyst bed (ml), is  $4200 \text{ h}^{-1}$  and the linear gas rate is 2.1 cm/s. The temperature is increased by a Eurotherm-controlled furnace at a rate of 9.6°C/min and measured with a Ni–Cr/Al–Cr type K thermocouple. The  $\text{H}_2$  consumption is measured with a four filament thermal conductivity cell kept at 20°C (10-077 wx T/C detector, Gow Mac). Each filament has a resistance of 30 Ohm when a current of 85 mA is applied to the Wheatstone bridge. The hot wire detector (HWD) signal (in mV) is amplified and registered on a recorder. The total  $\text{H}_2$  consumption due to reduction of Ni is measured by the integral of the HWD signal:

$$\begin{aligned} \text{mmole H}_2 &= \int \text{HWD} \cdot dT / 387 \cdot \text{sr} \\ &= \int \text{HWD} \cdot dT / 3715 \end{aligned} \quad (3)$$

where HWD is the HWD signal (in mV), dT the increment of the temperature (in °C), 387 a constant ( $\text{mV} \cdot \text{min} / \text{mmole}$ ), and sr the scan rate of 9.6°C/min.

#### XRD

X-ray diffraction profiles of the dried samples 1A through 5A are recorded on a Guinier-De Wolff camera ( $\text{Cu K}_{\alpha,1} = 1.5406 \text{ \AA}$ ). Ni particle sizes of the reduced samples 1A through 1F, 2A through 2F, 3B, 4B, and 5B are measured with XRD by broadening of the  $2\theta$  peaks of the reflections (200) and (220) of the cubic cell ( $a = 3.524 \text{ \AA}$ , JCPDS 4-850). The Ni particle size is calculated with the Scherrer equation:

$$L = 0.94 \cdot \lambda / 2\text{HW}(\theta) \cdot \cos(2\pi\theta/360) \quad (\text{nm}) \quad (4)$$

where L is the particle size (in nm);  $\lambda$  is 0.154 nm; and  $\text{HW}(\theta)$  the width of the diffraction peak at half maximum intensity, which is measured as a function of half of the diffraction angle  $2 \text{ rad } \theta$ , thus in  $\text{rad } \theta$  of the (200) or (220) reflections. The width of half height is corrected for the spectral line width of the instrument by  $\text{HW}(\theta)_{\text{corr}} = \sqrt{(\text{HW}^2(\theta)_{\text{meas}} - \text{HW}^2(\theta)_{\text{instr}})}$ , with  $\text{HW}(\theta)_{\text{instr}}$  is 0.0008  $\text{rad } \theta$  at (200) and 0.0012  $\text{rad } \theta$  at (220).

#### TGA

The weight loss of the Samples 1A, 2A, 4A, and 5A, which were dried at 120°C, was measured in a 50 ml/min  $\text{N}_2$ -flow as a function of the temperature, which increased from 20° to 900°C at a heating rate of 10°C/min. The initial weight is due to removal of interlayer water at 215°C (W1 in wt. %) (Miyata, 1980). Water of the double hydroxide sheet near Al (W2 in wt. %) is lost at 320°C and denoted as gibbsite dehydration. The water of the double hydroxide sheet near Ni (W3 in wt. %) and the  $\text{CO}_2$  are lost at 350°C and denoted as  $\text{Ni}(\text{OH})_2$  dehydration (Miyata, 1980). The temperature of dehydration of  $\text{Ni}(\text{OH})_2$  in the presence of  $\text{Al}_2\text{O}_3$  is about two times as high as the temperature normally observed with  $\text{Ni}(\text{OH})_2$ , viz., 180°C (in a reducing flow). Stabilization of  $\text{Ni}(\text{OH})_2$  by remaining  $\text{Al}_2\text{O}_3$  is assumed.

From the 0.5 g samples used in the TPR reactor experiments, the weight loss involved in the reaction of  $(\text{NiO} + \text{Al}_2\text{O}_3)$  to  $(\text{Ni} + \text{Al}_2\text{O}_3)$  (W4 in %) is reconstructed by measurement of the total weight loss (Wtotal in %). The weight loss W4 due to reduction of NiO to Ni is the subtraction of the total weight loss Wtotal by the combined weight losses  $W1 + W2 + W3$ , by  $W4 = W_{\text{total}} - (W1 + W2 + W3)$ . The amount of  $\text{H}_2$  needed for reduction of NiO is calculated with W4 by:

$$\text{mmole H}_2 = 10^3 \cdot W4(\%) \cdot 0.5 / 16 \cdot 100 \quad (5)$$

## RESULTS

#### X-ray diffraction

The XRD reflections of Samples 1A–5A, which have been dried but not reduced, are those of takovite (Table 2). Samples 2A and 3A prepared at the higher molar

Table 2. X-ray diffraction of synthetic takovite samples dried at 120°C and not reduced by H<sub>2</sub> (JCPDS 15-87).

1A 10 pH		2A 10 pH		3A 10 pH		4A 10 pH		5A 7 pH		Kruissink/van Reyen (1981)		
d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	hkl
7.72	100	7.82	100	7.82	100	7.74	100	7.69	100	7.72	100	003
4.92	w	4.87	w	4.87	w	4.92	w	4.87	w	—	—	—
4.48	w	4.87	w	4.52	w	4.48	w	—	—	—	—	—
3.85	w	3.88	27	—	—	3.86	11	3.85	21	3.85	90	006
2.57	45	2.59	32	2.59	34	2.59	26	2.57	42	2.57	40	012
—	—	—	—	—	—	—	—	2.30	20	2.29	80	015
—	—	—	—	—	—	—	—	1.95	21	1.95	—	018
1.524	47	1.527	32	1.527	25	1.524	23	1.52	23	1.520	80	110
1.496	40	1.500	27	1.521	25	1.496	18	1.49	20	1.492	80	113
1.420	8	1.422	5	—	—	1.40	w	1.39	w	1.414	30	116
1.311	9	—	—	1.28	w	1.29	w	1.29	w	1.308	50	119

w = weak.

Ni/Al ratio of 3 have large layer spacings with the d(003) reflections at 7.82 Å. Sample 1A with a molar ratio of 2.5 and sample 4A after the long reaction time of 20 hr have intermediate d(003) values of 7.72 and 7.74 Å. Sample 5A prepared at a low pH of 7 exhibits the smallest d(003) value of 7.69 Å.

#### Reduction of the samples

**Sample 1.** Sample 1 contains a large amount of Na as shown in Table 3 by the strong reflections of gamma NaAlO<sub>2</sub> after reduction with H<sub>2</sub>. The reduction profiles

of Samples 1A through 1F having a Ni/Al ratio of 2.5, when measured by hydrogen consumption in a TPR experiment, show different maxima and submaxima at 300°, 350°, 450°, 520°, 550°, 600°, and 700°C (Figure 1A). As can be seen in Figure 1A, calcination at a temperature ≥ 500°C causes the reduction peak to shift to levels ≥ 500°C (samples 1D through 1F). Apparently decomposition of the takovites leads to a mixed nickel-oxide/aluminum-oxide phase in which the Ni is difficult to reduce. The reduced Samples 1A–F are identified as to contain metallic Ni by XRD of a mean

Table 3. X-ray diffraction of takovite Samples 1A through 1F, Ni/Al = 2.5, with calcination temperatures of 120° to 850°C and reduced with H<sub>2</sub>.

1A 120°C		1B 260°C		1C 399°C		1D 493°C		1E 585°C		1F 850°C		Ni (JCPDS 4-850)		
d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	hkl
2.01	100	2.02	100	2.02	100	2.02	100	2.02	w	2.12	w	2.03	100	111
1.74	52	1.74	w	1.75	57	1.75	60	1.74	w	1.76	w	1.76	42	200
1.23	37	1.23	w	1.22	45	1.22	45	1.23	w	1.24	w	1.24	21	220
—	—	—	—	—	—	4.23	57	4.23	38	4.22	44	4.25	90	101
3.53	w	—	—	—	—	3.52	12	3.52	9	3.53	11	3.78	30	110
—	—	—	—	—	—	3.32	6	3.31	6	3.32	8	3.32	70	111
—	—	2.94	w	—	—	2.93	79	2.93	87	2.94	70	2.94	100	102
—	—	2.64	w	—	—	2.65	100	2.65	100	2.64	100	2.65	100	200
—	—	2.60	w	—	—	—	—	—	—	—	—	—	—	—
2.58	w	2.56	w	—	—	2.56	79	2.56	95	2.57	53	2.59	95	112
—	—	—	—	—	—	2.49	56	—	—	—	—	2.49	30	201
—	—	—	—	—	—	2.36	35	—	—	—	—	2.38	20	210
—	—	—	—	—	—	1.93	w	—	—	1.97	w	1.97	85	212
1.67	w	—	—	—	—	1.65	7	—	—	1.66	w	1.66	10	222
—	—	—	—	—	—	1.57	25	1.57	23	1.58	39	1.59	95	302
—	—	—	—	—	—	1.50	25	1.50	15	1.52	22	1.52	80	312
—	—	—	—	1.48	w	1.48	21	1.48	18	1.47	20	1.47	90	204
—	—	—	—	—	—	1.45	29	1.46	31	1.44	22	1.44	6	321
—	—	1.40	w	—	—	1.40	23	1.40	33	1.40	25	1.42	55	303
1.38	w	1.38	w	1.37	w	1.38	25	1.38	38	1.36	22	1.37	40	313
—	—	1.34	w	—	—	1.34	27	1.34	31	—	—	1.36	90	322
—	—	—	—	—	—	1.27	10	1.27	21	1.26	w	—	—	—
16		13		15		15		16		17		Nickel particle size L (nm)		

w = weak.

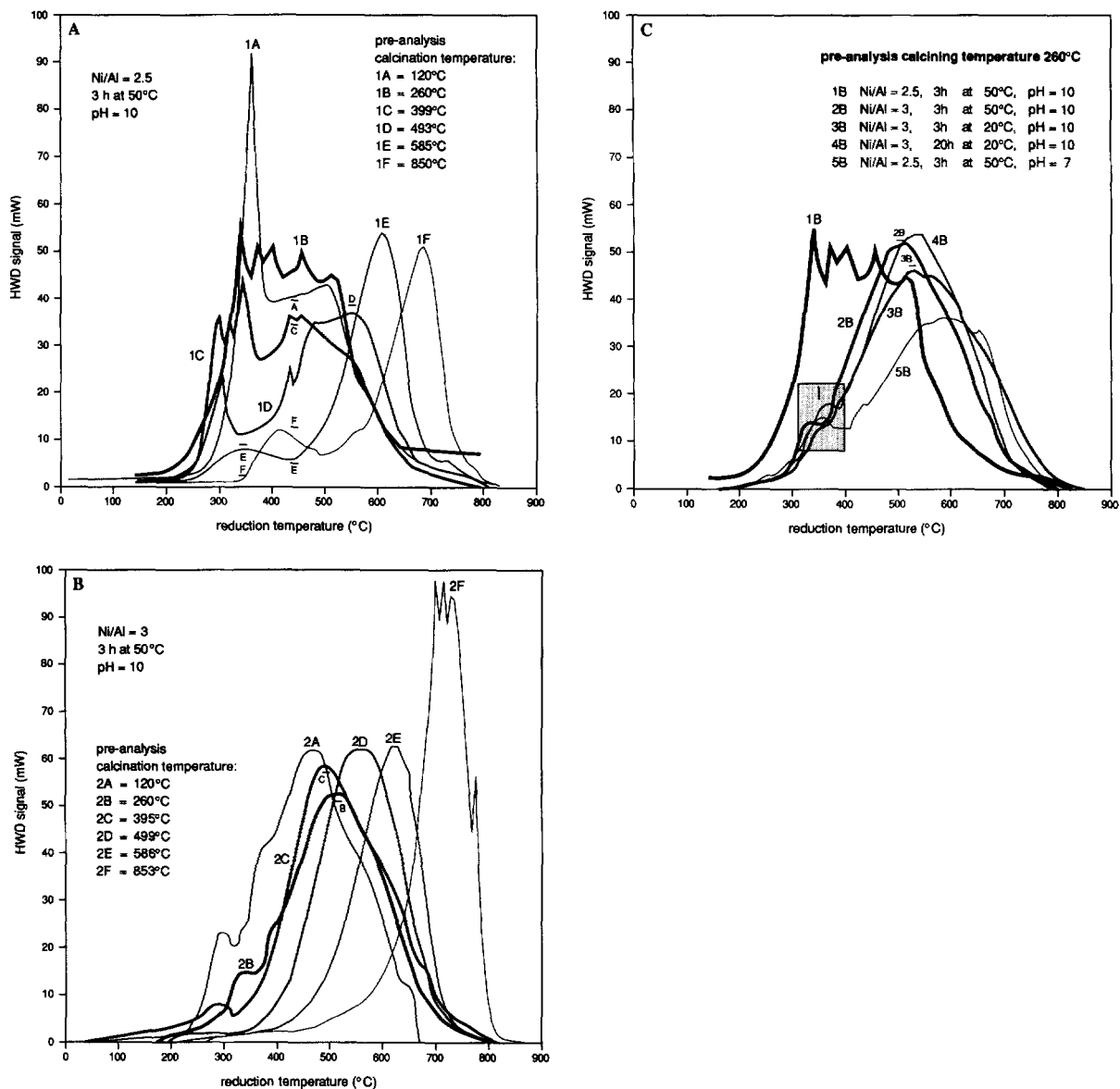


Figure 1. TPR profiles of takovite after calcination at increasing temperature: A) Ni/Al = 2.5, pH = 10, 3 hr at  $T = 50^\circ\text{C}$ , first calcined at  $120^\circ\text{C}$  (1A),  $260^\circ\text{C}$  (1B),  $399^\circ\text{C}$  (1C),  $493^\circ\text{C}$  (1D),  $585^\circ\text{C}$  (1E), and  $850^\circ\text{C}$  (1F); B) Ni/Al = 3, pH = 10, 3 hr at  $T = 50^\circ\text{C}$ , first calcined at  $120^\circ\text{C}$  (2A),  $260^\circ\text{C}$  (2B),  $395^\circ\text{C}$  (2C),  $499^\circ\text{C}$  (2D),  $586^\circ\text{C}$  (2E), and  $853^\circ\text{C}$  (2F); C) Samples 1B to 5B prepared at various conditions but calcined at  $260^\circ\text{C}$  before reduction at a temperature above the loss of interstitial water at  $215^\circ\text{C}$ .

particle diameter  $L$  of 15 nm (Table 3). There is, hence, no effect of the calcination temperature on the Ni particle size. Especially, the samples calcined above  $493^\circ\text{C}$  (1D through 1F) show strong reflections of the additional  $\gamma$   $\text{NaAlO}_2$  phase.

**Sample 2.** The reduction profiles of samples 2A through 2F with the higher molar Ni/Al ratio of 3 (Figure 1B) show a gradual shift of the reduction maximum to higher temperatures from  $450^\circ$  to  $700^\circ\text{C}$  at a calcination

temperature increasing from  $120^\circ$  to  $853^\circ\text{C}$ . The shift in the reduction temperature proceeds more smoothly with the precursor having a higher Ni/Al ratio of 3 and containing less Na. Shoulders at  $300^\circ$  and  $350^\circ\text{C}$  are seen with Sample 2A (and 2B), but are weaker than with 1A (Figure 1A). The smooth curved TPR maxima of 2A–2F are different from those of 1A–1F, which show sharp peaks and submaxima. The exception is sample 2F calcined at  $852^\circ\text{C}$ , which exhibits several peaks near  $730^\circ\text{C}$ .

Table 4. X-ray diffraction of takovite Samples 2A through 2F, Ni/Al = 3, with calcination temperatures of 120° to 853°C and reduced with H<sub>2</sub>.

2A 120°C		2B 260°C		2C 393°C		2D 585°C		2E 585°C		2F 850°C		Ni (JCPDS 4-850)		
d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	hkl
2.01	w	2.04	w	2.03	100	2.02	w	2.02	100	2.02	100	2.03	100	111
1.73	w	1.75	w	1.75	57	1.75	w	1.75	63	1.74	93	1.76	42	200
1.21	w	1.23	w	1.23	58	1.23	w	1.23	50	1.23	78	1.24	21	220
												NiO (JCPDS 22-1189)		
—	—	—	—	—	—	—	—	—	—	3.36 <sup>1</sup>	w	—	—	—
—	—	—	—	—	—	—	—	2.82	w	—	—	—	—	—
—	—	—	—	—	—	2.60 <sup>1</sup>	w	—	—	—	—	—	—	—
2.39	68	2.4	w	2.39	74	2.40	w	—	—	—	—	2.41	60	003
2.06	100	2.07	w	2.06	100	—	—	—	—	—	—	2.09	100	012
—	—	—	—	—	—	1.60 <sup>1</sup>	w	—	—	—	—	—	—	—
1.44	65	1.45	w	1.46	74	1.45	w	1.45	w	1.46	w	1.48	35	110
1.37	15	—	—	1.38	9	1.38	w	1.37	w	1.38 <sup>1</sup>	w	—	—	—
1.18	26	1.18	w	1.18	34	—	—	—	—	—	—	—	—	—
4–8		4–9		6		10		16		16		Nickel particle size L (nm)		

<sup>1</sup> Eventually NaAlO<sub>2</sub>.

w = weak.

Samples 2A–2F, after reduction, show only XRD reflections of Ni and an incompletely reduced DOSI phase (reflection 1.45 Å, Table 4). The Ni particle size of sample 2 increases from 4–8 to 16 nm with calcination temperatures increasing from 120° to 853°C.

*Samples 3–5.* In Figure 1C, samples 3B and 4B with Ni/Al = 3, synthesized at pH 10 and a temperature of 20°C for 3 and 20 hr, respectively, and calcined at 260°C display an identical TPR profile to 2B. Apparently, neither the temperature of the liquid during the preparation nor the duration of the precipitation strongly affect the reducibility of the catalyst precursor. The curves display maxima at 500°–550°C with shoulders at 350°C. Reflections of metallic Ni and an incompletely reduced DOSI phase are observed with XRD (reflection 1.46 Å, Table 5). Furthermore, the Ni particle diameter is small, 6 and 7 nm for 3B and 4B, and equal to 4–9 nm of 2B calcined at 260°C. The reduction profiles of sample 1B and 5B with the same Ni/Al ratio of 2.5, produced at pH of 10 and 7, respectively, are remarkably different (Figure 1C). Presumably, the difference is due to the Na content. The shape of the TPR curve of 5B is equal to that of 2B–4B and similar phase reflections are determined, but the TPR maximum is at a relatively high temperature of 600°C. Evidently the reduction proceeds with more difficulty at a lower Ni/Al ratio. The Ni particle size is again small, at 6 nm.

#### Quantity of reduced nickel

The weight losses in (%) of the initial 0.5 g takovite during calcination prior to reduction with H<sub>2</sub> are recorded in Table 6. It appears that experimental weight loss, W1(%) exp., with removal of interlayer water is 13–15%, which is substantially larger than the theo-

retical value of 10–11%. In contrast, the experimental weight loss with Al and Ni dehydroxylation and loss of carbonate, W2 + W3(%), is at 16–17% smaller than the 23–24% expected based on the stoichiometry of takovite. Some carbonate may, therefore, accompany the loss of interlayer water, which leads to larger values of W1(%) exp. and lower values of W2 + W3(%) exp.

In Table 6, the theoretical weight loss during reduction of Ni, W4(%) theor., ranging between 11% and 12%, is calculated from the stoichiometry of 0.5 g takovite. With calculation of the theoretical weight loss, it is assumed that Ni is fully reduced. The theoretical amount H<sub>2</sub> needed for this reduction, W4(mmol H<sub>2</sub>) theor., is 3.44 mmol with Ni/Al = 2.5, and 3.75 mmol

Table 5. X-ray diffraction of takovite samples 3B through 5B, dried at a temperature of 120°C, calcined at 260°C, and reduced with H<sub>2</sub>.

3B 260°C		4B 260°C		5B 260°C		Ni (JCPDS 4-850)		
d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	hkl
2.03	100	2.01	100	2.02	100	2.03	100	111
1.75	38	1.74	53	1.75	58	1.76	42	200
1.22	29	1.22	39	1.22	46	1.24	21	220
						NiO (JCPDS 22-1189)		
2.41	w	—	w	2.41	w	2.41	60	003
2.09 <sup>1</sup>	—	2.09 <sup>1</sup>	—	2.09 <sup>1</sup>	—	2.09	100	012
1.46	w	—	—	1.47	w	1.48	35	110
—	—	—	—	7.56	w	takovite ?		
—	—	4.46	2	—	—	takovite ?		
3.56	w	3.58	w	3.58	w	evt. NaAlO <sub>2</sub>		
1.38	w	1.38	w	1.39	w	evt. NaAlO <sub>2</sub>		
1.34	w	—	—	—	—	evt. NaAlO <sub>2</sub>		
6		7		6		Nickel particle size L (nm)		

<sup>1</sup> Partly under the 2.03 reflection of Ni.

w = weak.

Table 6. Thermogravimetric analysis (TGA) of synthetic takovite, dried at 120°C, with weight loss W1 (%) loss of interstitial water at 215°C.

Sample	Ni/Al	W1 (%)		W2 + W3 (%)		W4 (%)		W4 (mmole H <sub>2</sub> )		TPR after calcination at (mmole)	
		Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	120°C	260°C
1 <sup>1</sup>	2.5	15	10	16	24	9	11	2.81	3.44	3.1	3.3
2 <sup>2</sup>	3	13	11	17	23	3	12	0.94	3.75	4.1	4.0
4 <sup>2</sup>	3	13	11	16	23	7	12	2.19	3.75	—	3.9
5 <sup>1</sup>	2.5	15	10	16	24	13	11	4.06	3.44	—	3.2

W (%) exp. and theor. mean loss of weight during the experiments or by calculation of the theoretical loss with the stoichiometry of: <sup>1</sup>) Ni<sub>0.72</sub>Al<sub>0.28</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>0.14</sub> · 0.57H<sub>2</sub>O interstitial, and <sup>2</sup>) Ni<sub>0.75</sub>Al<sub>0.25</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>0.12</sub> · 0.63H<sub>2</sub>O interstitial.

W2 + W3 (%) due to dehydration of water bound to gibbsite and Ni(OH)<sub>2</sub> at 320° and 350°C and loss of CO<sub>2</sub>; and W4 (%) is the loss of weight by reduction of NiO. W1 through W4 are expressed in % of the initial weight of 0.5 g takovite.

with Ni/Al = 3. The experimentally measured weight loss with reduction, W4(%) exp., is mostly much lower with 3–13%. Consequently, the expected amounts of consumed H<sub>2</sub> based on these measured weight losses, W4(mmole H<sub>2</sub>) exp., have also too low values ranging between 0.94 and 4.06 mmole. The measured consumption of H<sub>2</sub> by TPR (mmole) of samples calcined at 120° and 260°C is also listed in Table 6. The TPR dihydrogen consumption values range between 3.1 and 4.1 mmole of the samples calcined at 120°C, and between 3.2 and 4.0 mmole of the samples calcined at 260°C. The amount consumed H<sub>2</sub> of TPR agrees well with that calculated from the theoretical weight loss,

W4(mmole H<sub>2</sub>) theor. Apparently the accuracy of the TPR consumption of H<sub>2</sub> is higher than that calculated from the experimental weight loss after reduction, W4(mmole H<sub>2</sub>) exp. This might be due to the slow desorption of produced water from the micro pores with reduction, which leads to too low values of W4(%) exp. (Table 6). Especially Samples 2 and 4 with a high Ni/Al ratio of 3 suggest a very low extent of reduction with 0.94 and 2.19 mmole H<sub>2</sub> in contrast with the TPR measurements with 4.0 ± 0.1 mmole.

It is interesting to study the effect of the temperature of the previous calcination on the reducibility of the Ni. Figure 2 shows the experimental hydrogen consumption calculated by integration of the HWD signal recorded during the TPR experiment. The hydrogen consumption is plotted as a function of the calcination temperature in Figure 2. The theoretical amounts of H<sub>2</sub> of 3.75 and 3.44 mmole needed for reduction of samples with molar ratios Ni/Al of 3 and 2.5 are plotted as horizontal lines in Figure 2. It can be seen that the samples with molar Ni/Al ratio of 3 at calcination temperatures ≤ 350°C exhibit an amount of H<sub>2</sub> larger than calculated for the amount of NiO. The apparently larger amounts of H<sub>2</sub> needed for reduction of the samples with Ni/Al = 3 are due to the formation of NiO<sub>1+x</sub>, where x is significantly higher than 0.01. It is well known that finely divided NiO takes up additional oxygen due to its partial oxidation to Ni(III). At higher calcination temperatures the non-stoichiometric oxygen is released and NiO assumes the green color of stoichiometric NiO instead of the grey color of NiO<sub>1+x</sub>. At still higher calcination temperatures, some Ni present as nickel aluminate cannot be reduced. After a first large consumption of H<sub>2</sub> at calcination temperatures between 100° and 200°C, the values decline at temperatures between 700° and 750°C.

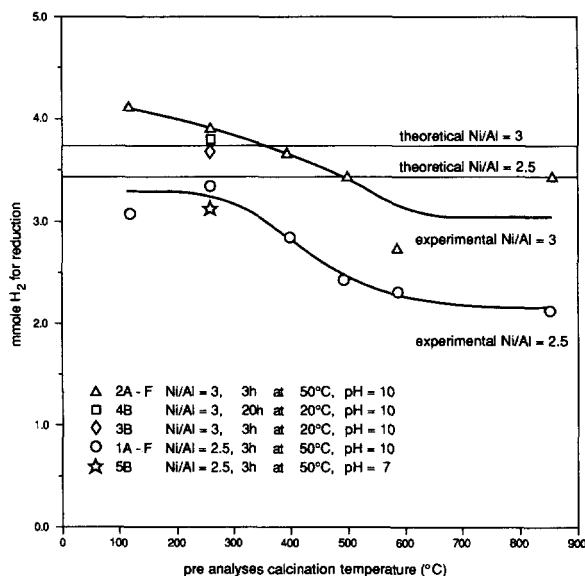


Figure 2. Integrated H<sub>2</sub> consumption upon reduction of synthetic takovite of different Ni/Al ratios of 3 and 2.5 as a function of the calcination temperature. The horizontal lines represent the theoretical H<sub>2</sub> consumption based on the stoichiometric amount of Ni in 0.5 g takovite. The curves of Sample 1 with Ni/Al = 2.5 and Sample 2 with Ni/Al = 3, represent the experimental H<sub>2</sub> consumption calculated from the surface integrals under the TPR profiles.

The extent of reduction of the samples with a molar ratio of 2.5 at all calcination temperatures is below the theoretically calculated level. Evidently reaction to a Ni–Al compound, which cannot easily be reduced, proceeds to a relatively higher extent. At calcination temperatures above 500°C, an appreciable amount of un-

reduced Ni results. It is likely that the Na present in the samples 1A through 1F promotes reaction of Ni(II) with the alumina.

## DISCUSSION

In the work of Kruissink *et al.* (1979), similar precipitates are described that are hydrothermally treated to reduce structural defects in the precipitates. The catalyst precursors prepared by Kruissink *et al.* (1979) exhibit a layer spacing of 7.58 Å after precipitation at a pH of 10, and of about 7.5 Å after precipitation at a pH of 7. The incorporation of nitrate ions during precipitation at pH 7 remains low, at about 10% of the amount of carbonate incorporated. Substantially higher contents of nitrate are obtained when the precipitation is performed at a pH of 5, or when sodium hydroxide is exclusively used in the precipitation. The layer spacings of Table 2 indicate accordingly no significant effect on the uptake of nitrate ions: The spacings vary from 7.82 to 7.69 Å. The lowest spacing is exhibited by Sample 5A, which is precipitated at a pH of 7, which leads to the most nitrate being incorporated. Kruissink *et al.* (1979) observed layer spacings of 8.92 and 9.0 Å only when much more nitrate was incorporated. The Ni particle size after reduction increased from 6 nm in the takovite with carbonate samples to 50 nm in the takovite with nitrate samples.

The size of the metallic Ni particles obtained after reduction also agrees well with the size of the Ni particles mentioned by Kruissink *et al.* (1979), at 4 nm. Kruissink *et al.* (1979) also mentioned that precursors containing Na exhibit lower catalytic activities in the hydrogenation of CO. We have confirmed the lower activity and established that the lower activity is due to the presence of large Ni particles.

Reduction of NiO by atomic hydrogen proceeds readily at room temperature. The dissociation of molecular hydrogen, therefore, is likely to be the rate-determining step in the reduction of nickel(II)oxide. Since the reduction of NiO to metallic Ni has been shown to initiate on a small number of sites at the surface of NiO, the dissociation of hydrogen will proceed on structural defects at the surface. Dissociation of the di-hydrogen and desorption of water from the surface proceed at a significant rate above 150°C as can be concluded from the onset of the reduction at temperatures around 150°C as displayed by Sample 1A in Figure 1A and Sample 2A in Figure 1B, respectively. Once metallic Ni has resulted from the reduction, the dissociative adsorption of hydrogen proceeds rapidly on metallic Ni and also the reduction.

Bulk Ni(OH)<sub>2</sub> loses water at temperatures of about 200°C. When bulk Ni(OH)<sub>2</sub> is heated in a flow of nitrogen, reduction immediately follows the dehydration of Ni(OH)<sub>2</sub>. The defect rich NiO formed with dehydration of Ni(OH)<sub>2</sub> is reduced readily by molecular

hydrogen. If Ni(OH)<sub>2</sub> is dehydrated in a flow of a non-reducing gas, defects in the resulting NiO are annealed. Subsequent reduction, therefore, proceeds less rapidly. As observed with experiments in our laboratory, reduction of well annealed NiO occurs above 450°C.

Structural defects present in takovite will not be able to dissociate molecular hydrogen. Consequently, reduction of the Ni ions will proceed only after decomposition of the takovite, which provides NiO, analogously to the behavior of Ni(OH)<sub>2</sub> being heated in a reducing gas flow. The higher stability of takovite as compared to that of Ni(OH)<sub>2</sub> causes the decomposition and the subsequent reduction to occur at temperatures around 350°C, which is at appreciably higher temperatures than that of Ni(OH)<sub>2</sub>.

The reduction profiles of Sample 2, which does not contain much Na and has a high Ni/Al ratio of 3 can be explained simply. After drying at 120°C, the dehydration of Ni-rich takovite starts at a temperature of about 220°C, with a first shoulder at 280°–320°C (Figure 1B). Additionally the precipitate produced at pH 10 contains some takovite with a lower Ni/Al ratio, which decompose to NiO at higher temperatures >320°C. The reduction of the NiO thus formed also proceeds at higher temperatures. A second shoulder to the main peak is shown at a temperature of about 350°C, while the main peak is at 450°C. We feel that the three different peaks at 280°–320°, 350°, and 460°C are due to the presence of takovites with different Ni/Al ratios. The second shoulder at 350°C coincides with the Al(OH)<sub>3</sub> (gibbsite) dehydration, perhaps catalyzing some Ni(OH)<sub>2</sub> decomposition, and the main peak, as mentioned before, is due to Ni(OH)<sub>2</sub> decomposition.

In our laboratory, the dissociation of di-hydrogen to be rate determining in reduction has been demonstrated on oxidized nickel single crystals that can be reduced at low temperatures exposed to hydrogen atoms produced on a hot filament. Dissociation of di-hydrogen on adsorption on metallic Ni has been shown to proceed by hydrogen-deuterium exchange experiments. It has also been observed that at a more elevated temperature hydrogen atoms are produced on metallic Ni, which can migrate to the surface of an oxidic support, a phenomenon known in the literature as spill over of hydrogen. Since collision of two hydrogen atoms on the support leads to desorption of di-hydrogen, the distance on the support that can be covered by hydrogen atoms is limited. The distance between the supported NiO particles can be so small that spill-over hydrogen can migrate from an already reduced Ni particle over the surface of the support to a NiO particle. The reduction will exhibit one relatively sharp peak in the TPR profile. The fact that the experimentally observed TPR profiles display three separate broad peaks indicates that the NiO particles present in our calcined takovite samples are separated and that spill-over hydrogen cannot migrate from one supported NiO par-



ticle to another. The occurrence of the three separate peaks is unexpected, since the three NiO phases are formed from uniform crystals of takovite, predicting close contact of the different NiO phases.

Calcination at 260°C of Sample 2 prior to the reduction leads to the formation of NiO slightly more difficult to reduce. When the calcination is performed at 395°C, more NiO results, which takes up additional oxygen to form NiO<sub>1+x</sub> during cooling to room temperature. Due to the excess amount of oxygen the reduction sets on at an extremely low temperature of 70°C (2C in Figure 1B), but due to the small amount of defects, the hydrogen consumption below 320°C remains low. With Sample 1C, calcined at 399°C the amount of NiO<sub>1+x</sub> is too small to become distinctly apparent by hydrogen consumption at low temperatures (Figure 1A).

Calcination at temperatures of 499°C or higher leads to reaction of NiO and Al<sub>2</sub>O<sub>3</sub> resulting from the decomposition of the takovite to nickel aluminate or to a DOSI (disordered oxide spinel intermediate) phase. It is well known that reduction of Ni spinel only proceeds at high temperatures as displayed by the curves 1D through 1F in Figure 1A, and by the curves of 2D through 2F in Figure 1B. The reaction to a spinel phase becoming more complete at higher temperatures is apparent from the gradual shift of the maxima of the reduction profile. The spinel structure does not contain the defects for the rapid dissociation of hydrogen.

Sample 1 contains a substantial amount of Na. It is assumed that the presence of Na promotes the reaction of nickeloxide with alumina to nickel aluminate. Drying at 120°C and calcination at 260° (1B) and 399°C (1C) lead to reduction profiles exhibiting a significant hydrogen consumption over a broad temperature range. After calcination at 585° and 850°C formation of nickel aluminate or a DOSI phase is apparent. Reduction of these phases is fairly difficult.

Reduction of Ni ions present in nickel aluminate or in a DOSI phase leads to relatively large Ni particles. At the more elevated temperatures required for the reduction of the Ni ions in nickel aluminate or a DOSI phase, the resulting Ni atoms are highly mobile over the aluminate or alumina. As a result the Ni atoms agglomerate to form Ni particles with a size of about 16 nm (Doesburg *et al.*, 1984).

At lower temperatures Ni atoms and small clusters of Ni atoms are less mobile, which result in smaller Ni particles. Accordingly reduction at lower temperatures leads to smaller particles of a size of 4 to 10 nm, which do not migrate or coalesce rapidly at higher temperatures. It is interesting that also reduction at relatively low temperature leads with sample 1, which contains Na, to large Ni particles. We attribute the formation of relatively large Ni particles to a high mobility of Ni metal atoms over spinel surfaces. The mobility of Ni metal atoms over NiO is lower than over

spinel surfaces, since the interaction of metallic Ni with NiO is higher than with a spinel surface.

From the experiments in this study we find the takovite with the molar Ni/Al ratio of 2.5, prepared at pH 10, and calcined below 260°C the most useful catalyst for the production of hydrogen and carbon monoxide flows from methane and steam. The catalyst can be either produced at 20° or 50°C in a period of 3 hr. The catalyst precursor must be thoroughly washed to remove Na. Calcination below 260°C provides nearly 100% reducible nickel and keeps the Ni particle diameter smaller than 8 nm, preventing the formation of carbon filaments in the reaction. Takovites of a higher Ni/Al ratio of 3 are less appropriate because the catalyst bodies are softer and the mechanical strength in the reactor is less. Disintegration leads to undesired pressure drops. Besides with combined gravimetric-TPR experiments is shown that water migrates less rapidly from the small micropores of the catalyst with Ni/Al = 3. A rapid diffusion of steam is needed for a proper performance of the catalyst.

## CONCLUSIONS

1) During the reduction of nickel in takovite, the molar Ni/Al ratio, the pH during precipitation, and the calcination temperature most significantly affect the shape of the TPR-profile, the solid phases after reduction, and the metallic nickel particle size. Less important are the temperature of the liquid during the precipitation and the period of time involved in the precipitation.

2) The main peak in the TPR profile of samples with a molar Ni/Al ratio of 3 shifts to higher temperatures when calcination is performed at higher temperatures, while the sample with a molar Ni/Al ratio of 2.5 containing Na shows a relatively broad TPR profile after previous calcination at temperatures up to 500°C.

3) Raising the temperature of the calcination from 120° to 853°C leads to an increase of the size of the nickel particles from 4–8 nm to 16 nm due to reaction to nickel aluminate at higher temperatures. The high transport rate of nickel metal atoms over sodium aluminate accelerates the growth of the Ni particles, and causes the size of the nickel metal particles to be 15 nm irrespective of the temperature of the previous calcination.

4) After calcination of the takovite precursors below 350°C, the nickel can be completely reduced to metallic nickel; calcination at higher temperatures produces nickel aluminate a fraction of which cannot be reduced to metallic nickel. The presence of Na promotes formation of aluminates and thus appreciably decreases the reducibility of nickel.

5) A thoroughly washed takovite with the molar Ni/Al ratio of 2.5, prepared at pH 10, and calcined ≤260°C before reduction is probably the most useful catalyst

for the production of hydrogen-carbon monoxide flows from methane and steam. The catalyst can be either produced at 20° or 50°C in a period of 3 hr.

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