

Reduction of 4-nitrotoluene over Fe–Mg–Al lamellar double hydroxides

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Received 17 January 1998; accepted 5 June 1998

Abstract

Fe–Mg–Al lamellar double hydroxides (LDHs) are shown to be efficient catalysts in the heterogeneous reduction of 4-nitrotoluene to 4-aminotoluene using phenylhydrazine or hydrazine hydrate as reducing agent. Catalysts based on Fe(III) and/or Fe(II) as well as Mg(II) and/or Al(III) were prepared by precipitation of metal sulfates with Na_2CO_3 . The samples were characterized by means of XRD, TG/MS, TPR, XPS and N_2 physisorption. The catalytic behavior was tested in a glass reactor under argon atmosphere at a temperature of 343 K using ethanol as a solvent. Selectivity to 4-aminotoluene amounted to 100% for all tested catalysts. Overall activity of the catalysts increased with increasing Mg(II) to Al(III) ratio and highest overall activity was obtained for an Al-free Mg–Fe(III) oxide/hydroxide. Highest specific rates referred to the Fe surface areas were observed for catalysts prepared from Fe(III) sulfate. The specific rate decreased with higher Fe(II) content of the precursor. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reduction of 4-nitrotoluene; Fe–Mg–Al oxide/hydroxide; Lamellar double hydroxide; LDH; Hydrotalcite-like compound; HTlc

1. Introduction

Catalytic reduction of nitroarenes to aminoarenes by hydrazines has been carried out using a wide range of hydrogenation catalysts, e.g., Pd/C, Rh/C, Raney–Ni, Cu, Fe [1,2]. In 1975, Hirashima and Manabe reported that compared to conventional hydrogenation catalysts aminoarenes can be produced in good yield and high purity using hydrazine hydrate in the presence of FeCl_3 /active carbon [3]. Yields of aminoarenes up to 100% (corresponding to nitroarene reactant) and lower consumption of

the reducing agent hydrazine have been obtained. However, activities in the reduction reaction were lower. It was assumed that the reaction is catalyzed by Fe oxide/hydroxide adsorbed on the active carbon [4,5]. Later on, the potential of several Fe oxides and Fe oxide/hydroxides for this reaction was tested [6,7]. It was proposed that highly dispersed Fe hydroxide acts as the catalytically active species [6]. The most active catalyst was obtained by precipitation of FeCl_3 using NaOH as base [7].

Lamellar double hydroxides (LDHs) are materials that contain highly dispersed metal cations [8]. They consist of positively charged metal hydroxide layers separated from each other by anions and water molecules. The layers

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contain metal ions of at least two different oxidation states. The most common case of di- and trivalent cations leads to the general chemical formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where x refers to the $M(III)/[M(II) + M(III)]$ ratio ranging between ca. 0.25 and 0.4 [9]. The positive charge of the metal hydroxide layers is compensated by interstitial layers built of anions A^{n-} and crystal water. In catalysis, LDHs are mainly used as precursors for the preparation of highly dispersed mixed oxides or metal/mixed oxide catalysts. Rarely, LDH catalysts are used in reactions under conditions where their layered structure is retained [10].

The aim of this study was to show the activity of different Fe–Mg–Al LDH catalysts, not subjected to previous thermal treatments, for the reduction of nitroarenes with phenylhydrazine and hydrazine hydrate. Additionally, new insight into the relation between textural and chemical properties of these catalysts and their catalytic activity in the reduction reaction should be obtained.

2. Experimental

2.1. Preparation

Various amounts of $MgSO_4$, $Fe_2(SO_4)_3$, $FeSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$ (total metal sulfates = 0.15 mol) were dissolved in 500 ml distilled water and transferred into a 1 l five-necked flask equipped with propeller mixer, reflux condenser, pH-meter (Metrohm 614 pH-meter), thermocouple and feeding unit for liquids (Metrohm 665 Dosimat). This system was equilibrated at 333 ± 2 K under vigorous stirring. Subsequently, 150 to 300 ml 0.75 M Na_2CO_3 solution were slowly added over a time period of 2 h until a pH of 8 was reached. The resulting suspension was stirred for 15 h at room temperature and filtered. The precipitate was intensively washed with distilled water and dried at 363 K for 24 h under reduced pressure

(< 10 kPa). All samples containing Fe(II) were prepared by performing precipitation, filtration and drying under argon.

2.2. Characterization

Catalyst materials were investigated with regard to their physical and chemical properties by means of powder X-ray diffraction (XRD), thermoanalytical measurements in combination with mass spectrometry (TG/MS), temperature programmed reduction (TPR), X-ray photo-electron spectroscopy (XPS), and N_2 physisorption.

XRD patterns were measured on a Siemens D 5000 powder X-ray diffractometer. Diffractograms were recorded with detector-sided Ni-filtered $Cu K\alpha$ radiation (40 mA, 40 kV) over a 2θ range of 2° to 70° and a position sensitive detector using a step size of 0.010° and a step time of 2.5 s. Measured patterns were compared with JCPDS data files [11].

Thermoanalytical measurements (TG, DTA) under Ar in the temperature range of 298 to 1323 K were performed on a Netzsch STA 409 using $\alpha-Al_2O_3$ as a reference and a heating rate of $10 K min^{-1}$. Evolving gases were monitored on-line using a Balzers QMG 420 quadrupole mass spectrometer connected to the thermoanalyzer by a heated capillary. Quantitative measurement of the evolved gases was performed by calibration of the system using a pulse method described by Maciejewski and Baiker [12] and Maciejewski et al. [13].

The apparatus used for the TPR studies has been described previously [14]. TPR profiles were measured under the following conditions: sample weight 60 mg, heating rate $10 K min^{-1}$, flow rate $75 ml min^{-1}$ of 5% H_2 in Ar (Carbagas).

XPS analysis was performed on a Leybold LHS 11 instrument with UCD using Mg $K\alpha$ radiation (240 W). The analyzer was operated at 150 eV constant pass energy in case of wide scans and at 38 eV in case of selected regions at a scale calibrated versus the Au $4f_{7/2}$ line at 84.0 eV. Spectra were recorded to achieve max-

imum resolution (better than 0.9 eV for Ag 3d_{7/2}). Corrections of the energy shift, due to the steady-state charging, were accomplished taking the C 1s line of adsorbed hydrocarbons at 285.0 eV as internal standard. For an estimation of the surface composition in mol%, the areas of the elemental peaks C 1s, O 1s, Fe 2p, Mg 2p and Al 2p were determined by the program SpecsLab 1.6 [15] applying a Shirley background. The resulting areas were divided by the corresponding atomic sensitivity factors [16].

BET surface areas (S_{BET}), mean cylindrical pore diameters ($\langle d_p \rangle$) and specific adsorption pore volumes (V_{p, N_2}) were obtained by physisorption of N₂ at 77 K using a Micromeritics ASAP 2000 instrument. Prior to measurement, the samples were degassed to 0.1 Pa at 363 K. S_{BET} were calculated in a relative pressure range between $0.05 < p/p_0 < 0.2$ assuming a cross-sectional area of 0.162 nm² for the N₂ molecule. Pore size distributions were calculated applying the Barrett–Joyner–Halenda (BJH) method [17] to the desorption branch of the isotherms [18].

2.3. Catalytic tests

Reduction of 4-nitrotoluene was carried out in a 200 ml double-walled glass reactor equipped with reflux condenser, thermocouple and sampling device. The reactor was heated by water pumped through the outer reactor shell ($\Delta T \pm 0.5$ K). The reaction mixture comprising 1.37 g (0.01 mol) 4-nitrotoluene, 100 mg catalyst (≤ 180 μm particle size) and 100 ml ethanol was stirred with a magnetic PTFE stirrer (0–1500 rpm). For equilibration of the system, the reaction mixture was kept at the desired reaction temperature for 30 min at 250 rpm. The starting procedure, which lasted about 10 s, involved the injection of 10 ml (0.1 mol) phenylhydrazine and the adjustment of the desired stirring speed (1000 rpm). The temperature effect of the phenylhydrazine injection had no significant influence on the reaction rates. All reactions were performed under argon to avoid decomposition

of phenylhydrazine due to the presence of oxygen.

Reference measurements with hydrazine hydrate as reducing agent were performed under argon atmosphere at 328 K using 200 mg [0 Fe(II)] as catalyst (denotation is explained in the first paragraph of the Results part), 1.37 g 4-nitrotoluene and 7.5 ml hydrazine hydrate.

4-Nitrotoluene conversion and selectivity to 4-aminotoluene were determined by GC analysis (HP1 column, FID). Conversions and selectivities were reproducible within $\pm 2\%$ and $\pm 5\%$, respectively. Initial reaction rates were determined by using experimental values in the conversion range 0–20% since in this region a linear dependence of conversion and reaction time was obtained. Reaction times for 50% conversion were determined by taking into account the corresponding value of a polynomial of the third degree which was fitted to the experimental data following the least square method.

3. Results

All LDHs prepared were based on Fe(III) and/or Fe(II) as well as Al(III) and/or Mg(II) (Table 1). Four out of the eight investigated samples contained 18 at.% of Fe(III) (related to total metal content) and no Fe(II). In these samples, the x value, i.e., the molar ratio of Al(III) and Fe(III) to total metal content, was varied between 0.33 and 0.25. The composition is fully defined by the x value and therefore the denotation [Fe(III) – x] is used for these samples [19]. In addition, four samples defined by a constant x value of 0.29 and a constant amount of Fe(II) + Fe(III) of 29 mol% (related to total metal content) were produced. In these samples, the amount of Fe(II), which is designated y value in the following, was varied between 0 and 29 mol%. The samples are fully defined by the y value and therefore the denotation [y Fe(II)] is used for these samples.

Table 1
Molar amounts of metals used in preparation of investigated LDH catalysts

Catalyst	x value ^a	$n[\text{Mg(II)}]$ (mol%)	$n[\text{Fe(II)}]^b$ (mol%)	$n[\text{Fe(III)}]$ (mol%)	$n[\text{Al(III)}]$ (mol%)
[Fe(III) – 0.25]	0.25	75	–	18	7
[Fe(III) – 0.28]	0.28	72	–	18	10
[Fe(III) – 0.30]	0.30	70	–	18	12
[Fe(III) – 0.33]	0.33	67	–	18	15
[0 Fe(II)]	0.29	71	–	29	–
[9 Fe(II)]	0.29	62	9	20	9
[19 Fe(II)]	0.29	52	19	10	19
[29 Fe(II)]	0.29	42	29	–	29

^a $n[\text{Al(III)} + \text{Fe(III)}]/n[\text{Mg(II)} + \text{Fe(II)} + \text{Fe(III)} + \text{Al(III)}]$, molar ratio of Al(III) and Fe(III) to total metal content.

^bDefines y value in the text.

3.1. Structural and chemical properties of catalysts

Surface areas, pore volumes and mean pore diameters of [Fe(III) – x] did not exhibit a singular trend (Table 2). For catalysts [y Fe(II)], the increase of the y value led to a decrease in surface area and to an increase of the mean pore diameters.

Crystalline phases of [Fe(III) – x] (not shown) and [y Fe(II)] catalysts (Fig. 1) before and after catalytic testing were determined by XRD. All samples showed reflections characteristic for the presence of a crystalline LDH phase (e.g., pyroaurite; JCPDS 25-0521) [11]. For the [y Fe(II)] catalysts, crystallinity of the prepared samples increased with increasing y value (Fig.

1a). After reaction, a crystalline Al(OH)₃ phase (doyleite; JCPDS 38-0376) [11] was identified (Fig. 1b) for the aluminum containing catalysts in addition to the LDH phase, which in general showed a slightly lower degree of crystallinity after catalytic testing. All XRD patterns of [Fe(III) – x] catalysts before and after reaction were similar to patterns of [19 Fe(II)].

Quantitative measurements of gases evolved during thermal decomposition of the catalysts in Ar were measured using a TG/MS instrument (Table 2). All [Fe(III) – x] catalysts generated comparable amounts of H₂O, CO₂ and SO₂ during heating. In contrast, the [y Fe(II)] catalysts produced increasing amounts of water with increasing y value. Evolution of CO₂ and SO₂ was similar for these catalysts except for the

Table 2
Textural properties and amount of gases evolved during thermal decomposition of LDH catalysts determined by N₂ physisorption and TG/MSy

Catalyst	S_{BET}^a (m ² g ⁻¹)	V_{p,N_2}^b (cm ³ g ⁻¹)	$\langle d_p \rangle^c$ (nm)	H ₂ O (wt.%)	CO ₂ (wt.%)	SO ₂ (wt.%)
[Fe(III) – 0.25]	150	0.67	18	22.7	1.9	5.2
[Fe(III) – 0.28]	217	0.78	14	22.1	0.9	6.6
[Fe(III) – 0.30]	181	0.77	17	25.1	1.1	6.4
[Fe(III) – 0.33]	141	0.75	21	23.8	1.2	6.3
[0 Fe(II)]	354	0.60	6	15.4	0.8	3.1
[9 Fe(II)]	161	0.71	16	18.0	3.5	5.7
[19 Fe(II)]	117	0.51	16	22.9	1.5	5.5
[29 Fe(II)]	94	0.66	22	24.0	5.8	5.4

^aBET surface area.

^bBJH cumulative desorption pore volume.

^cMean pore diameter $\langle d_p \rangle = 4V_{p,N_2}/S_{\text{BET}}$.

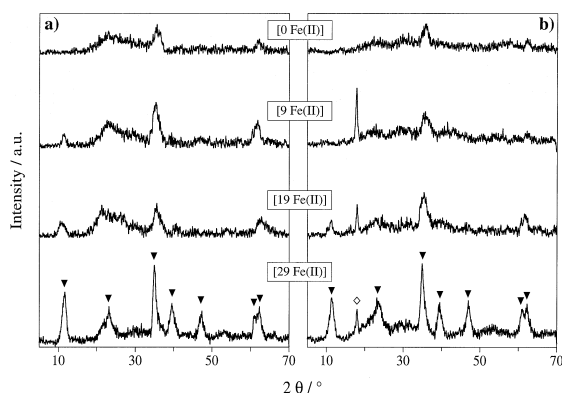


Fig. 1. X-ray diffraction pattern of [0 Fe(II)], [9 Fe(II)], [19 Fe(II)] and [29 Fe(II)]. (▼) hydroxalcalite-like phase (HT-phase), (◇) $\text{Al}(\text{OH})_3$. (a) before reaction, (b) after reaction.

aluminum-free sample, which showed generally lower amounts evolved.

For all catalysts, except [0 Fe(II)], similar TPR profiles have been obtained, showing a distinct maximum in H_2 -consumption at about 700 K followed by broad peaks at higher temperatures (Fig. 2). As to the [y Fe(II)] catalysts, the maximum in H_2 -consumption at about 700 K is broader for higher y values. The Al-free sample [0 Fe(II)] is more easily reduced than the other catalysts. The TPR profile is similar to those reported for small Fe_2O_3 particles [20,21].

Fe surface concentrations estimated from XPS measurements are listed in Table 3. Note that the Fe $2p_{3/2}$ peak was not deconvoluted into a contribution of Fe(II) and Fe(III). A similar binding energy of 710.9 eV (FWHM ca. 4.0 eV) was found for all catalysts. Referring to literature data, the Fe $2p_{3/2}$ peak of Fe(II) is located in the range 709.5–710.0 eV (FWHM 4–5 nm), and the corresponding peak of Fe(III) in the range 710.7–711.4 eV (FWHM 4–5 nm) [22–24]. This indicates that surface Fe(II) has been oxidized to Fe(III) upon exposure to air. However, it was reported that it is difficult to distinguish between different Fe oxides by XPS because the differences between these compounds are small and the FWHM rather large [22].

As regards the aluminum component, the Al surface concentrations of the [y Fe(II)] catalysts

increased with increasing y value, i.e., increasing Al bulk concentration (Table 3). Likewise, the Al surface concentration of the [Fe(III) – x] catalysts showed a similar trend as the Al bulk concentration with highest values being obtained for sample [Fe(III) – 0.33] (Table 3). The Mg:Al ratios of [Fe(III) – 0.25], [Fe(III) – 0.28], [Fe(III) – 0.30], [9 Fe(II)] and [29 Fe(II)] are within the same range, considering the uncertainty of the XPS analysis of porous materials (Table 3). In contrast, the ratios of [Fe(III) – 0.33] and of [19 Fe(II)] were substantially lower.

3.2. Catalytic properties of LDHs in the reduction of 4-nitrotoluene

The reaction rate of the reduction of 4-nitrotoluene with phenylhydrazine at 343 K was independent on stirring speed (> 250 rpm) and catalyst particle size (< 300 μm), indicating that the reaction rate was not influenced by

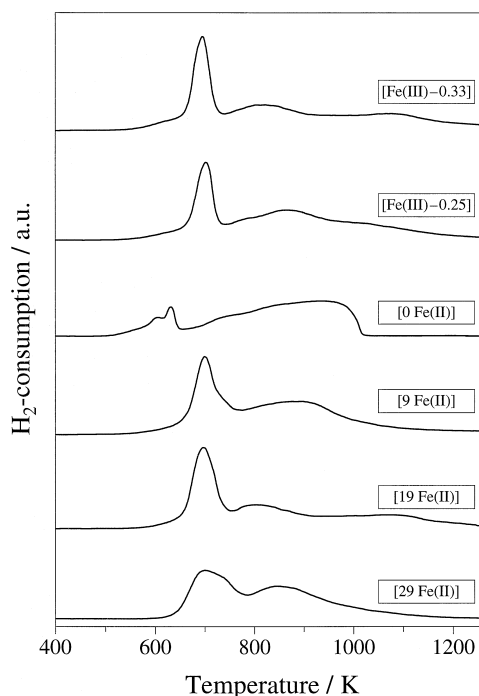


Fig. 2. Reduction behavior of [Fe(III)–0.33], [Fe(III)–0.25], [0 Fe(II)], [9 Fe(II)], [19 Fe(II)] and [29 Fe(II)] measured by TPR. TPR profiles of [Fe(III)–0.30], [Fe(III)–0.28] were similar to the corresponding profiles of [Fe(III)–0.33] and [Fe(III)–0.25] shown in this figure.

Table 3

Surface chemical compositions and catalytic properties of LDH catalysts in the reduction of 4-nitrotoluene by phenylhydrazine

Catalyst	Surface				Initial reaction rate		t_{50} (min)
	Concentration		Ratio	Area	Overall	Specific	
	Al (%)	Fe _{tot} ^a (%)					
[Fe(III) – 0.25]	11	4	0.60	6	0.20	3.3	260
[Fe(III) – 0.28]	12	3	0.60	7	0.16	2.5	310
[Fe(III) – 0.30]	12	3	0.60	5	0.15	2.8	330
[Fe(III) – 0.33]	14	3	0.35	4	0.03	0.7	1720
[0 Fe(II)]	–	18	–	64	1.57	2.5	25
[9 Fe(II)]	9	6	0.70	10	0.14	1.4	360
[19 Fe(II)]	11	8	0.10	9	0.06	0.6	950
[29 Fe(II)]	12	4	0.50	4	0.03	0.8	1740

Reaction parameters: 1.37 g 4-nitrotoluene, 100 mg catalyst, 10 ml phenylhydrazine, argon atmosphere, 343 K.

^aFe_{tot}, total amount of Fe, i.e., Fe(II) and Fe(III).

^bFe surface areas (m² g⁻¹) estimated by multiplication of XPS-derived Fe surface concentrations (%) with corresponding BET surface areas (m² g⁻¹).

^cOverall initial reaction rates determined by applying experimental values < 20% conversion.

^dSpecific initial reaction rates referred to Fe surface area S_{Fe} (m² g⁻¹).

interparticle or intraparticle mass transfer limitations in the chosen parameter range.

The selectivity to 4-aminotoluene (related to reactant 4-nitrotoluene) amounted to 100% for all reactions. Benzene and aniline were produced upon decomposition of the reducing agent phenylhydrazine. Phenylhydrazine was used in excess so that its consumption during reaction did not influence the reaction rate.

The catalytic activity of the LDHs is presented as overall initial reaction rate, specific initial reaction rate related to the Fe surface area and as reaction time for 50% conversion (t_{50}) (Table 3). For the [Fe(III) – x] catalysts overall initial reaction rates as well as specific initial reaction rates increased with decreasing x value, which reflects increasing Mg to Al ratios for these catalysts. Note that compared to the other samples of this series a significant drop in activity was observed for catalyst [Fe(III) – 0.33], although the estimated Fe surface concentration varied only from 3–4 mol% corresponding to an Fe surface area of 4–7 m² g⁻¹ (Table 3). In case of [y Fe(II)] catalysts, overall initial reaction rates, as well as specific initial reaction rates increased with decreasing y value. For all catalysts, the corresponding t_{50} values confirm

the observed trend for the initial reaction rates. Of all catalysts tested, [0 Fe(II)] provided the highest overall initial reaction rate, whereas [Fe(III) – 0.25] showed the highest specific initial reaction rate. [0 Fe(II)] showed no significant deactivation after multiple use.

To compare the performance of the best LDH catalyst of this study with that of iron oxide based catalysts reported in literature, a reference measurement was carried out, using [0 Fe(II)] as catalyst and hydrazine-hydrate as reducing agent (reaction conditions: 200 mg [0 Fe(II)], 1.37 g 4-nitrotoluene, 7.5 ml hydrazine-hydrate, 100 ml ethanol, argon atmosphere, 328 K). Under these conditions, the overall initial reaction rate of [0 Fe(II)] amounted to 0.4×10^{-3} mol l⁻¹ min⁻¹.

4. Discussion

In the following, the textural and chemical properties of the Fe–Mg–Al LDHs and their influence on the catalytic behavior in the reduction of 4-nitrotoluene are discussed.

The [Fe(III) – x] catalysts, containing a constant amount of Fe(III) and varying ratios of

Mg(II) to Al(III), did not exhibit a significant change in the investigated textural and chemical properties if the x value was changed, as emerges from comparing the pore volumes, the mean pore diameters, the thermal decomposition behaviors (Table 2), the crystalline phase compositions (Fig. 1) and the reduction behaviors towards H_2 (Fig. 2). Additionally, the estimated Fe surface concentration varied only from 3–4 mol% corresponding to an Fe surface area of 4–7 $m^2 g^{-1}$ (Table 3). Consequently, the observed decrease of the overall initial rates with increasing bulk x value (Table 3) cannot be explained by a variation of these parameters. The decrease of the overall initial rates is rather related to the bulk ratio of Mg(II) to Al(III) which decreases from 10.7 to 4.5 with increasing x value (Table 1). The low activity of [Fe(III) – 0.33] compared to the other three [Fe(III) – x] catalysts is attributed to the significantly lower Mg to Al ratio on the catalyst surface (Table 3). Regarding the specific initial rates, corresponding to 4-nitrotoluene converted per m^2 Fe surface area, similar values in the range $2.5\text{--}3.3 \cdot 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1} (S_{Fe})^{-1}$ are observed for the [Fe(III) – x] catalysts with x up to 0.3, whereas for catalyst [Fe(III) – 0.33], specific activity was markedly lower.

For the [y Fe(II)] catalysts prepared with constant x value but varying amounts of Fe(II), Fe(III), Mg(II) and Al(III), the textural and chemical properties changed substantially, if the y value, representing the amount of Fe(II) used in the preparations, was varied. Among all catalysts investigated, highest BET surface area and lowest mean pore diameter is observed for [0 Fe(II)], which contained only Fe(III) and Mg(II). In contrast, S_{BET} was lowest and $\langle d_p \rangle$ largest for [29 Fe(II)], prepared from Fe(II) as the iron precursor. For the other [y Fe(II)] catalysts, containing varying amounts of Fe(II) and Fe(III), as well as for the [Fe(III) – x] catalysts, S_{BET} and $\langle d_p \rangle$ were intermediate.

A similar picture emerges for the crystallinity of the catalysts. No indication for a crystalline hydrotalcite phase was observed for [0 Fe(II)],

whereas X-ray analysis revealed highest degree of crystallinity for [29 Fe(II)]. The other catalysts with intermediate y value showed only a weak reflection around $2\theta = 11.3^\circ$, indicating a hydrotalcite phase of low crystallinity.

The different amounts of water which evolved during thermal treatment of the [y Fe(II)] catalysts are correlated with the crystallinity of the samples. The evolved amount of water increased with increasing crystallinity of the samples (Table 2). It is assumed that more crystalline LDH structures possess higher water adsorption capacity due to a more developed layer structure. The examined dependency of BET surface area, crystallinity and amount of H_2O evolved, respectively, on the y value of the [y Fe(II)] catalysts cannot be explained by a varying Mg(II) to Al(III) ratio, as these properties did not vary significantly for the [Fe(III) – x] catalysts, which also contain a varying Mg(II) to Al(III) ratio. The observed dependencies can be rather explained by the absence of Al(III) and Fe(II) for catalyst [0 Fe(II)] and by the changing Fe(II) to Fe(III) ratio for the other [y Fe(II)] catalysts.

As to the surface concentration of Fe and Al, the values of the samples [y Fe(II)] were similar as the values of the [Fe(III) – x] catalysts, except for [0 Fe(II)] (Table 3). To understand the high Fe surface concentration of [0 Fe(II)], the Fe and Al surface concentrations of [0 Fe(II)] and [9 Fe(II)] have to be compared. The decrease of the Fe surface concentration from 18 to 6 mol% is attributed to a possible covering of the Fe sites by Al. This does not occur with sample [0 Fe(II)] which contains no Al.

Except for catalyst [0 Fe(II)], the TPR profiles of the samples [y Fe(II)] and [Fe(III) – x] were similar (Fig. 2), with the first reduction maximum being slightly broader for increasing y values. The TPR profile of [0 Fe(II)] is more similar to the TPR profile of small Fe_2O_3 particles than to the one of the other LDH samples, indicating that this catalyst contained no crystalline LDH phases as also corroborated by XRD (Fig. 1).

As to the catalytic performance of [y Fe(II)], the overall initial reaction rate of [0 Fe(II)] was significantly higher than for all other investigated catalysts (Table 3). The high activity of [0 Fe(II)] can be either attributed to a high number of active sites or to an increased activity of the sites themselves. Since the specific initial reaction rate of [0 Fe(II)] was comparable to the values obtained for the [Fe(III) – x] catalysts, the high activity of [0 Fe(II)] cannot be explained by an increased activity of the sites. It can be rather correlated to the number of active sites as [0 Fe(II)] possessed by far the largest Fe surface area (Table 3), which is a consequence of the large BET surface area and the high molar Fe surface concentration of this catalyst. The values for the overall initial reaction rates of the other [y Fe(II)] catalysts were of the same order of magnitude as the corresponding values of [Fe(III) – x] catalysts (Table 3). The overall initial reaction rates of the former decreased with increasing y value, i.e., increasing Fe(II) to Fe(III) ratio, as well as decreasing ratio of Mg(II) to Al(III) in the bulk. Taking into account the results obtained with the [Fe(III) – x] catalysts, it is assumed that the decrease in activity for the [y Fe(II)] catalysts is caused by the decreasing Mg(II) to Al(III) ratio. Regarding the specific initial reaction rates of the [y Fe(II)] catalysts, a decrease is observed for increasing y values, corresponding to an increasing Fe(II) to Fe(III) ratio. The result indicates a negative effect of Fe(II) used in the preparations on the intrinsic activity of the Fe surface sites, as for [0 Fe(II)] and [Fe(III) – x] catalysts, prepared from Fe(III), similar higher intrinsic activity of the Fe surface sites is observed. The low specific initial reaction rate of [Fe(III) – 0.33] and [19 Fe(II)] is attributed to the substantially lower Mg(II) to Al(III) surface ratio of these samples compared to the other catalysts.

Applying hydrazine hydrate as reducing agent resulted in higher reaction rates and for [0 Fe(II)], the most active catalyst of this study, an overall initial rate of $0.4 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1}$ was measured at 328 K. For an unsupported

iron oxide/hydroxide with $230 \text{ m}^2 \text{ g}^{-1}$ BET surface area, the most active catalyst described up to now, overall initial reaction rates up to $1.48 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1}$ have been reported for the reduction of 4-nitrotoluene with hydrazine hydrate at 328 K [7]. The higher activity of this unsupported catalyst may be traced to its higher Fe content. Miyata et al. [6] investigated various iron oxide and iron oxide/hydroxide modifications for the reduction of 4-nitrotoluene with hydrazine hydrate at 328 K. Among the catalysts tested, β -Fe(III) oxide hydroxide was reported to be most effective. Crystalline iron oxides resulted in substantially lower yields compared to the predominantly amorphous β -Fe(III) oxide hydroxide.

5. Conclusions

Fe–Mg–Al LDHs prepared by precipitation of metal sulfates with Na_2CO_3 are efficient catalysts for the reduction of 4-nitrotoluene to 4-aminotoluene using phenylhydrazine or hydrazine hydrate as reducing agent. The selectivity to 4-aminotoluene is 100% for all investigated catalysts.

Higher Mg(II) to Al(III) ratios increase the initial reaction rates. The highest overall initial reaction rate is obtained for a Mg–Fe(III) oxide/hydroxide possessing the largest Fe surface area. Complete absence of Al(III) significantly increases the Fe surface concentration of this catalyst. Highest initial reaction rates per Fe surface area are achieved for catalysts prepared from Fe(III) as iron precursor. Increasing the Fe(II) to Fe(III) ratio in the preparation of the catalysts lowers the intrinsic activity of the Fe surface sites and reaction rates.

Acknowledgements

Thanks are due to M. Maciejewski for performing thermoanalytical analyses. Financial support by the Swiss National Science Founda-

tion (Project No. 21-41850.94) is gratefully acknowledged.

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