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Synthesis and catalytic activity of silica supported iron(III)

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Abstract

Silica doped with iron(III) chloride, prepared in organic solvents (e.g. heptane, tetrahydrofuran) and converted with a metal alkyl (butyllithium or triisobutylaluminum) is used as catalyst for the hydrogenation of alkenes.

Keywords: Alkene; Hydrogenation; Iron(III); Silica; Supported catalysts

1. Introduction

Supported iron(III) is used in various catalytic reactions as a heterogeneous catalyst, mainly for the chlorination of alkanes [1–3] or aromatic rings [4,5]. Methane oxidation by oxygen under mild conditions in the presence of iron supported catalysts was published by Khenkin et al. [6]. Anhydrous ferric chloride dispersed on silica gel catalyses the alkylation of aromatic compounds in dry media [7]. The synthesis of ammonia by supported iron was examined by Baihe et al. [8].

Except for the Fischer–Tropsch synthesis [9–11] only a few catalytic systems based on supported iron(III) are known as hydrogenation catalysts today, e.g. the catalyst $\text{Ru/Ni}^{\text{II}}/\text{K}_4\text{Fe}(\text{CN})_6/\text{Al}_2\text{O}_3$ [12] for the hydrogenation of acetonitrile at 150°C and 30 bar H_2 , the hydrogenation of phenol to cyclohexanol [13] or the isomerization and hydrogenation of 1-hexene [14].

Soluble iron(III) halides combined with triisobutylaluminum are used as homogeneous catalysts in the hydrogenation of aliphatic double bonds [15]. Polar compounds, e.g. triethylamine, DMSO, which were added to these systems in various concentrations, increase the activity of these catalysts [16].

This paper reports on the preparation of iron doped silica in organic solvents and the examination of its catalytic activity, whereby the supported Fe(III) is converted with a metal alkyl (butyllithium – BuLi – or triisobutylaluminum – TIBA –) as cocatalyst for the hydrogenation of alkenes.

Silica is doped with iron(III) by the activation with BuLi in tetrahydrofuran (see Fig. 1) and the conversion with iron(III) chloride (separation of LiCl).

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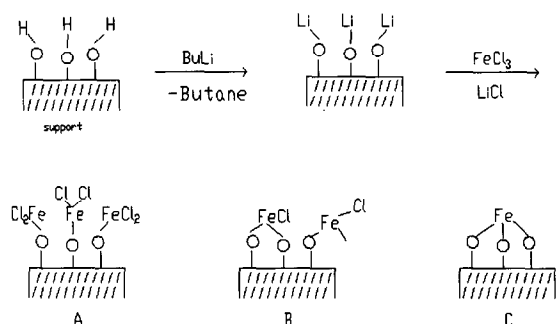


Fig. 1. Silanole groups of silica, activated by conversion with butyllithium in organic solvents, and the consecutive reaction with iron(III) chloride. Species A: single-bonded iron(III). Species B: double-bonded iron(III). Species C: triple-bonded iron(III).

2. Experimental

2.1. Materials and equipment

Silica, Merck 7733, used as supporting material, was washed in 1 M HCl, H₂O and dried at 200°C under vacuum (24 h, 12 hPa).

The other chemicals used were:

heptane	Fluka Nr. 51750
THF	Merck Nr. 9731
FeCl ₃	Merck Nr. 803945
butyllithium	Fluka Nr. 20160
triisobutylaluminum	Merck Nr. 818837
1-octene	Fluka Nr. 74902
cis-2-octene	ICN Biochem. Nr. 222274
1-heptene	Fluka Nr. 51860
1-decene	Sigma Nr. D-1889

Table 1

Experimental data of dotation of silica with FeCl₃

Charged FeCl ₃ /g SiO ₂ 7733		Supported Fe concentration		Relation of support Fe/charged Fe	Solvent
mmol/g	mg/g	% Fe	mmol/g		
0.62	100	1.07	0.19	0.31	heptane
0.18	30	0.44	0.08	0.44	heptane
0.06	10	0.11	0.02	0.33	heptane
0.92	150	1.34	0.24	0.26	THF
0.62	100	1.07	0.19	0.31	THF
0.18	30	0.38	0.07	0.38	THF

cyclohexene
1-dodecene
1-tetradecene
1-hexadecene
Alox B

Fluka Nr. 29230
Fluka Nr. 44150
Fluka Nr. 87189
Fluka Nr. 52280
Woelm Nr. 02087

molecular sieve 3Å
BHT(2,6-di-*tert*-butyl cresol)

Roth Nr. 8487
Fluka Nr. 34750

Heptane, dried over Alox B, was stored under argon over molecular sieve with a mean diameter of 4 Å and Cr^{II}/SiO₂ [17,18]. The alkenes were also dried over Alox B and stored under argon and molecular sieve.

THF was distilled under argon, 100 ppm BHT were added and the solution was heated for 1 h to reflux over molecular sieve. Afterwards it was also stored under argon over molecular sieve.

2.2. Synthesis of silica-supported iron by using the BuLi/heptane or BuLi/THF method

A solution of 20 ml (30 mmol) BuLi in 50 ml solvent was dropped to a stirred suspension of 20 g purified silica (Merck 7733) at room temperature during 1 hour (the colour of silica changed to yellow, the formation of butane was observed). The suspension was stirred for an additional hour, then 0.6 g (3.7 mmol) iron(III) chloride was added in two portions and the mixture was stirred again for two hours. Then the precipitate was washed in (50 + 50) ml solvent and dried in vacuo at room temperature (for experimental data see also Table 1 and [19]).

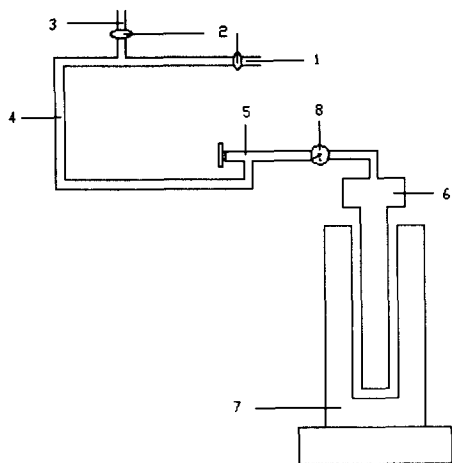


Fig. 2. Autoclave. 1. H₂ gas cylinder, 2. cocks, 3. aeration, 4. pressure line, 5. control valve, 6. autoclave, 7. magnetic stirrer, 8. manometer.

2.3. Activation of the supported Fe/SiO₂

Each 5 g of supported Fe(III) was heated under argon flow up to its activation temperature (150°C–700°C, heating rate 80°C/h); the maximum temperature was held for 1 h. Subsequently, the sample was cooled down under argon to room temperature.

The activation of the Fe/SiO₂ catalysts prepared in THF as a solvent could not be performed at a temperature higher than 200°C, because otherwise the adsorbed THF decomposed (colour of the support changed to black). For this reason, the maximum activation temperature of these Fe/SiO₂ catalysts was set to 150°C.

2.4. Hydrogenation process

Hydrogenation of alkenes under 60 bar pressure by using an autoclave

0.1 mmol of supported Fe/SiO₂ was suspended in 40 mmol of the 1-alkene and filled into the autoclave. 1 ml (1.5 mmol) BuLi was added and the autoclave was closed (see Fig. 2). Then the pressure line was filled with H₂ by using the cocks. H₂ was pressed into the autoclave until a pressure of 60 bar was reached. The suspension was stirred and the pressure was monitored by a manometer during the reaction. After 1 h, the reaction was

interrupted and the alkene/alkane mixture was examined by gas chromatography.

Hydrogenation of alkenes under normal pressure

The catalyst (0.1 mmol Fe/SiO₂) was suspended in 40 ml of heptane; 1 ml (1.5 mmol) BuLi and 20 mmol 1-alkene were added. H₂ was passed through the stirred suspension at a floating rate of 7 l/h. Every 15 min 0.2 ml of the reaction solution was withdrawn and examined by gas chromatography. The hydrogenation equipment is shown in Fig. 3.

A Carlo Erba HRGC 5300 instrument (fitted out with a glass capillary WCOT OV 101, carrier gas: nitrogen at 55 kPa, detection: FID) was used as gas chromatograph. A GCMS system – Hewlett Packard 5890 Series II, detector MSD 5971A EI – was used for the structure analysis of the intermediate products during the reaction.

3. Results

Only the Fe/SiO₂ catalysts combined with a metal alkyl – BuLi or TIBA – revealed hydrogenation activity, tested by hydrogenation of 1-octene at 60 bar H₂ pressure. Fe/SiO₂ or pure silica without Fe turned out to be inactive (Table 2). The oxidation state of the Fe on the silica gel was not determined.

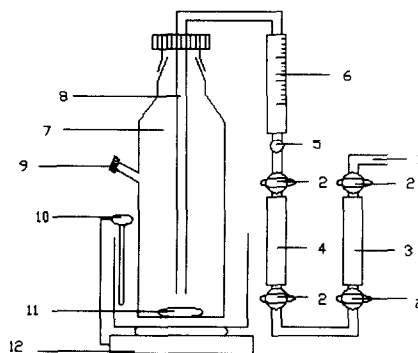


Fig. 3. Hydrogenation equipment. 1. to the gas cylinder, 2. glass cocks, 3. Mg(ClO₄)₂ column, 4. Cr^{II}/SiO₂-column, 5. needle valve, 6. flow meter, 7. hydrogenation flask, 8. H₂ inlet 9. septum, 10. thermometer, 11. agitating element, 12. magnetic stirrer with heating plate.

3.1. Reaction analysis by using 1-octene

During the hydrogenation process two differently competing reactions were observed. First it was the isomerization of 1-octene and second the hydrogenation of 1-octene (Fig. 4).

At the starting point of the reaction, nearly 100% 1-octene was found. After 30 min the concentration of 1-octene had decreased to 40%. At nearly the same time, the concentrations of the isomerization products reached their maximum. The isomerization products were now also hydrogenated; for this reason the concentration of octane increased from 8 to 70% during the next 20 min. In this case the reaction was complete after 150 min.

3.2. Catalysts synthesized by the BuLi/heptane method

The catalyst with the lowest supported iron concentration (0.11%) did not show any catalytic activity except when it was activated at 700°C. The other two catalysts (0.44% and 1.07%) showed catalytic activity: 100% yield was reached after 170 to 300 min. The highest activity was found for the catalysts which had been activated at 150°C (see Table 3).

3.3. Catalysts synthesized by the BuLi/THF method

Catalysts which were synthesized by the BuLi/THF method showed the highest catalytic activity.

Table 2
Hydrogenation^a of 1-octene under H₂ pressure (60 bar)

Catalyst	Co-catalyst	Remarks
Fe/SiO ₂ ^b	-	no reaction (stopped after 4 h)
SiO ₂ ^c	BuLi	no reaction (stopped after 6 h)
SiO ₂ ^c	TIBA	no reaction (stopped after 6 h)
Fe/SiO ₂ ^b	BuLi	100% yield after 50 min
Fe/SiO ₂ ^b	TIBA	90% yield after 1 h

^a Parameters: 6.2 ml (40 mmol) 1-octene, 1 g catalyst, 1 ml (1.5 mmol) co-catalyst TIBA or BuLi.

^b Fe/SiO₂ (1.07% Fe) synthesized by the BuLi/THF method.

^c Analogously treated SiO₂ (BuLi/THF-method), but not doped with FeCl₃.

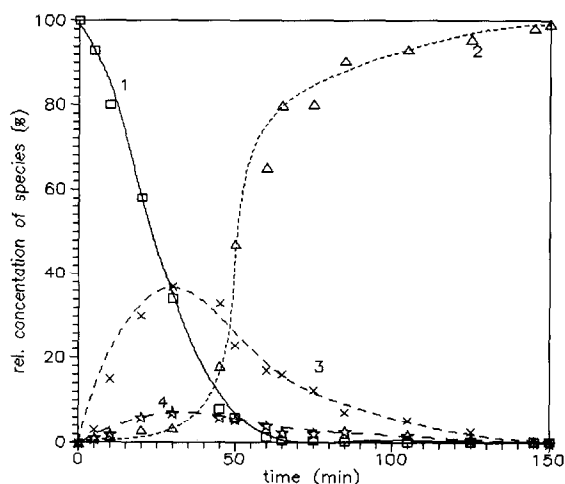


Fig. 4. Concentrations of educt, product and intermediates during the hydrogenation process of 1-octene under normal pressure using the Fe/SiO₂ catalyst. Curve 1: 1-octene curve, 2: octane curve, 3: *trans*-2-octene curve, 4: *cis*-2-octene. Parameters: 0.1 mmol supported Fe/SiO₂ (1.07% Fe), 40 ml heptane, 3.1 ml (20 mmol) 1-octene, 7 l/h H₂-floating rate, 1 ml (1.5 mmol) BuLi.

In particular the catalysts with supported iron concentration of 1.07% and 1.34% (both activated at 150°C) showed the highest hydrogenation activity. The experimental data are compiled in Table 4.

3.4. Influence of the ratio Fe/SiO₂/cocatalyst

In a second series of experiments the influence of the cocatalyst BuLi on the hydrogenation activity of the Fe/SiO₂ catalyst was tested. The ratio of the supported Fe/BuLi was varied between 1:1.5 to 1:60. The highest hydrogenation rate was found for the ratio of 1:15. At higher concentrations of BuLi a lower activity was observed, at the highest concentration (1:60) iron was even detached from the support (the colour of the solution changed to brown). In experiments with lower BuLi concentrations than 1:15, the catalytic systems showed lower activity (for experimental data see Table 5).

3.5. Effect of the temperature

Three temperatures (–15, 0, 25°C) were chosen to examine the influence of the reaction tem-

Table 3

Hydrogenation ^a of 1-octene at ambient conditions. Influence of the activation temperature and the supported iron concentration on the activity of the catalyst synthesized by the BuLi/heptane method

% Fe	T_{act} (°C)	t_{10} (min)	t_{50} (min)	t_{90} (min)	100% yield ^c (min)	Remarks
0.11	n.a. ^b	-	-	-	-	no reaction
	150	-	-	-	-	no reaction
	300	-	-	-	-	no reaction
	500	-	-	-	-	no reaction
	700	95	-	-	-	30% yield after 6 h
0.44	n.a. ^b	60	-	-	-	14% yield max.
	150	12	53	88	174	
	300	36	65	112	225	
	500	28	57	96	245	
	700	34	81	172	315	
1.07	n.a. ^b	53	163	225	> 300	
	150	12	43	53	180	
	300	8	44	86	205	
	500	25	63	116	240	
	700	34	81	172	302	

^a Parameters: 0.1 mmol Fe(III)/SiO₂, 1.5 mmol BuLi as co-catalyst, 3.1 ml (20 mmol) 1-octene in 40 ml heptane.

^b Not activated.

^c Time required to reach 100% octane in the solution.

perature on the activity of the catalytic system.

The rate constants and the order of the reaction were calculated on the basis of a plot $c_0 - c_t$ versus t for the three temperatures. The reaction order relating the decrease of 1-octene was zero (see Table 6), so the velocity constant was equal to the slope of the line $c_0 - c_t = kt$. The activation energy was calculated from a corresponding Arrhenius

plot to be $E_a = (23.7 \pm 0.7)$ kJ/mol (for experimental data see Table 6). Nearly the same value was found by J. Köhler [20] using a Ru/SiO₂ catalyst ($E_a = 18$ kJ/mol).

3.6. Effect of chain length of the alkenes

In order to examine the influence of the chain length and the structure (cycloalkenes) on the

Table 4

Hydrogenation ^a of 1-octene at ambient conditions. Influence of the activation temperature and the supported iron concentration on the activity of the catalyst synthesized by the BuLi/THF method

% Fe	T_{act} (°C)	t_{10} (min)	t_{50} (min)	t_{90} (min)	100% yield ^c (min)	Remarks
0.38	n.a. ^b	-	-	-	-	5% yield after 6 h
	150	8	29	45	103	
1.07	n.a.	15	64	127	-	
	150	6	24	36	95	
1.34	n.a.	24	73	139	185	
	150	4	24	43	75	

^a Parameters: 0.1 mmol Fe(III)/SiO₂, 1.5 mmol BuLi as co-catalyst, 3.1 ml (20 mmol) 1-octene in 40 ml heptane.

^b Not activated.

^c Time required to reach 100% octane in the solution.

Table 5

Hydrogenation^a activity in relation to the ratio of supported Fe/BuLi (catalyst synthesized by the BuLi/THF method)

support-Fe/BuLi rate (mol:mol)	t_{10} (min)	t_{50} (min)	t_{90} (min)	100% yield ^b (min)	Remarks
1:60	16	> 150	-	-	Fe was detached
1:30	35	94	152	278	
1:15	4	24	43	75	
1:7.5	6	32	47	92	
1:3.75	11	52	70	172	
1:1.5	6	51	-	-	52% yield max.

^a Parameters: 3.1 ml 1-octene in 40 ml heptane, 0.1 mmol Fe(III)/SiO₂, 7 l/h H₂ floating rate.^b Time required to reach 100% octane in the solution.

Table 6

Hydrogenation^a activity in relation to reaction temperature for the 1.35% Fe(III)/SiO₂ catalyst prepared by the BuLi/THF method

Temp. (°C)	t_{10} (min)	t_{50} (min)	t_{90} (min)	100% yield ^b (min)	Velocity constant k (mol/l min)
25	4	24	43	75	9.60×10^{-3}
0	21	75	109	175	3.79×10^{-3}
-15	66	139	190	> 250	2.21×10^{-3}

^a Parameters: 0.1 mmol Fe(III)/SiO₂, 1.5 mmol BuLi as co-catalyst, 7 l/h H₂ floating rate.^b Time required to reach 100% octane in the solution.

Table 7

Hydrogenation^a activity for different alkenes

1-Alkene	Solvent	t_{10} (min)	t_{50} (min)	t_{90} (min)	100% yield ^b
1-hexene	heptane	5	22	34	62
1-heptene	hexane	8	26	36	68
1-decene	heptane	8	34	45	79
1-tetradecene	heptane	7	34	44	92
1-hexadecene	heptane	10	32	45	90
cyclohexene	heptane	22	43	81	> 150

^a Parameters: 20 mmol alkene in 40 ml solvent, 0.1 mmol Fe(III)/SiO₂ (synthesized by the BuLi/THF method), 1 ml (1.5 mmol) BuLi, 7 l/h H₂ floating rate.^b Time required to reach 100% octane in the solution.

hydrogenation activity, some different alkenes were chosen. It turned out that the decrease of the hydrogenation rate is proportional to the chain length of the alkene (see Table 7). The structure

of the alkene also has an important influence, especially cyclohexene needed much more time to be hydrogenated than n-hexene.

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