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A. Autorenverzeichnis

Zeolite Supported Iron Oxide as Catalyst or Catalyst Precursor for Hydrocarbon Conversion Reactions

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Catalysis / Clusters / Iron on Zeolite / Materials Properties / Zeolite Y

When NaY saturated at room temperature with iron pentacarbonyl, is oxidized at room temperature in a very diluted oxygen flow, a zeolite encaged Fe_2O_3-phase is obtained as shown by Mössbauer spectroscopy, electron microscopy and X-ray diffraction. This catalyst contains 10% by weight of iron and serves as a good precursor of a Fischer-Tropsch (F.T.) catalyst. Unfortunately, the Fe_2O_3 phase is unstable under F.T. conditions, since it is shown that the iron phase migrates out of the zeolite matrix during reaction. – This encaged iron oxide phase can be hydrogen reduced giving finely dispersed and zeolite encaged iron, as is shown by physical and chemical methods. This system is a stable and active hydrogenolysis catalyst. Its selectivity is influenced by both particle size and support effects.

Introduction

Small iron clusters or iron oxide particles encaged in the pore or channel systems of zeolite supports, catalytically represent attractive systems. Substantial effort has already been reported as far as preparation and characterization are considered. Iron clusters can be generated in zeolites using indirect methods. The classical method, consisting of ion exchanging the zeolite with Fe(II) ions followed by their hydrogen reduction is only applicable to aluminum-rich faujasite-zeolites [1, 2]. Reduction with stronger agents is possible [3, 4], although this easily may result in severe sintering and formation of an extra-zeolitic iron phase. Alternatively, neutral iron complexes, as iron carbonyls, may be adsorbed. Depending on the exact decomposition method this gives rise to the formation of discrete dispersions and particle size distributions [5–13]. Thermal decomposition of sorbed pentacarbonyl inevitably gives a loss of iron [11–13].

A 1% loading of zeolite Y with α-Fe_2O_3 was obtained using the low temperature adsorption in the solution phase of iron-toluene adducts. Decomposition into α-Fe_2O_3 seems to occur under influence of residual water. In this way small particle α-Fe_2O_3 with a diameter of 2.5 ± 0.5 nm is obtained [15]. Recently, the preparation of Fe_2O_3 in the supercages of zeolite NaY with an iron loading of 10% by weight has been reported [16]. Iron pentacarbonyl was adsorbed on dry NaY, followed by exposure of the sample to oxygen at 77 K. In this way, the sorbed carbonyl was gradually oxidized into Fe_2O_3. Extensive physical characterization indicated this phase to be confined to the intracrystalline void volume of the zeolite. Unfortunately, this system was not stable in Fischer-Tropsch conditions. The reaction selectivity continuously changed till a bulk Hägg carbide phase is formed which exists externally to the zeolite.

In view of what precedes, it was the aim of this work to replace the low temperature oxidation of iron pentacarbonyl by a more realistic operation and to characterize physically and catalytically the solid thus obtained. An extensive comparison with more classically prepared catalysts is included.

Experimental

The preparation of NaY zeolite containing 10% by weight of iron as adsorbed iron pentacarbonyl was done as described earlier [16]. The sorbed $Fe(CO)_5$ was transformed into Fe_2O_3 by oxidation at room temperature using a flow of helium, containing 0.1% of oxygen. Reference iron catalysts were prepared by impregnation of silica and γ-alumina with aqueous $Fe(NO_3)_2$ solutions so as to obtain a loading of 10% Fe. These supports had a specific surface of 400 and 350 $m^2\ g^{-1}$, respectively.

Physical characterization of the zeolite-iron associations was done with TEM (transmission electron microscopy), Mössbauer spectroscopy and X-ray diffraction (XRD) spectrometry, in the way described earlier [16].

Catalytic experiments were performed in a continuous flow tubular reactor, the effluent of which was analyzed by on-line gas-chromatography [16]. For the FT experiments the gaseous hourly space velocity was 1000 at the reactor entrance. The reactant pressure was 2.0 M Pa and the CO/H_2 molar ratio 0.73. The n-decane hydrogenolysis was done at atmospheric pressure, using a weight hourly space velocity of 1.2 and a hydrogen/decane molar ratio of 10.

Results

Preparation and Physical Characterization of FeO_x on Zeolite NaY

Dry zeolite NaY was equilibrated in the dark at 295 K with iron pentacarbonyl and subsequently degassed purging the sample with dry helium. The sample contained on the average three residual $Fe(CO)_5$ molecules per supercage, which corresponds to 10% by weight of iron. To the purge gas was then added 0.1% of oxygen, in order to oxidize the adsorbed $Fe(CO)_5$ gradually and transform it into adsorbed Fe_2O_3. No overheating in the catalyst bed could be detected during the oxidation reaction. This sample will be denoted as NaY/FeO_x^* to discriminate it from the NaY/FeO_x sample described earlier [16], which was loaded with carbonyl in a similar way but overheating during oxidation was avoided by cooling the sample down to 77 K, exposing it to oxygen at this temperature and allowing it to warm up to room temperature.

The physical characterization of this sample was almost identical to the one described earlier, which was prepared much more cautiously but using rather irrealistic conditions [16]. The present sample shows a six-line Mössbauer pattern at 1.8 K, with a hyperfine field of 43 T and an isomer shift of 0.3 mm s^{-1} (Fig. 1). At room

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temperature, this six-line spectrum relaxes to give a symmetrical doublet with a quadrupole splitting of $V_{zz} = 1.0$ mm s^{-1}.

This Mössbauer behaviour also indicates that NaY/FeO$_x^*$ and NaY/FeO$_x$ are identical materials. TEM and XRD confirm this, since at magnifications of 300000 times, the supported iron system in both cases does not display any particles. In the XRD pattern, also no lines not ascribable to the NaY-zeolite could be detected.

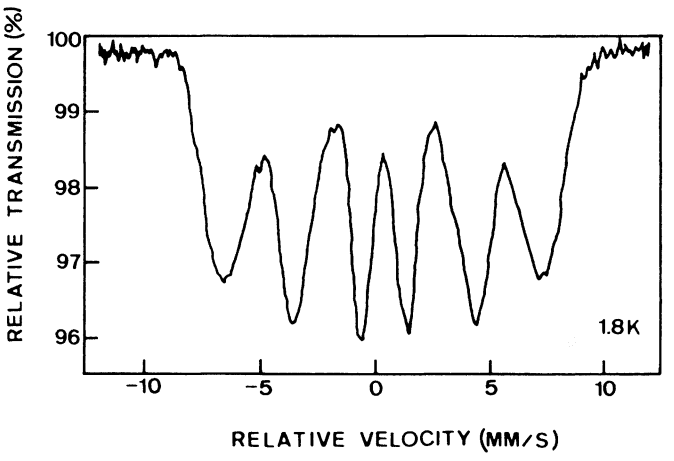

Fig. 1
Mössbauer spectrum of sample NaY/FeO$_x^*$ measured at 1.8 K. The lines are drawn by connecting the measured data points

Table 1
Comparison of NaY/FeO$_x^*$ and NaY/FeO$_x$[1] zeolites as Fischer-Tropsch catalysts at a temperature of 555 K

Catalyst	Time-on-stream (hours)	CO conversion (%)	Growth factor for C_3-C_8	Growth factor for C_8-C_{16}
NaY/FeO$_x$	0.5	36.8	0.644	–
NaY/FeO$_x^*$	0.6	38.0	0.649	–
NaY/FeO$_x$	120.0	25.8	0.657	0.875
NaY/FeO$_x^*$	127.0	26.3	0.651	0.861

[1] Data on this catalyst are from Ref. [16].

Behaviour of NaY/FeO$_x^*$ as a Fischer-Tropsch (F.T.) Catalyst

The F.T. behaviour of NaY/FeO$_x$ has been investigated in detail [16]. At increasing times-on-stream, this sample slightly deactivates and the hydrocarbon growth factor steadily increases for longer reaction times. This means that heavier hydrocarbons desorb from the catalyst at longer reaction times. In Table 1, some pertinent data are given, which compare the behaviour of catalyst NaY/FeO$_x$ to that of NaY/FeO$_x^*$. Within experimental error, both materials behave as identical F.T. catalysts. When two different growth factors are mentioned in Table 1, this indicates that two sets of active F.T. sites are present. This is true at steady state on both catalysts. The physical characterization of the equilibrium NaY/FeO$_x$ catalyst [16], indicates that during the F.T. reaction part of the active phase migrates out of the zeolite and is transformed into a Fe$_x$C phase.

Since this sintering is possibly caused by the steam atmosphere present during a F.T. reaction, the behaviour of sample NaY/FeO$_x^*$ in less demanding conditions was also investigated.

Characterization of Reduced NaY/FeO$_x^*$

NaY/FeO$_x^*$ is a suitable precursor for zeolite supported iron since the Fe_2O_3-phase is confined to the cages of the zeolite. A NaY/Fe catalyst was generated during reduction of this precursor either at 573 or 873 K. Reference catalysts carry equal amounts of iron on the classical supports γ-alumina and silica. The latter were prepared via an impregnation with Fe(NO$_3$)$_3$, drying, calcination at 823 K and subsequent reduction at 573 and 873 K, respectively.

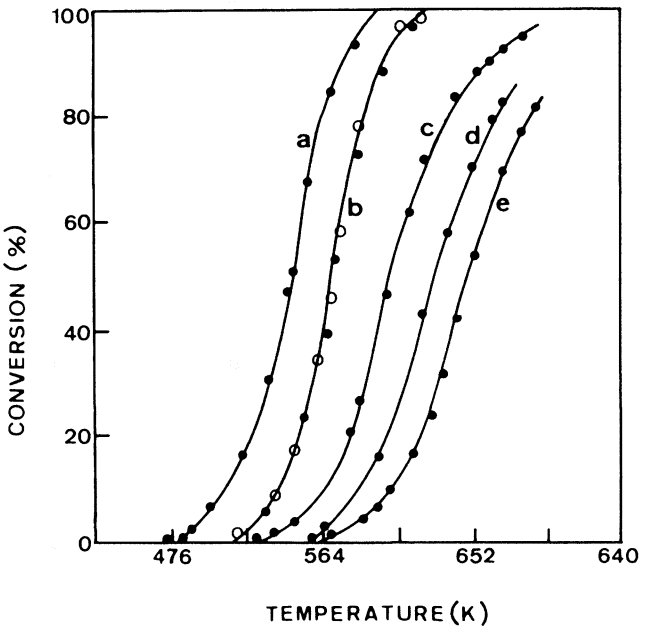

Fig. 2
n-Decane hydrogenolysis over 10% Fe on support catalysts: a) silica-873; b) silica-573 (open points); b) NaY-873 (full points); c) NaY-573; d) alumina-873 and e) alumina-573

The characterization of reduced Fe_2O_3, on NaY, alumina and silica by CO chemisorption, Mössbauer spectroscopy and XRD spectrometry is given in Table 2. The Mössbauer data indicate that in every case the Fe_2O_3 supported phase is reduced completely. At the two reduction temperatures used, all iron is kept inside the cages of the zeolite as shown by X-ray diffraction. Also on alumina, the dimensions of the iron particles remain in both cases below the detection limit of this technique, while on silica definitely larger iron particles are formed in comparable conditions. These trends are confirmed by the CO-chemisorption data. Indeed, on alumina and NaY a similar degree of metal dispersion is achieved, while on silica, the metal dispersion is lower. For all catalysts, an increased degree of sintering is found after the high temperature reduction.

Hydrogenolysis of n-Decane over Supported Iron Catalysts

Catalytic data for the hydrogenolysis of n-decane over the iron catalysts discussed above are presented in Table 3 and 4 and Fig. 2. While an apparent activation energy is found in the small range from 34 to 41 kJ mol^{-1} for all catalysts, a strong effect of the catalyst on the reaction rate can be observed (Table 3). With all three supports a higher reaction rate is noted when iron oxide is reduced at higher temperature. This treatment results in a lower iron dispersion. Iron dispersion however, is not the only rate determining parameter. At approximately 70% iron dispersion (Table 3), the hydrogenolysis rate is support dependent and decreases as follows:

silica > NaY > alumina .

Further insight into the structure-sensitivity of the decane hydrogenolysis reaction is obtained if the detailed product selectivities are compared (Table 4).

Table 2
Characterization of reduced Fe_2O_3 on different supports

Support	Reduction temperature (K)	CO chemisorption CO/Fe × 100	Mössbauer hyperfine splitting (T)	Isomershift relative to bulk Fe (mm s^{-1})	Intensity of Fe(111) reflection
NaY	573	90	33.1	0.0	– [1]
	873	68	33.1	0.0	–
alumina	573	90	33.1	0.0	–
	873	72	33.1	0.0	–
silica	573	75	33.1	0.0	+ [2]
	873	50	33.0	0.0	+ + [3]

[1] absent; [2] visible; [3] fairly, intense.

Table 3
Reaction rates for n-decane hydrogenolysis on supported iron catalysts[1]

Catalyst	Iron dispersion[2] (%)	Reduction temperature (K)	Reaction rate (r) at 540 K (mmol g^{-1} s^{-1} 10^8)	Apparent activation energy (E_a) (kJ mol^{-1})
Fe/NaY-573	90	573	1830	37.50
Fe/NaY-873	68	873	2650	34.50
Fe/alumina-573	90	573	324	41.08
Fe/alumina-873	72	873	1320	–
Fe/silica-573	68	573	4550	39.70
Fe/silica-873	50	873	6830	–

[1] Containing each 10% by weight of iron.
[2] From Table 2.

Table 4
Distribution of the hydrogenolysis products from n-decane over 10% Fe on support catalysts

Catalyst	Fe dispersion[1] (%)	Conversion (%)	Product distribution per carbon number (mol per 100 mol converted)								
			C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
alumina-573	90	10	524	16	10	9	8	8	8	10	9
NaY-573	90	10	399	16	14	13	10	10	10	10	15
NaY-873	68	10	213	26	8	8	6	6	5	21	44
silica-573	75	10	113	33	17	6	6	6	3	5	67
alumina-873	72	60	657	17	8	7	6	5	5	5	5
NaY-873	68	60	582	21	12	9	8	8	7	6	7
silica-873	50	60	135	15	12	10	10	10	9	10	11

[1] From Table 2.

The catalytic stability of the iron on NaY catalyst is remarkably good. The presented trends derived from kinetic and product distribution data obtained after 2 hours on-stream, remain virtually unchanged after 24 hours on stream.

Discussion

The assignment of the Mössbauer spectra of NaY/FeO_x to α-Cl or γ-Fe_2O_3 associated with the zeolite has been discussed earlier [16]. In this work a survey of literature Mössbauer parameters of supported and bulk α and γ-Fe_2O_3 and of Fe_2O_4 is made and compared to those of the NaY/FeO_x sample. If follows that the NaY/FeO_x and consequently the NaY/FeO_x^* sample consists of a α-Cl or γ-Fe_2O_3 phase intimately associated with the zeolite. The other physical measurements (XRD and TEM) confirm this and suggest that the iron oxide is dispersed in the intracrystalline void volume of the Y zeolite.

The F.T. behaviour of both materials also is identical, confirming the conclusions drawn from the physical characterization measurements. Characterization of an equilibrium NaY/FeO_x catalyst in a F.T. experiment has shown that during the transient behaviour a significant part of the iron sinters out of the zeolite and is transformed into a Fe_xC phase. The similarity in catalytic behaviour between NaY/

FeO_x and NaY/FeO_x^*, suggests that the same transformations occur on the NaY/FeO_x^* sample, prepared according to the presently presented method. The presence of two discrete hydrocarbon chain growth factors is in line with the presence of two sets of active sites, a bulk carbide phase located externally tot the zeolite crystals and residual iron still present in the zeolite cages. The present data do not allow to make any conclusions as to the nature of the latter phase: oxidic, metallic or carbidic.

The absence of any deactivation during the hydrogenolysis reaction clearly indicates that sintering of finally dispersed iron oxide during the F.T. reaction is not caused by the presence of a hydrocarbon atmosphere, but rather by the high partial pressure of water generated during the F.T. reaction. On the other hand, it seems that hydrogen reduction of Y zeolite supported Fe_2O_3, prepared by mild oxidation of adsorbed pentacarbonyl, constitutes a gentle method for the preparation of finely dispersed iron in the cages of zeolite Y. This is not possible when Fe(III)-exchanged Y zeolite is used as starting material [1, 2].

The decane hydrogenolysis reaction rate on zeolites, just like on other supports is shown to be dispersion-dependent. The higher the iron dispersion, the lower is the hydrogenolysis rate. This behaviour is expected for a structure-sensitive reaction [18]. The data also indicate that at comparable iron dispersion the hydrogenolysis rate is support dependent. The observed decrease in hydrogenolysis rate according to the sequence:

silcia > NaY > alumina

has been found earlier with other materials (Pt, Pd) and for other reactions (e.g. benzene hydrogenation) [17]. It corresponds to an increasing acidity or electron withdrawing capability of the respective supports. The dependence of catalyst activity upon the degree of dispersion and the nature of the support remains unchanged over the whole conversion range of the feed molecule, as can be derived from Fig. 2. The unchanged activation energy suggests that similar reaction paths exist on the iron surface of the catalysts, whereas the strong dependence of activity on metal dispersion is the result of an increased number of active sites available on the iron phase as its dispersion decreases. This classifies the n-decane hydrogenolysis as a structure-sensitive reaction, in agreement with the earlier findings of Sinfelt [18].

As far as the reaction mechanism is concerned this indicates that preferentially C_1 species are chopped from the longer hydrocarbon chain (Table 4). Although this seems to be a property of iron as catalyst, it can be amplified by increasing the dispersion of the metal or at a given dispersion by increasing the electron accepting properties of the support. These influences fit nicely in the Sinfelt picture [17] for ethane hydrogenolysis. The intermediates in this reaction are highly unsaturated hydrocarbon residues multiply bonded to surface metal atoms. The reaction is therefore dependent on the presence of specific geometric arrangements of surface atoms or of their electronic properties. The existence of both phenomena is evidenced by alloy dilution experiments and correlations with the percentage d-character of the catalytic elements respectively [18].

The two parameters determining the activity are found to influence the product distribution as well. It is obvious that with higher dispersion of iron an increased selectivity for methane compared to all other products is observed. At both conversion levels, the support effect at identical dispersion on the methane selectivity is clearly present. Indeed, the methane yield increases as follows:

at 10% conversion: silica-573 < NaY-873
at 60% conversion: NaY-873 < alumina-873 .

The molar distribution among C_5 is still asymmetrical even when abstraction is made from C_1 and C_9. This asymmetry is more pronounced at the high conversions.

It is well established that the nature of the catalytic element determines also the product distribution in the hydrogenolysis reaction. Ni attacks selectively the ends of alkane chains, whereas Pt is the other extreme since it breaks statistically all C–C bonds [19]. The iron catalysts represent examples of the former type of cleavage, with preference for attack at the end of the hydrocarbon. This preference is definitely less pronounced on iron compared to nickel, but it seems that degree of metal dispersion and support influence can modify this behaviour.

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References

[1] Y. Y. Huang and J. R. Anderson, J. Catal. *40*, 143 (1975).
[2] R. L. Garten, W. N. Delgass, and M. Boudart, J. Catal. *18*, 19 (1970).
[3] F. Schmidt, W. Gunsser, and J. Adolph, A.C.S. Symp. Ser. *40*, 291 (1977).
[4] L. B. Lee, J. Catal. *68*, 27 (1981).
[5] D. Ballivet-Tkatchenko, G. Coudurier, H. Mozzanega, and I. Tkatchenko, Fund. Res. Homog. Catal., p. 257, ed. Tsutsui, New York 1979.
[6] D. Ballivet-Tkatchenko and G. Coudurier, Inorg. Chem. *18*, 558 (1974).
[7] D. Ballivet-Tkatchenko, N. D. Chau, H. Mozzanega, M. C. Roux, and I. Tkatchenko, A.C.S. Symp. Ser. *152*, 187 (1981).
[8] D. Ballivet-Tkatchenko, C. Coudurier, and N. D. Chau, Stud. Surf. Sci. Catal., Elsevier *19*, 123 (1982).
[9] L. F. Nazar, G. A. Ozin, F. Hugues, J. Godber, and D. Rancourt, J. Molec. Catal. *21*, 313 (1983).
[10] J. B. Nagy, M. van Eenoo, and E. G. Derouane, J. Catal. *58*, 230 (1979).
[11] F. Schmidt, Th. Bein, U. Ohberich, and P. A. Jacobs, Sixth Int. Zeolite Conf., p. 151, eds. D. Olson and A. Bisio, Butterworth 1984.
[12] Th. Bein, F. Schmidt, and P. A. Jacobs, Int. Symp. Zeolites, Portrose 1984, in press.
[13] A. X. Trautwein, E. Bill, R. Bläs, G. Doppler, F. Seel, B. Wolf, R. Klein, and U. Gonser, Surf. Sci. *156*, 140 (1985).
[14] D. G. Rancourt, S. R. Julian, and J. M. Daniels, J. Magnet. Magn. Mater. *49*, 305 (1985).
[15] L. F. Nazar, G. A. Ozin, F. Hugues, J. Godber, and D. Rancourt, J. Mol. Catal. *21*, 313 (1983).
[16] Th. Bein, G. Schmiester, and P. A. Jacobs, J. Phys. Chem. 1986, in press.
[17] F. Figueras, R. Gomez, and M. Primet, Adv. Chem. Ser. *121*, 480 (1973).
[18] J. H. Sinfelt, Catal. Rev. Sci. Eng. *9*, 147 (1974).
[19] J. E. Germain, "Catalytic Conversion of Hydrocarbons", p. 119, Academic Press 1969.

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