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Characterization of Nickel Dispersions in Reduced Nickel Faujasites by Transmission Electron Microscopy

Metal dispersions with narrow particle size distributions are of great interest for the study of correlations between the structure and function of metal catalysts (*1*, *2*). The zeolite matrix proves to be especially suited for the preparation of finely divided metals with a narrow particle size range (*3*). Recently metal aggregate phases within the faujasite framework were found with aggregate sizes ranging from 3 nm for Pd (*4*) or 4 nm for Ru (*3*) to 8 nm for Pt (*5*). Among the methods applied for the identification of highly dispersed metals, transmission electron microscopy has turned out to be a unique tool for the characterization of supported metal phases and particle size distributions. In the following, transmission electron micrographs of reduced nickel faujasite catalysts are presented and discussed.

The preparation of the nickel faujasites used in the study (Table 1) has been described in detail elsewhere (*6*). All pretreatments of the samples (the temperature-programmed dehydration, the reduction by hydrogen, and catalytic reaction) have been carried out in a fluidized bed reactor where shallow bed conditions are maintained rather than deep bed conditions. All samples were analyzed by X-ray diffraction in parallel with transmission electron microscopy.

For electron microscopy samples were embedded in an epoxy resin and specimens (50–80 nm thick) were cut by an ultramicrotome (OMU 3; thermal advance; diamond knife). The micrographs were obtained by transmission electron microscopy (Zeiss EM 10; resolution ~0.5 nm; accelerating potential, 100 kV).

Micrographs, which are representative for each sample in the freshly reduced and catalytically applied states, are given in Figs. 1–3. The phase contrast imaging of the faujasite lattice, obtained with properly tilted specimens (Fig. 4), demonstrated that the metal aggregates can be clearly distinguished from the support. The reduced samples (Figs. 1a–3a) show mainly monodispersed nickel with mean aggregate sizes of 6–8 nm (NiCaX 5), 8–10 nm (NiCaX 1.1), and 12–14 nm (NiX 17). There was no indication for sintering caused by the focused electron beam. It can be concluded from the following facts that the monodispersed nickel aggregates of round shape are located inside the faujasite bulk: (i) all splintered chips (average thickness ~50 nm) that are cut from faujasite crystals (average size ~1000 nm) contain nickel particles; (ii) the nickel particles are randomly distributed without any accumulation at the border of the chips. Following the catalytic carbon monoxide hydrogenation reaction only the sample NiCaX 5 contains monodispersed nickel with narrow aggregate size distribution (Fig. 1b). The slight increase of the mean aggregate size, which results from the analysis of a series of micrographs indicates an additional reduction during the catalytic reaction. The samples NiCaX 1.1 (Fig. 2b) and NiX 17 (Fig. 3b) exhibit bidispersed nickel with aggregates of round shape (10–20 nm) inside the bulk as well as particles of crystal forms with corners and plane surfaces (20–50 nm) outside the zeolite crystals.

Samples containing monodispersed nickel in the electron micrographs do not show distinct nickel lines in the X-ray diagrams (Fig. 5a), while samples showing bidispersed nickel of larger particle size in the electron micrographs exhibit X-ray diffraction lines due to nickel (Fig. 5b). The X-ray diagrams prove that the overall crystalline structure of the zeolite was maintained. The maintenance of the crystalline structure is also confirmed by the phase contrast imaging of the zeolite lattice (Fig. 4). The determination of the mean nickel aggregate

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TABLE 1

Composition and Catalytic Properties of the Nickel Faujasites Analyzed by Transmission Electron Microscopy[a]

Abbreviation	Composition	Catalytic activities[b]					
		250°C		300°C		350°C	
		1 hr	6 hr	1 hr	6 hr	1 hr	6 hr
NiCaX 5[c]	$Ni_{9.6}Ca_{10.6}Na_{45.5}X$	14	27	209	214	499	520
NiCaX 1.1[d]	$Ni_{10.1}Ca_{10.7}Na_{44.5}X$	4	4	82	103	164	70
NiX 17	$Ni_{7.6}Na_{70.8}X$	53	46	242	242	786	544

[a] From Ref. (6).

[b] Hydrocarbon yields [mg(hydrocarbon)/g(nickel) · hr] in the carbon monoxide hydrogenation reaction; 1 bar; $CO/H_2 = 3/7$; 300 GHSV; 1 and 6 hr time on stream; fluidized bed reactor.

[c] Simultaneous ion exchange of calcium and nickel.

[d] Consecutive ion exchange of calcium and nickel.

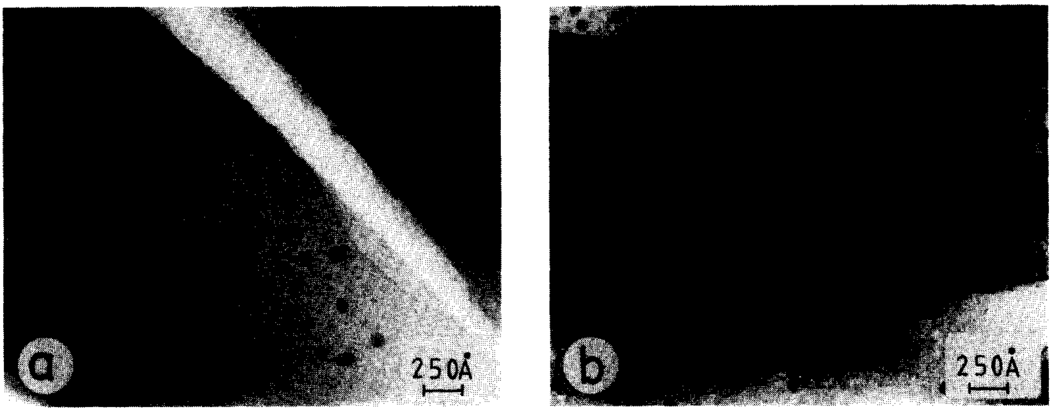

FIG. 1. Transmission electron micrographs of nickel aggregates in sample NiCaX 5: (a) following reduction (H_2, 1 bar, 300°C, 25 hr); (b) following the catalytic reaction.

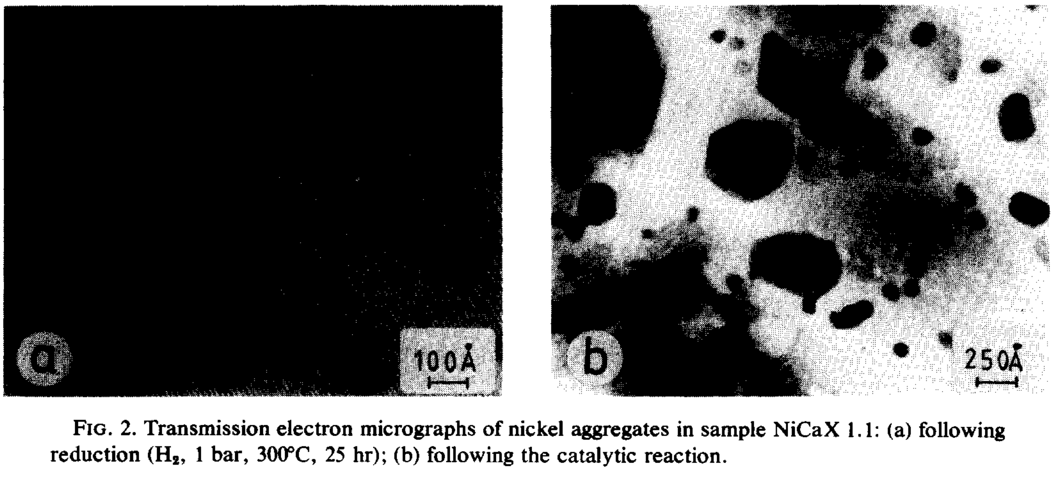

FIG. 2. Transmission electron micrographs of nickel aggregates in sample NiCaX 1.1: (a) following reduction (H_2, 1 bar, 300°C, 25 hr); (b) following the catalytic reaction.

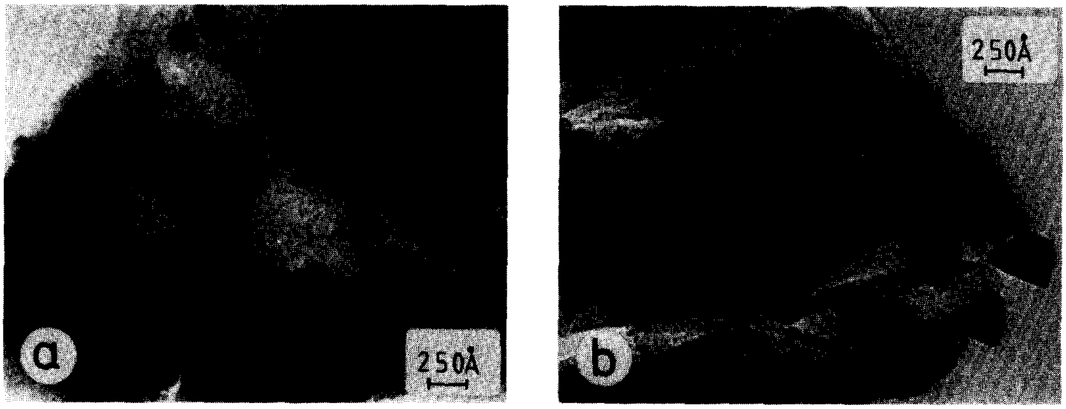

FIG. 3. Transmission electron micrographs of nickel aggregates in sample NiX 17: (a) following reduction (H_2, 1 bar, 300°C, 25 hr); (b) following the catalytic reaction.

FIG. 4. Transmission electron micrograph of a nickel aggregate in sample NiX 17 following the catalytic reaction with phase contrast imaging of the zeolite lattice.

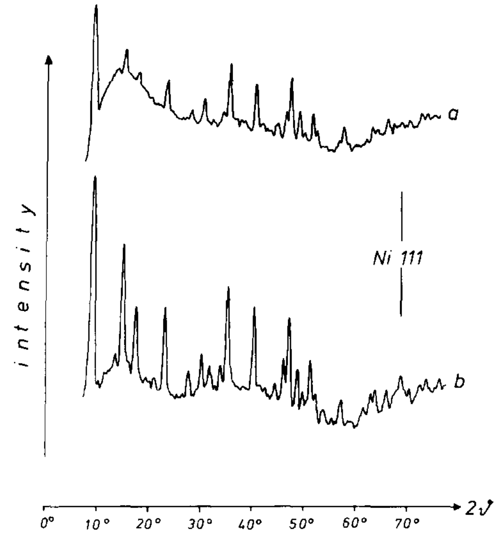

FIG. 5. X-Ray diagrams of the sample NiCaX 1.1: (a) following reduction (H_2, 1 bar, 300°C, 25 hr); (b) following the catalytic reaction.

size within the faujasite bulk from the X-ray diagrams suffers from the lack of significant signals probably due to a strong scattering effect by the zeolite matrix.

The transmission electron micrographs of reduced nickel faujasites prove that besides the well-known phase of nickel particles outside the zeolite crystals also nickel aggregates up to 14 nm can grow in the zeolite bulk (*13*). A monodispersed nickel phase of this new type with a narrow aggregate size distribution (6–9 nm) remains stable with respect to sintering (Fig. 1b) and catalytic activity (Table 1) up to 350°C, if the faujasite was loaded with nickel and calcium ions simultaneously in the ion exchange step of the preparation procedure.

Recently some insight into the reduction mechanism of nickel ions in the faujasite framework has been obtained (*6–11*). There is an increasing agreement that in carefully dehydrated samples nickel will be reduced preferentially in the S I positions in the hexagonal prisms (*6, 7, 10, 11*). Here the nickel ions are in a surrounding which is close to an octahedral symmetry and which will be occupied preferentially due to the favorable ligand field stabilization. Additionally introduced calcium ions can unfavorably influence the nickel reduction process, as can be drawn from the lower initial catalytic activity of the calcium containing samples (Table 1, columns 4 and 5). If the calcium is introduced first in a consecutive ion exchange procedure (sample NaCaX 1.1), then the nickel ions are unable to reach the favorable S I positions, because they have to pass the cubooctahedra (*12*), which could be filled with calcium ions. This results in a relatively low occupation of the S I positions by nickel ions prior to the reduction and a low initial catalytic activity. The situation is more favorable if the nickel ions are introduced simultaneously with the calcium ions, because now they can compete for the hidden positions from the beginning, thus increasing the occupation of the S I sites prior to reduction resulting in a higher initial catalytic activity.

Ideas about the growth of metal aggregates within the zeolite framework, which are much larger than the supercages, have not yet been put forward. Small nickel clusters of a few atoms should be mobile enough to move through the lattice until they can agglomerate to large and immobile aggregates, which will be randomly distributed within the zeolite bulk. Immobile anchored aggregates can grow further by attaching nickel ions, which will be reduced more readily on the hydrogen activating metal phase. The reduction process produces protons, which can cause bond ruptures or local destructions in the faujasite framework surrounding the metal aggregate. The aggregate containing holes in the bulk are continuously enlarged in this way, thus enabling the metal particle growth to proceed.

In this context the stabilizing role of the simultaneously introduced calcium ions toward sintering has to be elucidated. Presumably the enhancement of the thermal stability of the faujasite lattice by polyvalent, unreducible cations will be highest if these ions are evenly distributed throughout the zeolite framework, which is achieved best by a simultaneous exchange together with reducible cations.

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