Characterization of Iron Catalysts Prepared by Chemical Vapor Deposition on Nonzeolitic Supports †

Juan D. Henao, Bin Wen,[§] and Wolfgang M. H. Sachtler*

Center for Catalysis and Surface Science, Institute for Environmental Catalysis, Northwestern University, 2137 Tech Drive, Evanston, Illinois 60208

Received: January 27, 2004

Chemical vapor deposition (CVD) of FeCl₃ has been used to deposit Fe^{3+} ions on the surface of sulfated zirconia (SZ) and silica-alumina (SA). Upon exposure to $FeCl_3$ vapor most Brønsted acid sites and silanol groups are replaced by Fe, as evidenced by IR. With SZ the concentration of the acid sites and thus the retention of Fe increase with the sulfate loading up to \sim 45% of a monolayer, followed by an abrupt decrease at higher loadings. This indicates condensation of sulfate groups to polysulfates, which is in line with a lower number of Brønsted sites per sulfate. Release of HCl due to the reaction of Brønsted sites with FeCl3 peaks at 85 °C for SZ but only at 345 °C for SA. After replacing Cl^- by OH^- and calcining, the materials were tested as De-NOx catalysts and characterized by temperature-programed reduction (TPR) with H₂ or CO. Mononuclear and dinuclear oxo-ions of Fe coexist with Fe oxide particles in calcined Fe/SA, resulting in a low selectivity for NO_x reduction. During reduction of Fe/SA up to 800 °C, a significant fraction of the Fe forms a chemical compound with SA, possibly an aluminate. In Fe/SZ the Fe dramatically increases the reducibility of the sulfate groups, from 57% partial reduction to SO_2 in the absence of Fe, to 90% deep reduction to S²⁻ ions in its presence. Formation of Fe sulfide is indicated by the enhanced sulfur retention upon reduction. Fe/SZ is active for NO_x reduction with isobutane. Catalysts with low Fe content that are prepared by controlled sublimation are superior to those prepared by impregnation. At 450 $^{\circ}$ C and GHSV = 30 000 h⁻¹, 65% of NO_x is reduced to N₂ in excess O₂.

Introduction

Heterogeneous catalysts, exposing transition metal ions as active sites on high-surface-area supports, are usually prepared by impregnation, coprecipitation, or ion exchange from aqueous solution. In recent years two novel techniques, chemical vapor deposition (CVD) and solid state ion exchange (SSI), have been added to this toolbox.^{1,2} They have mainly been applied to zeolites, for instance, Fe/MFI and Co/MFI (the MFI zeolite is often called ZSM-5), which are remarkably active and selective catalysts for the selective reduction of NO and NO2 to N2 with hydrocarbons as reductants.³⁻⁶ As these catalysts operate in an atmosphere containing O2 and H2O vapor in large excess over NO_x, the demands on activity and selectivity are very high. Since it would be desirable to achieve a similar performance with supports of higher thermal stability, the question arises whether the same preparation techniques are also applicable to highsurface-area supports such as silica-alumina or sulfated zirconia. The present paper addresses this issue.

For zeolites it is certain that catalysts prepared by CVD or SSI expose sites that are qualitatively different from those obtained by ion exchange from solution or by impregnation.^{3,7,8} As the number of exchange positions in a zeolite is given by the number of Al-centered tetrahedra, N(AI), conventional ion exchange of an Fe³⁺ solution with a Na-zeolite is limited to a ratio of Fe to Al ions $N(Fe)/N(AI) = \gamma = 1/3$. In contrast, the

CVD technique using FeCl₃ vapor interacting with the acid sites of H-MFI leads to $\gamma = 1.0$, a value easily obtained experimentally, as IR data confirm that all Brønsted protons of H-MFI are swiftly replaced by [FeCl₂]⁺ ions:

$$H^{+}_{zeol} + (FeCl_{3})_{vapor} \rightarrow [FeCl_{2}]^{+}_{zeol} + HCl_{vapor}$$
(1)

As most zeolites have lattice imperfections and silanol groups leading to additional acid sites, the experimental value of γ will exceed unity. This confirms that for the CVD technique the strong Brønsted acidity characteristic of zeolites is not required, which is an additional argument for exploring the potential of applying this preparation technique to less strong solid acids.⁷

Exchange of the Cl⁻ ions against OH⁻ groups by hydrothermal treatment transforms [FeCl₂]⁺ ions to Fe-hydroxo ions which can reorganize themselves during calcination to oxo-ions, Fe oxide nanoparticles, and bare ions. Techniques exist to limit the formation of the usually undesirable oxide particles far below the amounts obtained by conventional impregnation.^{3,9} Oxoions and oxide particles are also formed on amorphous supports such as Al₂O₃ when using traditional impregnation, but they readily form solid solutions or aluminates which make it impossible to distinguish the oxygen ligated to the active metal from that of the support. For CVD-prepared Fe/MFI catalysts, however, isotope exchange with gaseous ¹⁸O₂ distinguishes clearly between the oxygen atoms in oxo-ions and those of the zeolite lattice.¹⁰ In addition to the higher value of γ , this propensity that zeolite-supported oxo-ions have their own oxygen ligands which are not shared with the supporting oxide could be a major cause of the specific catalytic qualities of CVDprepared transition metal/zeolite catalysts. An objective of the

[†] Part of the special issue "Michel Boudart Festschrift".

^{*} Corresponding author. Phone: (847) 491-5263. Fax: (847) 467-1018. E-mail: wmhs@northwestern.edu.

[§] Present address: Nano Dynamics Inc., 901 Fuhrmann Blvd., Buffalo, NY 14203.

present study is to find whether similar catalytic qualities can be attained with nonzeolite systems by preparing them with the CVD technique.

The notable Brønsted acidity of silica–alumina makes this material suitable for anchoring iron by CVD. Varying the silica/ alumina ratio permits modification of its acidity and catalytic activity.^{11–13} Sulfated zirconia is an even stronger acid; both Lewis and Brønsted acid sites are exposed. One OH group per sulfate is bound through its H atom to a surface oxygen,¹⁴ while sulfur retains its oxidation state of +6.15 Sulfated zirconia is usually prepared by impregnation of Zr(OH)₄ with (NH₄)₂SO₄ or H₂SO₄ followed by drying and calcination at 500–750 °C.¹⁶ The structure, texture, and catalytic activity of **SZ** depend on the pH used to precipitate Zr(OH)₄, the source of the sulfate and its concentration in the solution, and the calcination temperature.^{17–19}

In the present work, the CVD technique is used in the preparation of Fe/SZ and Fe/SA. Temperature-programed reduction, FTIR, and XRD have been used to characterize the anchored iron and other structural elements related to the catalytic activity. Catalytic tests were done on the reduction of NO_x with isobutane in the presence of excess oxygen and water vapor.

Experimental Section

Catalyst Preparation. Commercial silica–alumina (**SA**) (Aldrich, 76% SiO₂, 13% Al₂O₃) with a BET surface area of 475 m²/g has been used as a support. Sulfated zirconia (**SZ**) was prepared by stirring a slurry of 32 g of Zr(OH)₄ (Magnesium Elektron Inc., 70.4% ZrO₂; BET area 100 m²/g) and 25 mL of an aqueous solution of sulfuric acid (Mallinckrodt, 96.1%) at 80 °C until a dry powder was obtained (usually after 1 h). Seven samples were prepared by varying the H₂SO₄ concentration while keeping the amount of Zr(OH)₄ constant. The materials were dried overnight at 110 °C, then calcined in O₂ at 600 °C for 4 h. At this temperature tetragonal ZrO₂ is formed, while decomposition of the SO₄ groups is prevented.^{20,21}

Temperature-programed surface reaction (TPSR) runs were done with **SA** and **SZ** to establish the temperatures for maximum rate of iron deposition from the FeCl₃ vapor. An amount of 1 g of either support (**SA** or **SZ**) was loaded in a U-shaped quartz reactor and heated for 1 h at 550 °C in an Ar flow. After cooling the sample to room temperature, 0.5 g of FeCl₃ was loaded in the opposite side of the U-shaped reactor. Under a flow of Ar through both beds the reactor was heated from 25 to 500 °C with a ramp of 5 °C/min. The HCl produced was quantified by using a Dycor M200 mass spectrometer (MS).

SA and seven **SZ** samples of different sulfate content were submitted to isothermal CVD of FeCl₃ at the previously determined optimum temperature. Typically, 10 g of sample, 3 g of FeCl₃, and 120 mL/min of Ar were used. While [FeCl₂]⁺ ions were formed at the surface, the released HCl was absorbed in an NaOH solution. The reaction stopped when all reactive protons were replaced by [FeCl₂]⁺ ions; the excess FeCl₃ vapor passed through the solid bed without being retained.

The Fe-loaded samples were washed with 2-fold deionized water to replace Cl⁻ ions by OH⁻ groups, then dried at 110 °C and calcined in flowing O₂ at 500 °C (600 °C for SZ) for 2 h. Due to the different sulfate loads in each of the SZ samples, their capacity to retain iron during sublimation was found to be different. We will refer to them as Fe/SZ-*j*, with *j* = 1, 2, ..., 7. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) shows that the Fe/S ratio in the Fe/SZ samples varies between 0.10 and 0.75, whereas the Fe/Al ratio in Fe/SA was ~0.25.

For comparison, two Fe/SZ samples were prepared by impregnation. In this case, iron was loaded as iron(II) oxalate dihydrate (Aldrich, 99%) dissolved in water; 0.3 mL of this solution was dosed per gram of solid. The materials were dried overnight and calcined in an O₂ flow at 600 °C for 2 h. These samples will further be labeled as Fe/SZ-1-I and Fe/SZ-5-I; their Fe content is equal to that of the CVD-prepared samples Fe/SZ-1 and Fe/SZ-5, respectively.

Characterization. FTIR was used to determine the effect of iron deposition on the acid sites; data were acquired with a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a DTGS detector by recording 150 scans with a resolution of 1 cm⁻¹. Sample wafers of $8-10 \text{ mg/cm}^2$ were placed into a flow-through quartz cell sealed with NaCl windows. They were calcined in O₂ at 450 °C before analysis; spectra of materials at different stages of preparation were collected in the transmittance mode in a dry He flow at room temperature.

In order to identify the oxidation state of the iron, H₂-TPR and CO-TPR measurements were performed. For H2-TPR the samples were put in a quartz reactor, calcined in flowing O2 at 500 °C for 2 h, and then cooled to room temperature. Flowing oxygen was then replaced by Ar for 1 h before admitting the reducing mixture (5% H₂/Ar at 40 mL/min). The sample was heated under this reduction gas from 25 to 800 °C at a rate of 8 °C/min, while the H₂ consumption was monitored with a Gow-Mac thermal conductivity detector (TCD) located downstream of a cold trap. For Fe/SZ an n-pentane/N2 trap (-131 °C) was used to retain H₂S and SO₂, whereas a dry ice trap (-78.5 °C)was used to retain the water generated by reduction of Fe/SA. CO-TPR was only done with Fe/SA; the sample was first calcined in O₂ at 500 °C for 2 h, cooled to room temperature, purged with He, and then contacted with a CO/Ar (2%) flow at 75 mL/min. A Dycor M200 mass spectrometer (MS) was used to monitor the consumption of CO (m/e = 28, 14) and the evolution of CO₂ (m/e = 44, 28), H₂O (m/e = 18), and H₂ (m/e= 2), while the temperature was increased from 25 to 760 $^{\circ}$ C at a ramp of 8 °C/min. The contribution of CO_2 to the m/e =28 signal was subtracted before calculating the CO consumption.²² The TCD and MS detectors were calibrated for H₂ and CO consumption by using known amounts of CuO. Temperature-programed oxidation (TPO) in an O₂/He (5%) mixture was carried out between 25 and 760 °C to quantify any carbon deposits.

XRD patterns were recorded in a Rigaku DMAX diffractometer, using Ni-filtered Cu K α radiation ($\lambda = 1.540598$ Å); scanning was conducted from $2\theta = 5^{\circ}$ to $2\theta = 70^{\circ}$ at a scan step of 0.1°. Surface areas were determined with a Micromeritics ASAP 2010 liquid nitrogen analyzer, after degassing the samples overnight at 0.1 Pa and 350 °C.

Catalytic Tests. Catalytic reduction of NO_x with isobutane was studied in a microflow reactor using a 200 mL/min feed gas containing 0.1% of a NO + NO₂ mixture (from a cylinder that originally contained pure NO₂), 0.1% *i*-C₄H₁₀, 2% O₂, and 1% H₂O. The actual NO/NO₂ ratio at the catalyst depends, of course, on the temperature and will be higher at high temperature. Catalytic data will, therefore, be expressed in terms of NO_x conversion and N₂ yield, with NO_x = NO + NO₂. The catalyst was either 550 mg of Fe/SZ or 200 mg of Fe/SA, resulting in a GHSV of 30 000 h⁻¹. In a typical test, the sample was loaded in a U-shaped quartz reactor, calcined in flowing O₂ at 500 °C for 2 h, then cooled to 150 °C before feeding the reaction mixture. The effluent gas was monitored while the temperature was raised stepwise from 250 to 550 °C. Sampling was performed 30 min after reaching each preset temperature.



Figure 1. HCl generated by CVD of FeCl₃ onto (a) SZ-1 and (b) SA as determined by TPSR experiments. MS signal normalized per unit surface area.

Reaction products were analyzed on-line by GC-TCD using Alltech 13X molecular sieve and Porapak Q columns. To prevent water condensation, all lines were kept at 80-100 °C by means of heating tapes. An ice-water trap was positioned before the GC to condense most of the water vapor and protect the packed columns. The N₂ yield was calculated from the N₂ formation, while the hydrocarbon combustion was quantified from the amounts of CO and CO₂.

Results

To determine the most favorable temperatures for deposition of FeCl₃ onto **SZ** or **SA**, preliminary TPSR runs were carried out by mass spectrometrically monitoring the HCl that is produced when FeCl₃ vapor reacts with surface protons. The results are shown in Figure 1; the features are characteristic of the reactivity of the acid sites toward FeCl₃. Sulfated zirconia displays two types of H⁺ sites: one type is very active at a relatively low temperature; sites of the other type are less active but much more numerous, giving the dominant TPR peak at 285 °C. The width of the feature between 60 and 200 °C suggests a rather wide distribution in reactivity of the former sites. The TPSR profile of **SA** is dominated by one large, asymmetric feature, peaking at 345 °C; the shoulder at 300 °C is representative of the Brønsted sites.

On the basis of these results, sulfated zirconia and silica– alumina were exposed to FeCl₃ vapor at 285 °C and 345 °C, respectively. Saturation was attained after 3 h for **SA** and after 4-5 h for **SZ**. The capacity of **SZ** samples to retain iron from the vapor depends on their sulfate load. Once saturation is achieved, no further uptake of iron or change in color is registered, even if exposure to the FeCl₃ vapor is continued for 4 additional hours. Values of the ICP-AES chemical analysis, including the impregnated samples, are compiled in Table 1.

Figure 2 shows how the sulfate content in **SZ** is crucial for its capacity to retain iron. The iron uptake increases with sulfate content; it reaches a maximum at 30×10^{-5} mol SO₄²⁻/g catalyst (0.96% S) but precipitously decreases at higher sulfate concentrations. At this stage the surface coverage of zirconia with sulfate is 45% of the monolayer coverage calculated for a size per sulfate group of 0.25 nm². Higher coverage of the surface with sulfate results in much lower retention of Fe from FeCl₃.

IR results are shown in Figure 3. As each spectrum was measured with a different wafer, different intensities of a given



Figure 2. Effect of sulfur content on (a) sulfated zirconia capacity to retain iron and (b) sulfate surface coverage.

 TABLE 1: Chemical Composition of Catalysts Prepared by

 CVD and Impregnation

		molar ratio		
sample	wt (%) Fe	Fe/S	Zr/S	Fe/Al
Fe/SZ-1	0.19	0.10	19.7	
Fe/SZ-2	0.26	0.14	24.1	
Fe/SZ-3	0.46	0.25	24.1	
Fe/SZ-4	0.50	0.75	65.4	
Fe/SZ-5	0.61	0.54	39.2	
Fe/SZ-6	0.64	0.44	30.4	
Fe/SZ-7	0.74	0.45	23.6	
Fe/SZ-1-I	0.16	0.05	12.4	
Fe/SZ-5-I	0.59	0.19	13.2	
Fe/SA	2.41			0.24

band in different spectra reflect, in part, different thicknesses of these wafers and should not be used for quantitative evaluations. The bands corresponding to the OH groups vanish after CVD, indicating complete substitution of H⁺ by [FeCl₂]⁺, both in **SZ** and **SA**. Trace a in Figure 3A shows the spectrum for **SZ-1** after calcination at 450 °C in flowing O₂. It exhibits the characteristics typical of sulfated zirconia and metalpromoted sulfated zirconia;^{15,23,24} the band at 3645 cm⁻¹ is assigned to its strong Brønsted acid sites.^{25,26} In Figure 3B trace a shows the spectrum of **SA**, where the band at 3743 cm⁻¹ represents free hydroxyl groups, while the broad band between 3690 and 3530 cm⁻¹ is due to the Brønsted acid sites.^{11,27,28} Exposure to FeCl₃ affects both the Brønsted sites and the



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Figure 3. Infrared spectra of **SZ-1** (Panel A) and **SA** (Panel B): (a) fresh, (b) after CVD, and (c) after CVD and hydrolysis. All samples were calcined at 450 $^{\circ}$ C in O₂ flow.



Figure 4. H₂-TPR profiles of (a) SZ-1, (b) Fe/SZ-1 after calcination in O₂ flow at 500 $^{\circ}$ C.

terminal silanol groups, lowering their band intensity to almost zero, as is clear from traces b in Figure 3. Subsequent washing and calcination regenerates the OH sites. In the case of sulfated zirconia, a new band arises at 3770 cm⁻¹ (see Figure 3A, trace c) which is similar to that of the terminal OH groups (3780 cm⁻¹) on sulfate-free zirconia.^{29,30} This suggests that upon washing some OH groups are formed that are similar to those on sulfate-free zirconia, which is a weaker acid than **SZ**.

Figure 4 shows the H₂-TPR profiles of **SZ-1** and Fe/**SZ-1**; they are representative of the set of sulfated zirconias used in this study. The profile of **SZ-1** displays one large feature starting at 500 °C and peaking at 738 °C; this peak is attributed to



Figure 5. XRD patterns of (a) SZ-1, (b) SZ-7, (c) Fe/SZ-1, and (d) Fe/SZ-7 after calcination in O_2 flow at 600 °C.

TABLE 2: H₂ Consumption in TPR Experiments over SZ-1, SZ-7, Fe/SZ-1, and Fe/SZ-7 Samples

	Fe		S^{6+} to S^{4+}	S^{6+} to S^{2-}	peak temp
sample	(wt %)	H ₂ /(S+Fe)	(%)	(%)	(°C)
SZ-1	0	2.1	57	43	738
SZ-7	0	2.1	57	43	732
Fe/SZ-1	0.19	3.2	10	90	499
Fe/SZ-7	0.74	2.8	11	89	486

reduction of the sulfate groups, as previous experiments showed that no reduction of unsulfated zirconia takes place in this temperature region.³¹ In the presence of Fe this peak is shifted to lower temperature by more than 200 °C, indicating that Fe strongly catalyzes the reduction of sulfate groups. The peak positions for Fe/SZ-1 and Fe/SZ-7 (see Table 2) suggest that the reduction temperature varies with the Fe load and is lower for higher iron loads. This has been confirmed for other Fe/SZ samples not shown here.

Integration of profiles a and b, and those not shown of SZ-7 and Fe/SZ-7, provides the data in Table 2. While SZ-1 and SZ-7 consume roughly four H atoms per S atom (H₂/S = 2.1), the hydrogen consumption in Fe/SZ-1 and Fe/SZ-7 is much higher, suggesting complete reduction of the Fe³⁺ ions and most of the sulfate to sulfide. As previous work showed that SO₂ and S²⁻ ions are preferred reduction products of sulfate groups in SZ, the results are rationalized by assuming that no other reduction products are formed. This leads to the result that sulfate groups in SZ-1 and SZ-7 are reduced by ~57% to SO₂ and by 43% to sulfide ions. Upon applying the same assumption to the samples loaded with iron, it follows that ~90% of the surface sulfate groups are reduced to S²⁻ ions.

XRD patterns for iron-free and iron-doped **SZ-1** and **SZ-7** in Figure 5 indicate that both supports were present in the tetragonal modification $(2\theta = 30.3^{\circ})$; a small amount of monoclinic zirconia $(2\theta = 28.7^{\circ})$ was also detected in Fe/SZ-**1**. Formation of FeSO₄ $(2\theta = 18.1^{\circ}, 19.8^{\circ})$, Zr(SO₄)₂ $(2\theta =$ $13.6^{\circ}, 20.5^{\circ})$, hematite $(2\theta = 33.3^{\circ}, 35.7^{\circ})$, wüstite (ferrous oxide; $2\theta = 36.1^{\circ}, 41.9^{\circ})$, or magnetite $(2\theta = 30.1^{\circ}, 35.4^{\circ})$ was not apparent from the XRD data. The CVD method is known to prevent the formation of large iron oxide clusters. The XRD patterns for the samples prepared by impregnation, that is, Fe/SZ-1-I and Fe/SZ-5-I, have the same characteristics as those of Figure 5.

H₂-TPR profiles of Fe/**SA** are shown in Figure 6. Profile A displays six overlapping peaks, some of which may be due to stepwise reduction of a given species in the original sample. Blank experiments confirmed the absence of any TPR peaks



Figure 6. H₂-TPR profiles of fresh Fe/SA (Panel A) and CO-reduced Fe/SA (Panel B). Fresh Fe/SA calcined in O_2 flow at 500 °C before reduction.

for **SA**. Formation of iron oxide nanoparticles that are not detectable by XRD is indicated by the TPR data. To get more information on the nature of the iron species, we decided to also use CO-TPR, as this method discriminates between Fe oxoions (and oxide particles) and bare Fe ions. Reduction of bare Fe ions by H_2 implies removal from Fe of positive charge which ends up in protons. Reduction of neutral oxide particles implies removal of oxygen only; this can be done either by hydrogen or by carbon monoxide. Reduction of Fe oxo-ions requires removal of both oxygen and charge. These two phenomena can be separated by first using CO-TPR to remove oxygen, followed by H_2 -TPR to remove the charge.

Figure 7 shows the CO consumption and the CO₂ formation during CO-TPR. The results indicate the presence of large amounts of oxo-ions, indicating dinuclear (or multinuclear) oxygen-bridged species in which two Fe³⁺ are easily reduced to Fe²⁺ by removal of the bridging oxygen. An inherent complication of the CO-TPR technique is that water gas shift and the Boudouard reaction will also consume CO and produce CO₂. In the present work the temperature was kept below the value where the Boudouard reaction is known to take place. Formation of H₂ was monitored, and it was found that the peak at 527 °C is largely caused by water gas shift; this peak will further be disregarded in the analysis of the oxidation states of iron. The first two peaks correspond to true reduction of iron oxide particles and iron oxo-ions.

As reduction of Fe oxide particles with CO will give Fe⁰, but that of Fe oxo-ions will create bare Fe ions, one can discriminate between both types by H₂-TPR after CO-TPR. The



Figure 7. CO consumed (Panel A) and CO₂ generated (Panel B) by CO-TPR of fresh Fe/SA. Fresh Fe/SA calcined in O_2 flow at 500 °C before reduction.

result of such a second H_2 -TPR run is shown in Figure 6B. The difference between profiles A and B in that figure illustrates the abundance of oxo-ions in calcined Fe/**SA**. A tentative assignment of the peaks will be presented in the Discussion.

The materials were probed as catalysts in the reduction of NO2 with *i*-C4H10 in a "wet" feed. Figure 8A shows the temperature dependence of the N2 yield for the samples prepared by CVD while Figure 8B compares the activities of Fe/SA and the iron-impregnated samples. Fe/SA is found to have a very low catalytic activity for this reaction, but some of the Fe/SZ samples display higher N₂ yields. While yields are lower than those observed with good Fe/MFI catalysts, it is of interest that the Fe/SZ with the lowest Fe content converts 65% of NO_x to N_2 at 450 °C. The N_2 yield at 300 °C is comparable to that achieved with Fe/MFI. This could mean that in Fe/SZ-1 some Fe is present in a structure similar to that identified for Fe/ MFI, prepared by sublimation, but more research will be needed to check this. The selective nature of the NO_x reduction is also manifest from the CO2/CO ratio in the product as evidenced by parts A and B of Figure 9. The selective catalyst Fe/SZ-1 produces a significant amount of CO; even at 550 °C the CO2/ CO ratio remains near unity. This is typical for selective catalysts with very low concentration of Fe oxide particles which are selective for deep oxidation to CO₂. By contrast, over the SZsupported catalyst with the highest metal loading, Fe/SZ-7, combustion to CO_2 is significant. Over this catalyst the CO_x contains less than 30% CO at 400 °C and even less at higher temperature, signaling a catalytic signature reminiscent of Fe oxide. Comparison of Fe/SZ-1 and Fe/SZ-1-I is quite relevant. Table 1 shows that both have a very similar iron content, but



Figure 8. N₂ yield for Fe/SZ samples prepared by CVD (Panel A) and Fe/SA and Fe/SZ-I-1 (Panel B). Reaction mixture: 0.1% NO₂, 0.1% *i*-C₄H₁₀, 2% O₂, 1% H₂O; GHSV = 30 000 h⁻¹.

Figure 8 reveals that below 350 °C the catalyst prepared by sublimation gives a N_2 yield near 50%, while the N_2 yield of the impregnated sample remains below 20% at this temperature.

Discussion

Whereas a very high acid strength seems not to be a prerequisite for the deposition of Fe from FeCl₃, the present data show that acidity does matter. Deposition of Fe and release of HCl take place at a lower temperature on the support with the higher acidity, sulfated zirconia, than on silica alumina. The former solid acid exposes a small number of strong acid sites that are apparently responsible for Fe retention and HCl release below 100 °C. Silica-alumina is able to retain more Fe at higher temperature, in agreement with its high surface concentration of active OH groups. The IR spectra in Figure 3B confirm that the terminal hydroxyl groups in SA contribute most to the production of HCl during CVD. These groups appear at a higher wavenumber (Figure 3B) and release HCl from FeCl₃ at higher temperature (Figure 1). Integration of trace a and of the deconvoluted trace b in Figure 1 shows that SZ-1 has roughly twice as many Brønsted sites per unit area as SA; the surface density of silanol groups on SA is roughly equal to that of the Brønsted sites on SZ-1. The presence of two well-defined peaks for sulfated zirconia in Figure 1 indicates that two kinds of Brønsted sites are present. It has been proposed^{14,32} that the remarkable acidity of SZ is due to the existence of Brønsted and Lewis site pairs; their density reaches a maximum at a Brønsted/Lewis ratio near unity.33 In addition to these groups,



Figure 9. CO (Panel A) and CO₂ (Panel B) yield for samples prepared by CVD and impregnation. Reaction mixture: 0.1% NO₂, 0.1% *i*-C₄H₁₀, 2% O₂, 1% H₂O; GHSV = 30 000 h⁻¹.

a small number of sites release HCl at much lower temperature. The pattern reflects the microscopic heterogeneity inherent to the impregnation process of zirconium hydroxide with H_2SO_4 .

A new finding is that a very high surface coverage of sulfate groups on zirconia leads to an abrupt drop of its propensity to retain Fe from FeCl₃. This suggests that at surface coverages above 45% neighboring sulfate groups undergo condensation reactions of the type

$$-S-OH + HO - S \rightarrow -S - O - S - H_2O \qquad (2)$$

This type of chemistry is known for phosphate groups, which change from ortho via meta to pyrophosphate, and for chromates giving dichromate. We are not aware of previous reports of such condensation of adjacent sulfate groups decorating the surface of zirconia. That such condensation takes place is also in line with the IR data (not shown) of SZ-1 and SZ-7, that is, two materials with a high and a relatively low sulfate loading (see Figure 2). With the use of the band at $\sim 1025 \text{ cm}^{-1}$ of the O_{S-O} stretching mode³⁴ as an internal standard, the relative concentration of Brønsted sites (\sim 3645 cm⁻¹) per sulfur can be calculated for both materials. This estimate shows that the number of Brønsted sites per sulfur atom is lower by a factor of 2 for SZ-1 (with high sulfate loading) than for SZ-7 (see Table 5), indicating that appreciable condensation of adjacent sulfate groups takes place at the sulfate coverage where the Fe retention from FeCl₃ decreases precipitously.

The effect of iron on the reduction of sulfated zirconia is rather dramatic and very similar to that of platinum in Pt/SZ.³¹

 TABLE 3: Normalized H₂ and CO Consumption from TPR

 Experiments over Fe/SA^a

		H ₂ /Fe or CO/Fe (mol ratio)		
experiment	sample	peak I	peaks II-IV	peaks V-VI
H ₂ -TPR	fresh	0.05	0.51	0.41
H_2 -TPR	CO reduced		0.28	0.44
CO-TPR	fresh	peak I 0.06	peak II 0.23	peak III

^a Refer to Figures 6 and 7 for peak labeling.

 TABLE 4: Effect of H₂ Reduction on Sulfur Content of SZ-1 and Fe/SZ-1

	before H ₂ -TPR		after H ₂ -TPR	
sample	Fe/S	S/Zr	Fe/S	S/Zr
SZ-1 Fe/ SZ-1	0 0.10	0.08 0.05	0 0.13	0.02 0.04

TABLE 5: Brønsted Sites Per Sulfur Atom on SZ-1 and
SZ-7 a

	peak area (abso	rbance \times cm ⁻¹)	ratio
sample	1025 cm^{-1}	3645 cm^{-1}	Brønsted/total sulfate
SZ-1 SZ-7	181.4 135.8	67.1 106.8	0.4 0.8

 a Normalized by using the area of the peak at ${\sim}1025$ cm^-l, corresponding to the O_{S-O} stretching mode(s) of all surface sulfates.^{34}

In both systems reduction of the transition metal facilitates dissociative chemisorption of H₂. Whereas reduction by H₂ of Fe-free SZ-1 requires a high temperature and transforms \sim 57% of the sulfate groups to SO₂ but only \sim 43% to S²⁻, the presence of Fe induces a spectacular effect on the temperature and the extent of reduction, as \sim 90% of the surface sulfate groups in Fe/SZ are reduced to S^{2-} ions. The fact that H₂ is reversibly adsorbed on zirconia without any bond cleavage³⁵ illustrates the high resistance of that material against chemical reduction. This situation is completely changed when Fe is present; both the position of the TPR peaks and the level of sulfate reduction are strongly affected. As with Pt/SZ,³⁶ dissociation of H₂ takes place, followed by surface migration of atomic hydrogen leading to reduction of sulfur S^{6+} to S^{2-} (see Table 2). The relative position of the peaks in Figure 4 indicates that once sites are formed where H₂ molecules can dissociate, swift reduction of nearby sulfate groups will follow.

Reducing sulfur in sulfate ions to sulfide ions or H_2S results in a high hydrogen consumption ratio of $H_{cons}/S = 8$:

$$SO_4^{2-} + 4H_2 \rightarrow 4H_2O + S^{2-}$$
 (3)

which is much larger than the H_2 consumption per Fe (H_{cons}/Fe = 3) in the reduction of Fe₂O₃

$$Fe_2O_3 + 3 H_2 \rightarrow 2Fe + 3 H_2O \tag{4}$$

It is, therefore, not meaningful to derive a value for the final oxidation state of Fe from the TPR data. However, the fact that Fe strongly promotes the reduction of the sulfate groups in a way similar to platinum shows that a significant fraction of the iron must be present as Fe^0 or as an iron sulfide that is capable of dissociating H₂ molecules. Chemical analysis of **SZ-1** and Fe/**SZ-1** before and after H₂-TPR (see Table 4) shows that with **SZ-1** much sulfur has been removed (mainly as SO₂), but in Fe/**SZ-1**, 70–80% of the sulfur is retained. This indicates that with Fe/**SZ-1**, iron sulfide is formed. As dissociative chemisorption of H₂ will have a lower activation energy than migration of the H atoms over the surface of sulfated zirconia, the rate of

the overall reduction will increase with decreasing distance between Fe (or Fe-sulfide) clusters and sulfate groups and thus with increasing Fe loading, as is indeed observed.

This could have important consequences for the durability of such catalysts. It is well-known that sulfate groups protect the metastable tetragonal phase of zirconia against transformation to the more stable, but for catalysis less desirable, monoclinic modification.^{16,17,20} If catalysts are reduced and subsequently reoxidized, the sulfur which is retained can continue to exert its protective function. Likewise, the acid sites associated to sulfate groups will be regenerated. If, however, sulfur escapes as SO₂ during a reducing cycle, the protective function of the sulfate and its effect on catalyst acidity will be permanently lost.

As to Fe/SA, six deconvoluted H₂-TPR peaks in Figure 6 indicate six discernible states of Fe, some of which may be the result of stepwise reduction of one original species. The CO-TPR data show that after calcination most of the iron is present as oxide particles and/or oxo-ions. As to their nature, it is known that dinuclear ions [HO-Fe-O-Fe-OH]²⁺ can be easily reduced to [HO-Fe-D-Fe-OH]2+, but mononuclear [Fe= O⁺ ions, if isolated and immobile, would give highly unstable Fe⁺. We therefore assume that such ions are only reducible if they can migrate and dimerize or, more probably, dock on other Fe oxide or Fe metal particles. As ion migration over the surface of an oxide is known to be strongly facilitated by H₂O ligands,^{37–39} such reduction of docked [Fe=O]⁺ ions is expected to be more facile under conditions of H₂-TPR when H₂O is formed than under CO-TPR conditions. This is confirmed by the present data. The TPR data in Figures 6 and 7 can be tentatively interpreted on this basis. We assign the peaks at 376 and 434 °C in Figure 7 to the reduction of (1) oxide nanoparticles to Fe^0 and (2) dinuclear oxo-ions to bare Fe^{2+} ions. The larger number of peaks in Figure 6A then shows that besides these two species there are bare Fe³⁺ ions that can only be reduced by H₂. There also appear to be mononuclear Fe oxoions present that require water or OH ligands to migrate and dock before they can be reduced to Fe⁰.

Figure 6B can be deconvoluted to three peaks at 381, 454, and 597 °C, which we tentatively attribute to the reduction of (1) bare Fe^{3+} ions, (2) Fe^{2+} ions that were created by the preceding CO reduction of dinuclear Fe^{3+} oxo-ions, and (3) mononuclear Fe oxo-ions that cannot be reduced by CO because they are immobile in the absence of hydroxyl or water ligands. Admittedly, this interpretation is speculative and requires independent verification.

Adding up the H₂/Fe ratios in the first row of Table 3 gives a value of 0.96, whereas a value of 1.5 would be expected for the total reduction of all Fe from Fe³⁺ to Fe⁰. This finding shows that a significant fraction of the Fe in **SA** remains unreduced. Apparently this Fe is stabilized in the support; a solid state reaction takes place either with the silica or the alumina or both. From the standard Gibbs free energy it appears that formation of an aluminate is more favorable than formation of a silicate:⁴⁰

$$\operatorname{Fe}_{2}\operatorname{SiO}_{4} + 2\operatorname{Al}_{2}\operatorname{O}_{3} \rightleftharpoons 2\operatorname{FeAl}_{2}\operatorname{O}_{4} + \operatorname{SiO}_{2},$$

$$\bigtriangleup G^{0} = -11 \text{ kcal/mol} (5)$$

It is well-known that Al_2O_3 provides octahedral holes in the oxygen sublattice which are attractive for transition metal ions such as Cr^{3+} in gems. We therefore assume that this escape route protects the Fe against reduction to Fe⁰. Phase diagrams show that solid solutions exist of FeAl₂O₄ and Fe₃O₄; the formation of this aluminate and similar Co and Cu aluminates

has been reported by Bolt.⁴¹ Formation of Cu aluminate in Cu/ZSM-5 was shown by Yan et al.^{42,43}

As to the catalytic activity for NO_x reduction, the data show the behavior expected for catalysts containing a variety of Fe species. It is well-known that Fe oxide particles catalyze the combustion of hydrocarbons and, therefore, display a low selectivity for NO_x reduction in the presence of oxygen in excess. With Fe/MFI our previous work showed that N₂ yields exceeding 80% have been obtained near 350 °C; dinuclear oxygen-bridged Fe ions are believed to be responsible for this selective catalysis. The present data show that with Fe/SA the maximum N_2 yield is 10% at 350 °C. To understand this striking difference two points should be considered: First, comparison of the H₂-TPR and CO-TPR spectra in ref 44 and the present paper reveals significant differences in the population of Fe sites. With Fe/MFI a sharp H2-TPR peak at 400 °C identifies dinuclear oxygen-bridged Fe sites, and a second peak above 600 °C has been ascribed to Fe oxide clusters. The CO-TPR pattern of calcined Fe/MFI shows one predominant sharp peak at 400 °C, ascribed to the same dinuclear oxo-ion as the H₂-TPR peak at 400 °C. The H₂-TPR pattern of Fe/SA in Figure 6 of the present work is markedly different; its deconvolution reveals six Fe species of potentially catalytic relevance. The second point is the escape of some Fe complexes from the surface of SA to its interior. The present data suggest that the most selective sites preferentially disappear, when Fe aluminate is formed. As the catalytic tests were done at a rather high partial pressure of water and the catalyst was held at each temperature for considerable time, it makes sense that under these conditions elusive oxocomplexes react with the support and form a stable aluminate, whereas in the case of the crystalline support that solid state reaction will have a much lower rate.

The catalytic data of the **SZ**-based materials display a different picture. Samples with high Fe loading appear, again, to display a signature typical of Fe oxide particles. In contrast, the Fe/**SZ** catalysts with low Fe loading show a remarkable selectivity for NO_x reduction and deserve further study. Some of the samples have a yield of 65%. The fairly high selectivity of Fe/**SZ-1** in comparison to Fe/**SZ-7** is encouraging as it could indicate that the presence of sulfate prevents excessive combustion. A similar effect of sulfate content on combustion activity has been observed with Pd/**SZ** in NO reduction by CH₄.⁴⁵ In Fe/**SZ-1**, the sulfur and iron contents provide sufficient sites for NO₂ activation but prevent excessive isobutane combustion. Interestingly, the mass balance shows that below 350 °C the carbon oxides are mainly due to oxidation by NO₂, not the O₂ which is present in large excess.

Conclusions

The CVD method permits complete replacement by Fe of the Brønsted sites and silanol groups in sulfated-zirconia and silica-alumina. The rate of this substitution correlates with the acid strength. The iron uptake by sulfated zirconia during CVD initially increases with sulfate content but drops precipitously above a critical coverage near 45% of monolayer. This indicates condensation of sulfate ions to "pyro" or polysulfate groups.

Iron has a dramatic effect on the reducibility of the sulfate groups in sulfated zirconia. It strongly lowers the reduction temperature and significantly enhances the depth of sulfate reduction inducing formation of iron sulfide. The performance of sulfated zirconia-supported iron in NO_x reduction with isobutane in a wet feed reveals a strong effect of the preparation procedure and the Fe loading. Catalysts prepared by sublimation are more active than those prepared by impregnation. Within the group of catalysts prepared by sublimation the materials with low Fe content perform best. Results confirm that some iron sites selectively catalyze NO_x reduction to N₂. Other sites, such as Fe oxide particles, promote the combustion of i-C₄H₁₀. Sulfate appears to enhance the selectivity of catalysts with low Fe load.

Under redox conditions the **SZ** materials that are decorated with Fe are expected to display a better durability than those without a transition metal, because in the reduction mode sulfur is better retained and thus will exert its protective function against transformation to monoclinic zirconia in the oxidation mode.

On silica-alumina, the CVD technique deposits iron in the form of dinuclear and mononuclear iron oxo-ions, in addition to oxide particles. Upon reduction at elevated temperature some 36% of the Fe forms a solid compound, presumably iron aluminate, in which Fe^{2+} is stabilized against further reduction. The low N₂ yield with Fe/SA contrasts strongly with the high yield, exceeding the 80% obtained with Fe/MFI tested in the same lab with the same equipment. Clearly, applying the same CVD technique is no warranty for obtaining catalysts with similar performance. A probable chemical cause for the strikingly different performance of Fe catalysts using crystalline or amorphous supports is suggested by the TPR data. In the case of Fe/MFI they show that one type of site prevails; the physical characterization by a number of research groups suggests that the selective centers are dinuclear oxo-complexes of iron. In the case of Fe/SA, however, the TPR data in the present paper show a wide variety of Fe sites. The inferior catalytic selectivity for NO_x reduction is presumably due to the high reactivity of the most selective sites which form an aluminate with the support or agglomerate to oxide particles. It thus seems that the higher stability of the crystalline support and the fairly localized nature of the acid sites in zeolites are favorable factors for the highly selectivity of catalysts of this type.

Acknowledgment. This work was supported by the EMSI program of the National Science Foundation and the U.S. Department of Energy Office of Science (CHE-9810378) at the Northwestern University Institute for Environmental Catalysis. It made use of central facilities supported by the MRSEC program of the National Science Foundation (DMR-0076097) at the Materials Research Center of Northwestern University.

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