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Assessment of the free surface area of magnesia-supported magnesium ferrite particles using selective oxygen chemisorption

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The free surface area of iron oxide catalysts supported on magnesium oxide has been determined using selective oxygen chemisorption at room temperature. The oxygen chemisorption experiments were performed on reduced catalysts. It has appeared to be essential that the iron oxide phase, which is present as $MgFe_2O_4$ in the fresh calcined catalysts, is reduced uniquely to FeO, prior to the chemisorption experiment. Crystallite sizes typically in the range of 20–23 nm have been found independent of the catalyst loading and the type of precursors. A higher iron loading does not lead to larger crystallites, but rather to more crystallites of about the same average size. Results are in very good agreement with those obtained by X-ray line broadening and electron microscopy.

Introduction

It is of great interest to determine the free surface area of the active component of a supported catalyst, since it allows one to determine the catalytic conversion per unit of surface area. A very direct approach to obtain the free active surface area is applying selective chemisorption techniques. A simple nitrogen Brunauer–Emmett–Teller (BET) measurement would not satisfy, since it provides the total surface area including the contribution of the support. Selective chemisorption techniques, especially with hydrogen and carbon monoxide, are frequently used for the characterization of supported metal catalysts. Comparable procedures for supported metal oxide catalysts are scarce, since common probe molecules, such as, hydrogen, carbon monoxide, and nitrogen oxide generally do not exhibit simple chemisorption or decomposition with oxidic catalysts [1]. To solve this problem by completely reducing the oxidic active phase to the corresponding metal would lead to great inaccuracies, because of the introduction of effects, such as, sintering.

An alternative procedure, namely, selective chemisorption of oxygen onto partially reduced oxide catalysts, however, has proven to be fairly accurate. This method has been applied on supported V_2O_5 catalysts by van Dillen [2]. Weller has reviewed results of oxygen chemisorption on supported and unsupported Cr_2O_3 and MoO_2 catalysts [3]. Van der Wal [4] and van de Berg *et al.* [5] have adsorbed oxygen selectively onto supported and unsupported α-Fe_2O_3 catalysts, respectively. In this paper we will discuss oxygen chemisorption onto iron oxide dehydrogenation catalysts supported on magnesium oxide. Previous studies have shown that the iron oxide phase in these catalysts is present as finely divided magnesium ferrite, $MgFe_2O_4$, on the magnesium oxide support [6].

Some oxides, such as, V_2O_5, and Fe_2O_3, do not chemisorb oxygen to the extent of about a monolayer, since sorption of oxygen has to be accompanied by a charge transfer from the catalyst to the oxygen [2, 4]. To endow the surface with the ability to adsorb oxygen, the oxide will have to be reduced to a lower oxidation state. The active surface area is subsequently determined by re-oxidizing the surface by admitting oxygen pulses to the catalyst. A prerequisite is that oxygen sorption is carried out at temperatures where surface oxidation proceeds rather rapidly and bulk oxidation is slow or even inhibited. Then, if pulses of oxygen are admitted to the reduced catalyst, the time required to take up one dose rises appreciably when surface oxidation changes into bulk oxidation.

Since surface oxidation is probably not limited to the first monolayer, the amount of oxygen adsorbed cannot be directly related to the active oxidic surface area. Therefore, the method will have to be calibrated. This can be done by independently determining the surface area of unsupported magnesium ferrite by nitrogen adsorption using the BET method. The amount of oxygen required to oxidize the surface of partially reduced unsupported magnesium ferrite can be used to determine the surface area per molecule of oxygen taken up. This calibration factor enables one to calculate the surface area of supported magnesium ferrite. It is necessary to assume that the calibration

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factor, relating the magnesium ferrite surface area to the amount of oxygen adsorbed, is the same for supported and unsupported magnesium ferrite. The oxidation process, as to rate and mechanism, might depend on the type of lattice planes exposed and thus on the particle size. The demand of a common calibration factor can therefore be best met with by applying finely divided unsupported magnesium ferrite of a particle size of the same order of magnitude as with the supported catalyst. Using this procedure, at least a reliable comparison of relative free surface areas within a group of analogous supported catalysts is possible.

Previously, we have discussed the reduction behaviour of magnesium ferrite particles supported on magnesium oxide [7]. It has been found that magnesium ferrite is reduced to an FeO phase partly *via* Fe_3O_4 at temperatures of about 633 K. The FeO phase is stabilized by the magnesium oxide support by formation of a solid solution. Upon further reduction at higher temperatures the FeO phase is reduced to metallic iron. The success of the estimation of the free $MgFe_2O_4$ surface area by oxygen chemisorption depends on converting the Fe^{3+} ion reliably and reproducibly into a known lower valence state. Since only part of the magnesium ferrite is reduced *via* Fe_3O_4, FeO is chosen to be the desired state, prior to oxygen chemisorption. Therefore, the reduction temperature is optimized so as to obtain the FeO phase after reduction. Complete formation of FeO is checked after the surface oxidation experiment by subsequent titration of the bulk to complete oxidation with oxygen pulses at increased temperatures. In general FeO is non-stoichiometric (Fe_xO, $0.85 \leqslant x \leqslant 0.95$) but nevertheless will be referred to as FeO [8].

To obtain information about the phase changes that take place during the surface and the bulk oxidation experiments, the catalysts have also been studied magnetically *in situ* during the oxygen sorption experiments. As discussed earlier [7], iron compounds all have rather different magnetic properties. Therefore, a well based distinction can be made among several iron compounds using magnetic methods. For this purpose a low-field magnetic method is used [9]. A prerequisite for using a low-field magnetic method is that particles behave superparamagnetically at the temperature at which the magnetization measurements are performed. The property of superparamagnetism is exhibited by ferro- or ferrimagnetic compounds of very small particle sizes. Superparamagnetic particles are single domain, which means that they are in a uniform state of magnetization at any applied field. They can be magnetized by a coherent rotation of their magnetic moments and therefore behave just like a system of paramagnetic atoms only with a much larger magnetic moment. Using the calculation method of Bean and Livingstone [10] and using magnetic data given by Bartels *et al.* [11], the critical particle size below which $MgFe_2O_4$ behaves superparamagnetically can be calculated to be 30 nm in diameter at 293 K.

The particle sizes calculated from the oxygen chemisorption results are compared to those obtained from X-ray line broadening and electron microscopy. Part of these results have been presented previously [6].

2. Experimental procedure

2.1. Catalyst preparation

Catalysts were prepared by means of the incipient wetness impregnation of preshaped magnesium oxide support bodies (Engelhard, Mg-0601 T 1/8″) using badly crystallizing organometallic complexes [6]. As organometallic complexes pure ammonium iron(III) EDTA (Merck, Fotopur) and ammonium iron(III) citrate (BakerGrade) were applied. After impregnation the catalysts were dried at atmospheric pressure first at room temperature and then at 393 K, at both temperatures for 16–24 h. Finally, the catalysts were calcined in air for 16–24 h usually at 973 K to decompose the metalorganic precursors. The iron loadings of the catalysts in weight percentage iron were determined by an indirect titration method with EDTA [6]. The iron loading is expressed as the calculated weight percentage metallic iron on the magnesium oxide support.

Unsupported magnesium ferrite was prepared by air oxidation of an aqueous suspension containing both Mg^{2+} and Fe^{2+} ions in a 1:2 ratio [12]. The starting solution was prepared by mixing 50 ml of aqueous solutions of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (0.44 mole) and $MgSO_4$ (0.22 mole). For simultaneous precipitation of both hydroxides $Mg(OH)_2$ and $Fe(OH)_2$, the starting solution was added to a solution of 100 g NaOH in 1000 ml of water under a nitrogen gas flow. A green precipitate was formed. This suspension was heated and kept at 328 K, while air was bubbled through the suspension, until the green precipitate had changed into a brown precipitate of the ferrite. The precipitate was then separated from the solution by centrifuging and repeatedly washed with deionized water. Finally, the ferrite was calcined in air at 973 K for 36 h.

2.2. Oxygen chemisorption

Chemisorption experiments were performed in a conventional glass vacuum apparatus. Fig. 1 shows a schematic representation of the apparatus. The apparatus allowed chemisorption experiments in combination with *in situ* low-field magnetization measurements. For this purpose the catalysts were fragmented into particles with sizes between 0.50 and 0.85 mm. Samples could be reduced *in-situ* in a 10% H_2/N_2 flow at temperatures ranging from 293–823 K. For chemisorption experiments pressures as low as 0.133 mPa (metered with a Leybold Heraeus Ionivac IM 30) could be established using an oil diffusion pump (Leybold Heraeus PD 400). For chemisorption O_2 (Hoekloos, 99.995%) was applied. Oxygen pulses were metered using a Bourdon-type precision pressure gauge (Texas Instruments, model 145).

Prior to the chemisorption experiment, a catalyst was reduced overnight in a 10% H_2/N_2 gas flow at about 633 K. Subsequently, the sample cell was evacuated at the reduction temperature. After 1 h the sample

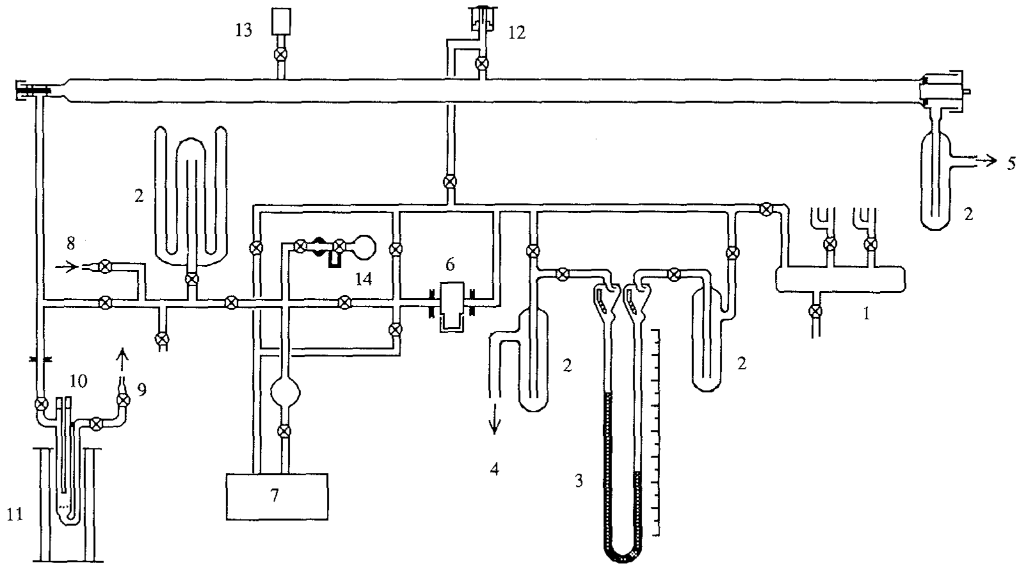

Figure 1 A schematic representation of the chemisorption apparatus: Position *1*: oxygen gas inlet system; Position *2*: cold trap 77 K; Position *3*: mercury U-tube; Position *4*: rotation pump (Leybold Heraeus D6A, 0.133Pa); Position *5*: oil diffusion pump (Leybold Heraeus PD 400,0.133 mPa); Position *6*: needle valve; Position *7*: Bourdon pressure gauge (TI, PG145); Position *8*: inlet for pretreatment gas; Position *9*: outlet for pretreatment gas; Position *10*; glass reactor with catalyst; Position *11*: oven, range 293–823 K; Position *12*: ionization pressure gauge (Leybold Heraeus Ionivac IM-10; range 0.133 μPa–2.7 mPa); Position *13*: pressure gauge (Leybold Heraeus, range 0.133 Pa–0.1 Mpa); Position *14*: calibration volume.

cell was cooled down to room temperature, while evacuation was continued. The catalyst was evacuated until the pressure was finally below 0.6 mPa. Next, small oxygen doses of about 20–70 Pa (dose volume 200 ml) were admitted at room temperature, while the adsorption time was monitored. It appeared useful to define the adsorption time as the time required to take up about 95% of the dose admitted. After the adsorption times had increased appreciably and surface oxidation had changed into bulk oxidation, the temperature was increased to 633 K. Next, to oxidize the bulk, oxygen pulses were admitted until adsorption of oxygen had ceased. From the total amount of oxygen sorbed, the initial oxidation state of the reduced oxide phase could be calculated.

During the adsorption experiments, the magnetization of the catalyst was measured at room temperature in a low-field a.c.-permeameter, analogous to the one described by Selwood [9] and Geus *et al.* [13]. Technical data are given by Erkelens and Wösten [14]. The alternating (260 Hz) magnetic field was detected by a lock-in amplifier (Princeton Applied Research, model 5101).

2.3. Other characterization techniques

The BET surface area of unsupported magnesium ferrite was determined by nitrogen physisorption using a Sorptomatic 1800 instrument (Carlo Erba). Nitrogen adsorption was measured statically at 77 K. Prior to the physisorption experiment, the samples were outgassed in vacuum (0.27 Pa) at 393 K for 3 h.

The reduction behaviour was studied with temperature programmed reduction (TPR). Hydrogen consumption by a catalyst was determined as a function of the temperature. Experiments were performed in a conventional atmospheric flow reactor, as described earlier [7].

By means of a vibrating sample magnetometer it was established whether the supported magnesium ferrite catalysts behaved superparamagnetically. In this apparatus magnetic field strengths up to 0.95 MA m^{-1} could be established. The magnetization of the catalyst samples was measured as a function of the field strength at 293 and 77 K. More details on the apparatus are given by van Stiphout *et al.* [15].

X-ray diffraction measurements were performed in a Philips powder diffractometer mounted on a Philips PW 1140 X-ray generator with Fe $K_{\alpha1,2}$ radiation ($\lambda = 0.193735$ nm).

Finally, the materials were characterized using transmission electron microscopy (Philips EM 420).

3. Results and discussion

3.1. Unsupported magnesium ferrite

As explained above, finely divided unsupported magnesium ferrite has been prepared to be used for calibration of the oxygen chemisorption technique. An X-ray diffractogram of unsupported magnesium ferrite prepared by coprecipitation of Fe^{2+} and Mg^{2+} ions is shown in Fig. 2. As can be seen, the calcined precipitate mainly consists of magnesium ferrite. Only very weak diffractions of α-Fe_2O_3 and MgO are found at 42.2 and 47.0° 2θ, respectively. Measurement of the X-ray line broadening does not provide an unambiguous mean value for the magnesium ferrite crystallite size.

The BET surface area of the unsupported magnesium ferrite has been determined using N_2 adsorption. The surface area of magnesium ferrite is 26.82 $m^2 g^{-1}$. From this surface area an average crystallite size of about 50 nm is calculated, which indicates that the unsupported magnesium ferrite is rather finely divided.

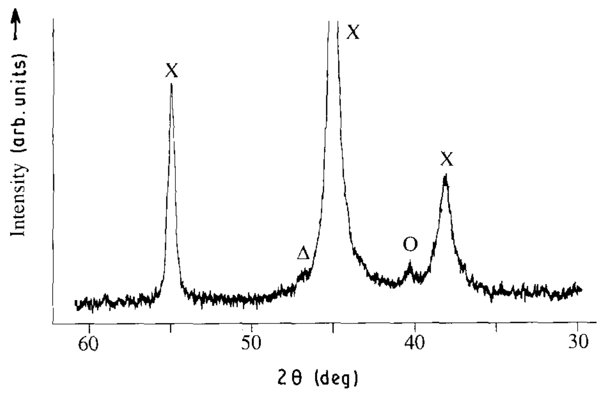

Figure 2 X-ray diffractogram of bulk magnesium ferrite prepared by coprecipitation from Fe^{2+} and Mg^{2+} ions. The sample was dried and calcined at 973 K. (×): $MgFe_2O_4$; (O): α-Fe_2O_3; (Δ): MgO.

In order to determine how reduction of the unsupported magnesium ferrite proceeds, a temperature programmed reduction experiment has been performed. Fig. 3 shows the TPR profile. Two large reduction peaks are found with a ratio of the areas of roughly 1:2. The first reduction peak shows a small shoulder on the low temperature side. Evidently reduction of unsupported magnesium ferrite proceeds in a comparable manner as was found for supported magnesium ferrite particles [7], i.e., reduction *via* Fe_3O_4 to an FeO phase and next to metallic iron. The onset temperature for reduction was about 600 K.

Oxygen chemisorption has to be performed on a reduced oxidic phase. Since an FeO phase has been chosen to be the desired phase after the reduction pretreatment, the unsupported magnesium ferrite was reduced in a 10% H_2/N_2 flow at 633 K, i.e., at the steep rise of the first reduction peak. Magnetization measurements on a supported magnesium ferrite catalyst have shown that at this temperature magnesium ferrite is fully reduced to a FeO phase [7]. Next an oxygen chemisorption experiment has been performed on the prereduced ferrite. Fig. 4 shows the time required to take up a dose of O_2 that is admitted at room temperature, plotted against the total amount of oxygen sorbed per gram of magnesium ferrite. Initially the oxygen doses are adsorbed very rapidly, i.e., in about 30 s. During this stage surface oxidation is proceeding. After 16 pulses the adsorption time increases steeply. At the steep rise of the adsorption time surface oxidation has changed into bulk oxidation. During this final stage the oxidation rate has become controlled by diffusion of oxygen through the oxidized surface layer and proceeds only very slowly. The amount of oxygen required to oxidize the surface is defined as the amount V_{ads} at the intersection of the two solid lines shown in Fig. 4. It can be seen that the unsupported magnesium ferrite used in this experiment, after reduction at 633 K, takes up 8.02 ml STP O_2 per gram of magnesium ferrite. By increasing the temperature to about 633 K and admitting oxygen doses at that temperature, the bulk of the magnesium ferrite is oxidized. From the total amount of oxygen taken up by the reduced ferrite during both surface and bulk oxidation, i.e., 60.1 ml STP O_2 per gram, it is calculated that the degree of reduction to the FeO phase was indeed 100%. No Fe_3O_4 or Fe was present after the reduction at 633 K.

From this result and the magnesium ferrite BET surface area, the calibration factor, relating the specific magnesium ferrite surface area to the amount of oxygen required to oxidize the surface, can be calculated. This calibration factor is found to be 3.34 $m^2\,ml^{-1}$ STP O_2. In all experiments discussed hereafter, this factor will be used to calculate the surface area of supported magnesium ferrite from the amount of chemisorbed oxygen. From the crystallite size of 50 nm and the amounts of oxygen required for oxidation of the surface and the bulk of the particles, respectively, it can be calculated that surface oxidation of the FeO phase proceeds as deep as about 1 nm, which is considerably more than one monolayer, as was discussed in the introduction.

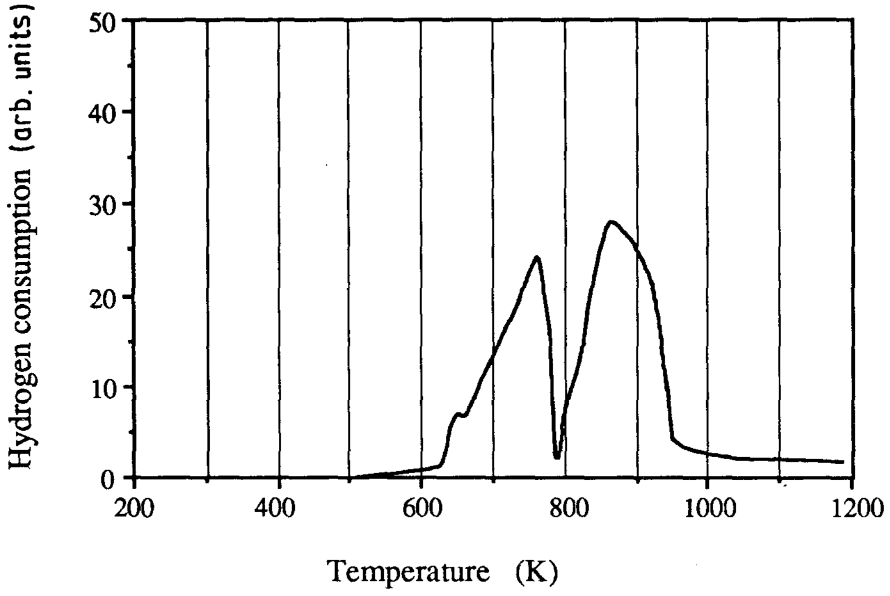

Figure 3 Temperature programmed reduction profile (TPR) of unsupported magnesium ferrite prepared by coprecipitation from Fe^{2+} and Mg^{2+} ions.

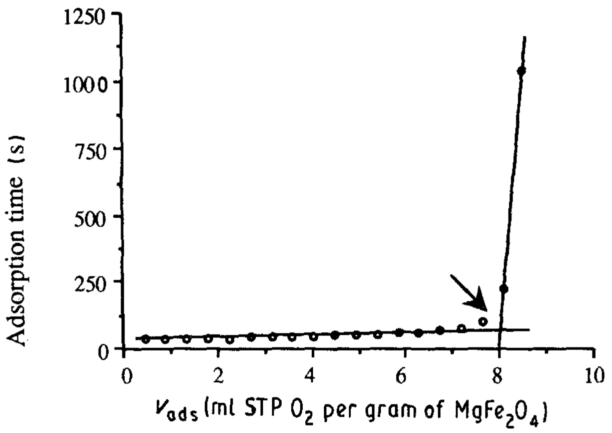

Figure 4 Oxygen sorption plot of unsupported magnesium ferrite after reduction at 633 K. The amount of oxygen required for surface oxidation at room temperature is indicated by the intersection of the two solid lines.

3.2. Supported magnesium ferrite catalysts

3.2.1. Oxygen chemisorption

It has already been mentioned that the reliability of the results should depend on reacting the iron species to a known lower valence state in a controlled way. First of all, therefore, the temperature of reduction prior to the oxygen chemisorption experiment has been varied, to determine the reliability of the thus obtained surface areas. Next, the reduced samples have been titrated at room temperature to establish surface oxidation, followed by titration at 633 K to establish bulk oxidation of the reduced catalyst. Plots representing bulk oxidation performed at 633 K for a 1.0 wt % Fe/MgO catalyst (ex citrate) prereduced at different temperatures are shown in Fig. 5. In this figure the amount of oxygen sorbed at 633 K is plotted against the oxygen pressure. From the total amount of oxygen required for complete oxidation at 633 K, the initial oxidation state after reduction can be deduced. The dashed lines indicate the amounts of oxygen required if the state of the catalyst after reduction pretreatment would be either Fe_3O_4, FeO or metallic iron. If after complete oxidation a value for the required amount of oxygen is obtained being between two dashed lines, it is considered that both compounds are present simultaneously. The relative amounts of each can be calculated from the total amount of oxygen required for complete oxidation and the total amount of iron present. For these calculations the FeO is assumed to be stoichiometric. It can be seen that after reduction of the 1.0 wt % Fe/MgO catalyst at about 653 K all iron is present as FeO. Beyond this value a considerable amount of metallic iron is formed upon reduction, e.g., at 673 K about 20% of the iron is present as Fe^0. Below 653 K Fe_3O_4 is formed next to FeO. The amount of Fe_3O_4 increases as the temperature of reduction pretreatment is lowered.

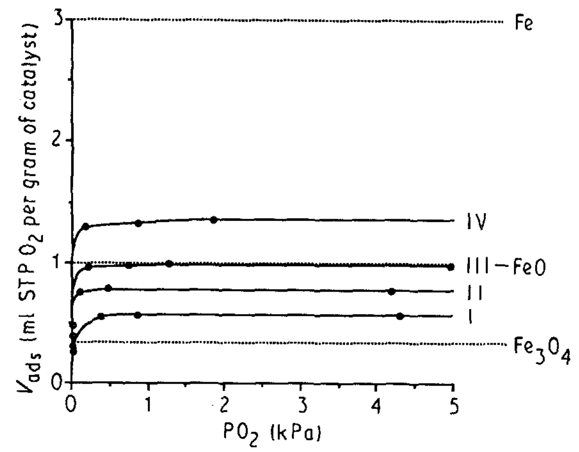

Figure 5 Oxygen bulk oxidation plots for a 1.0 wt % Fe/MgO catalyst (ex citrate) performed at 633 K. Catalysts have been prereduced at: (I) 613; (II) 633; (III) 653 and (IV) 673 K. The dashed lines indicate the amount of oxygen required if iron in the reduced catalyst was present solely as either Fe_3O_4, FeO, or Fe.

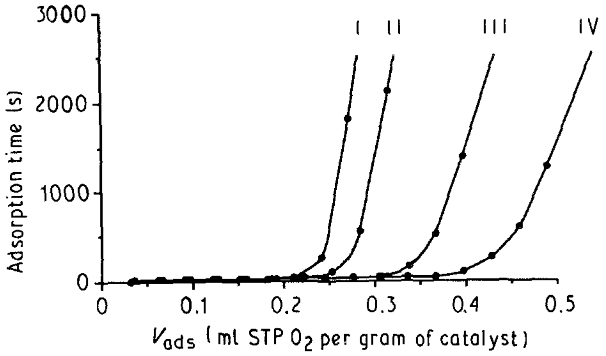

Figure 6 Oxygen sorption plots of a 1.0 wt % Fe/MgO catalyst (ex citrate) performed at room temperature. The temperature of the reduction pretreatment was varied between 613 and 673 K: (I) 613; (II) 633; (III) 653 and (IV) 673 K.

The influence of the initial oxidation state after the reduction on the amount of oxygen required for surface oxidation is shown in Fig. 6. In this figure time–adsorption plots of the 1.0 wt % Fe/MgO catalyst measured at room temperature after reduction at several temperatures ranging from 613 to 673 K are shown. When the temperature of the reduction pretreatment is increased and the composition of the reduced catalysts changes from Fe_3O_4 *via* FeO to Fe (Fig. 5), the amount of oxygen required for surface oxidation at room temperature also strongly increases. It is evident that the presence of iron species other than the desired FeO phase, i.e., Fe_3O_4 or Fe, strongly influences the obtained results. So, for each catalyst to be studied with oxygen chemisorption, the reduction temperature is optimized so as to obtain a maximum amount of FeO, and a minimum of both Fe_3O_4 and Fe.

For catalysts prepared by impregnation of magnesium oxide with ammonium iron(III) citrate, with loadings of 1.0, 2.1, and 3.1 wt % Fe, the oxygen adsorption plots are shown in Fig. 7. For all these catalysts the iron is almost completely present as Fe^{2+} after reduction pretreatment, as has been determined by bulk oxidation at 633 K afterwards. Reduction temperatures and iron loadings are given in Table I. It can be seen in Fig. 7 that when the iron loading is increased, the amount of oxygen taken up by the surface also increases. It is also apparent that as the catalyst loading is increased and thus the amount of ferrite in the sample cell, the sharp change from

TABLE I. Oxygen chemisorption data and results in comparison with other techniques

	Loading (wt % Fe)	Reduction temp. (K)	Spec surf. area ($m^2 g^{-1}$ cat.)	Crystallite size (nm)		
				O_2-sorption	XRLB	TEM
Citrate	1.0	653	1.17	20	–	–
	2.1	613	2.28	22	19	18
	3.1	633	3.22	23	18	19
EDTA	0.9	633	0.96	22	–	22
	1.7	623	1.94	21	–	22
	2.8	593	3.68	18	–	18
	4.4	618	4.24	25	18	24

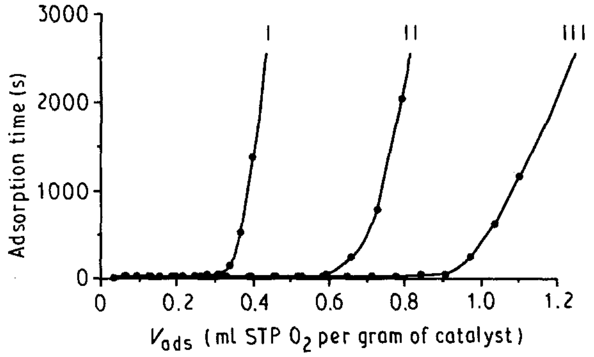

Figure 7 Oxygen sorption plots of magnesia-supported magnesium ferrite catalysts (ex citrate) performed at room temperature: (I) 1.0; (II) 2.1; (III) 3.1 wt % Fe/MgO.

surface to bulk oxidation is gradually obscured. The amounts of oxygen required for surface oxidation, the calculated surface area, and the crystallite sizes are given in Table I, together with the results from transmission electron microscopy (TEM) and X-ray line broadening (XRLB) [6]. For catalysts prepared by impregnation with ammonium iron(III) EDTA the results are also given in Table I. For the calculation of the crystallite sizes, the particles are assumed to be of a spherical shape. Generally, for catalysts prepared from either of the complexes, crystallite sizes of about 20–23 nm are found using oxygen chemisorption. This is equivalent to a specific surface area of about 60 m^2 per gram of magnesium ferrite. At higher loadings the crystallite sizes tend to increase, as is clearly observed for a 4.4 wt % Fe/MgO catalyst (ex EDTA). Furthermore, the value of 18 nm obtained for a 2.8 wt % Fe/MgO catalyst (ex EDTA), which is observed with oxygen chemisorption, is rather low if compared to values obtained for other iron loadings. The high extent of oxygen sorption and, hence, the small size can be explained by the presence of about 5% metallic iron next to the FeO phase directly after reduction pretreatment, in spite of the low reduction temperature of only 593 K. Lowering the reduction temperature before the oxygen chemisorption experiment even further, to prevent the formation of metallic iron, results in an unreduced layer within the catalyst bed, which would surely lead to unreliable results. The formation of metallic iron even at 593 K might point to the presence of some α-Fe_2O_3, which is not reduced via the stabilized FeO phase, but via Fe_3O_4 directly to metallic iron. However, no α-Fe_2O_3 diffraction lines are observed in the fresh catalyst using electron diffraction. Still the value of 18 nm is not very anomalous, since transmission electron microscopy also gives a rather low value of 18 nm.

As mentioned above, in Table I the crystallite sizes are also given, these have been obtained from transmission electron microscopy (TEM) and X-ray line broadening. For the catalysts prepared from ammonium iron(III) citrate, crystallite sizes of about 18–19 nm are found using both methods. These values are essentially the same as those that have been found using the chemisorption technique. For the 1.0 wt % Fe/MgO catalyst (ex citrate) catalysts the diffraction intensities of X-ray diffraction pattern were too low to allow the determination of crystallite sizes. This is also the case for the EDTA catalysts with low iron content. The particle sizes obtained with TEM are in good agreement with those obtained with oxygen sorption.

3.2.2. Magnetization measurements

As found above, the sizes of the magnesium ferrite particles within the catalysts studied are about 20 nm. As mentioned in the introduction, the particles are therefore expected to behave superparamagnetically. This has been checked by high-field magnetic measurements using a vibrating sample magnetometer. The magnetization of the 3.1 wt % Fe/MgO catalyst (ex citrate) has been measured as a function of the field strength at 293 K. The catalyst did not show remanence, nor did it show the flattening in a plot of the magnetization against the reciprocal field strength, which is characteristic for non-superparamagnetic behaviour [13, 15]. The magnesium ferrite particles thus behave superparamagnetically.

The magnetization of a partially reduced 4.4 wt % Fe/MgO catalyst (ex EDTA) has been monitored in a low-field a.c.-permeameter, during oxygen sorption first at room temperature and then at 633 K, and finally during oxidation at 773 K. The magnetization measured has been normalized to the magnetization of the fresh catalyst before reduction, i.e, M_0. Hence, the magnetization of the fresh catalyst is defined as being unity. When the catalyst is reduced at 627 K, which is indicated as stage I in Fig. 8, the relative magnetization M/M_0 strongly decreases from 1.0 to a value of 0.14. This decrease confirms the results of magnetization measurements described earlier [7],

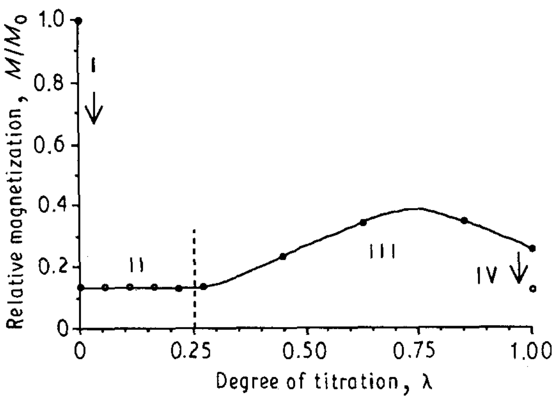

Figure 8 Magnetization plotted as a function of the amount of oxygen required to oxidize a partially reduced 4.4 wt % Fe/MgO catalyst (ex EDTA). Surface oxidation has finished at $\lambda = 0.26$: (I) reduction at 628 K; (II) surface oxidation at 293 K; (III) bulk oxidation at 633 K; (IV) heating in oxygen at 773 K.

and clearly shows that the $MgFe_2O_4$ particles are reduced to an anti-ferromagnetic FeO phase. The remaining signal is ascribed to a slight amount of Fe_3O_4.

Next, oxygen pulses have been admitted to the reduced catalyst. Firstly, the surface is oxidized at 293 K and, secondly, the bulk is oxidized at 633 K. Fig. 8 shows the relative magnetization plotted as a function of the relative amount of oxygen that has been sorbed. The amount of oxygen has been normalized to the total amount of oxygen sorbed during both oxidation steps and is referred to as the degree of titration, λ. Surface oxidation at 293 K, designated as stage II, has ended at $\lambda = 0.26$, which equals about 1.15 ml STP O_2 per gram of catalyst. At $\lambda = 1.0$ the bulk oxidation is complete. As can be seen in Fig. 8 during the surface oxidation the magnetization remains constant. From this it can be derived that oxidation of the anti-ferromagnetic FeO phase proceeds either to some supersaturated form of Fe_xO, with a low value of x, or to anti-ferromagnetic α-Fe_2O_3. On the basis of these results solely no discrimination can be made between either of the two possibilities. Since in general FeO is not stable at temperatures below 843 K [16, 17], the authors are inclined to prefer the latter explanation involving the α-Fe_2O_3, not denying the stabilizing role which magnesium oxide might play. Since beyond $\lambda = 0.26$, the uptake of oxygen at 293 K ceases, the oxygen sorption experiment was continued at 633 K. This is referred to as stage III. After a dose of oxygen was admitted at 633 K and taken up, the sample cell was cooled to room temperature, after which the magnetization was measured. As was shown before, at 633 K bulk oxidation proceeds. In Fig. 8 it can be seen that at first the relative magnetization increases. Above about $\lambda = 0.75$ the relative magnetization decreases again. Since the rate of bulk oxidation is limited by the transport of oxygen through the oxidized surface layer, the FeO phase is not rapidly oxidized to α-Fe_2O_3. Rather the oxidation proceeds slowly and stepwise *via* an Fe_3O_4 phase. This phase is ferrimagnetic. Subsequently, as the oxidation proceeds, the Fe_3O_4 is gradually transformed into anti-ferromagnetic α-Fe_2O_3. This explains the initial increase followed by a decrease of the magnetization.

The oxidation of Fe_3O_4 has been extensively studied by Feitknecht and co-workers [18–20]. He found that, ferrimagnetic γ-Fe_2O_3 is formed, when Fe_3O_4 is carefully oxidized at temperatures below about 573 to 673 K. γ-Fe_2O_3 rapidly transforms into α-Fe_2O_3 at about 773 to 873 K. At about 623 K this transformation proceeds slowly. According to the observations of Feitknecht and co-workers [18–20], some γ-Fe_2O_3 might therefore have been formed next to α-Fe_2O_3 during the bulk oxidation experiment at 633 K. To establish formation of γ-Fe_2O_3, the catalyst has been kept at 773 K at the end of the bulk oxidation experiment at 633 K. The effect on the magnetization is indicated in Fig. 8 by stage IV. If any γ-Fe_2O_3, which is ferrimagnetic, is present, it should rapidly transform into anti-ferromagnetic α-Fe_2O_3 at 773 K. A decrease of the magnetization of $M/M_0 = 0.26$ to 0.14 is observed, which indicates that next to α-Fe_2O_3 some γ-Fe_2O_3 has been formed during the bulk oxidation at 633 K.

4. Conclusions

As far as the preparation of unsupported magnesium ferrite is concerned, X-ray diffraction and nitrogen physisorption experiments have shown, that rather finely divided magnesium ferrite is obtained by coprecipitation of Mg^{2+} and Fe^{2+} ions and subsequent oxidation. Using the thus prepared magnesium ferrite, the calibration factor relating the magnesium ferrite surface area to the oxygen chemisorption has been found to be 3.34 $m^2\,ml^{-1}$ STP O_2. Applying this calibration factor, the free surface area of the supported magnesium ferrite is found to be about 60 m^2 per gram of magnesium ferrite independent of the catalyst loading and the type of precursors. This corresponds to an average crystallite size of about 22 nm. Essentially, the same values have been obtained using X-ray diffraction and transmission electron microscopy. At high loadings the crystallite sizes are not significantly higher. It can be concluded that a higher iron loading does not lead to larger crystallites but rather to more crystallites of the same size.

From the magnetization measurements it can be concluded that during the surface oxidation at 293 K the FeO phase at the surface is rapidly oxidized to α-Fe_2O_3. This confirms earlier observations that FeO is not homogeneously dissolved in the MgO phase [6], but is concentrated at the surface of the particles. After the surface has been rapidly oxidized, further oxidation proceeds slowly. The rate is controlled by oxygen diffusion through the oxidized surface layer. At 633 K bulk oxidation proceeds at a much higher rate, but not directly to α-Fe_2O_3. FeO is oxidized *via* Fe_3O_4 to both γ-Fe_2O_3 and α-Fe_2O_3.

The conformity of the results from oxygen chemisorption on the one hand, and X-ray diffraction and transmission electron microscopy on the other, is very good, taking into account the entirely different background of these techniques. It justifies the use of the calibration factor, that relates the magnesium ferrite surface area to the amount of oxygen sorbed, for both supported and unsupported magnesium ferrite. This was achieved by applying finely divided unsupported magnesium ferrite for calibration.

The other requirement is involved with the reduction pretreatment. It appears to be highly important that the magnesium ferrite is uniquely reduced to an FeO phase and that the presence of other iron species, such as, Fe_3O_4 or Fe is prohibited. From Fig. 6 it can be concluded, that all three magnesia-supported iron compounds take up different amounts of oxygen per unit surface area. A final bulk titration experiment at increased temperatures after the surface oxidation, however, has proven to be a reliable method to determine the oxidation state after the reduction pretreatment.

A remark has to be made about the catalyst texture. The catalyst support used for the preparation of the catalysts studied here contained pores with an average radius of about 90 nm [21], allowing for rapid oxygen transport through the pores of the support to the iron containing particles. However, care has to be taken with catalysts containing much smaller pores. Then the rate of surface oxidation will be controlled by oxygen diffusion through the pores, just like bulk oxidation is controlled by oxygen diffusion through the oxidized layer. This will obscure the change from surface to bulk oxidation. The effect is similar to what is observed, when the catalyst loading is increased, as has been shown in Fig. 7.

Selective oxygen chemisorption is an excellent technique for the determination of the active surface area of magnesium ferrite catalysts supported on magnesium oxide. It is applicable to many other catalyst systems. The prerequisite, however, remains that oxidation of the surface proceeds at much higher rate than that of the bulk. The results also depend on the ability to convert the metal oxide reliably and completely into a known lower oxidation state. When these requirements are fulfilled, oxygen sorption is able to provide an accurate average value for the free active surface area and, hence, a reliable mean value for the crystallite size.

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