

Characterization of Fe/ZSM-5 by isotopic exchange with $^{18}\text{O}_2$

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Abstract

Exchange of $^{18}\text{O}_2$ with O atoms in two groups of Fe containing ZSM-5 catalysts was studied. One class was prepared by sublimation of FeCl_3 onto H-ZSM-5 with various Si/Al ratios. These materials are highly active and selective catalysts in the reduction of NO_x with alkanes. A second group, further called $\text{Fe}_2\text{O}_3/\text{ZSM-5}$, was prepared by impregnation. Significant differences in the exchange behavior were found between both groups; the exchange rate is higher for $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ than for Fe/ZSM-5, in accordance with the higher selectivity for alkane combustion of $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ and its low selectivity for NO_x reduction. The data suggest that negligible amounts of iron oxide particles exist in the Fe/ZSM-5 catalyst. For Fe/ZSM-5 catalysts the exchange is not limited to the oxygen atoms directly attached to iron; some zeolite oxygen is also exchanged, although this does not occur for the metal-free zeolite. Kinetic analysis shows that with $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ the R^2 exchange mechanism prevails in which $^{18}\text{O}_2$ is exchanged in one step against two ^{16}O atoms. For the selective Fe/ZSM-5 catalyst R^1 exchange prevails at low temperature, i.e., $^{18}\text{O}_2$ molecules exchange only one O atom against an atom of the solid. The qualitative difference between both types of catalyst indicates that Fe/ZSM-5 catalysts owe their selectivity in NO_x reduction to Fe oxo-ions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fe/ZSM-5 catalyst; Oxygen isotope exchange; Selective reduction of NO_x ; Exchange mechanisms; Chemical vapor deposition

1. Introduction

More than 20 years ago, the research group of professor Tetsuro Seyama opened up the field of NO reduction over zeolite catalysts containing transition metal ions in their cavities [1,2]. By using ^{15}N -labeled ammonia and unlabeled

beled ^{14}NO , they showed that 90% of the N_2 molecules formed in this process were heteronuclear $^{15}\text{N}^{14}\text{N}$ [3]. In the work of our group on NO_x reduction with propane over Cu/ZSM-5 it appeared that the alkane reacts with adsorbed NO_y complexes and possibly forms an oxime with NO. Exposure of Cu/ZSM-5 covered with this oxime to labeled $^{15}\text{NO}_2$, resulted in the formation of N_2 of the predominant composition $^{15}\text{N}^{14}\text{N}$ [4], as in Seyama's earlier work. This indicates important common elements in the catalytic chemistry of NO_x reduction over zeolite based catalysts. This line has been con-

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tinued to our recent work with Fe/ZSM-5 catalysts, which are of interest because of their high activity even in the presence of an excess of H₂O in the feed [5,6].

Oxygen isotope exchange has often been applied to characterize oxidation catalysts. It was found by Winter [7] and confirmed by numerous other authors, that two types of processes can be discerned: for instance an ¹⁸O₂ molecule contacting a solid containing ¹⁶O atoms, either exchanges only one atom, so that the primary product is an ¹⁸O¹⁶O molecule, or both atoms are exchanged during one interaction of the molecule with the solid, i.e., ¹⁶O₂ is a primary exchange product. The former mechanism is usually termed R¹, the latter R². In this terminology, an exchange of ¹⁶O₂ with ¹⁸O₂ without apparent contribution of a solid is conventionally called R⁰. Boreskov showed that for ZnO, MnO₂, Co₃O₄, V₂O₅, WO₃ and CuO the diatomic R² exchange was roughly one order of magnitude faster than the monoatomic R¹ exchange [8].

As to zeolite-supported transition metal ions, Valyon and Hall reported that with Cu/ZSM-5 the heteromolecular exchange of ¹⁸O₂ is disguised by fast homomolecular exchange, but with Cu/Y hetero-exchange prevailed [9]. Their data suggest that an O₂ molecule is adsorbed as a precursor state at one point, while another O₂ molecule is released elsewhere. Surprisingly, the exchange was not confined to O atoms bonded to Cu, but more O atoms are exchanged from Cu/ZSM5 than correspond to the redox capacity of Cu. Brabec et al. studied oxygen isotope exchange with a variety of Fe/ZSM-5 systems that were prepared in different ways [10]. For the most active catalyst they found that the ratio of exchangeable oxygen to iron exceeded that of the formula Fe₂O₃. As in the work of Valyon and Hall this extensive exchange took place at a temperature at which no exchange was observed for the metal-free zeolite.

Cu/ZSM-5 and Fe/ZSM-5 are active catalysts for the reduction of NO_x with hydrocar-

bons in the presence of excess oxygen. At high metal loading, they are assumed to contain binuclear oxo-ions with bridging oxygen atoms, [Cu–O–Cu]²⁺ and [HO–Fe–O–Fe–OH]²⁺ respectively. If such complexes are isolated from each other, it is difficult to imagine how they can release O₂ molecules or how both atoms of an O₂ molecule can be exchanged with such complexes in one step without simultaneous participation of some oxygen ions of the zeolite. Panov et al. reported that their Fe/ZSM-5 catalysts contain so called α-oxygen which is generated by dissociative chemisorption of nitrous oxide [11]. They observed an extremely fast exchange between this α-oxygen and ¹⁸O₂ molecules, but in the same paper these authors also claim that over such catalysts the exchange rate of ¹⁶O₂ and ¹⁸O₂ is four orders of magnitude lower than over Fe₂O₃.

In the present paper isotope exchange data are reported for Fe/ZSM-5 catalysts that were prepared by chemical vapor deposition, in this case, sublimation of FeCl₃. They have been found to be very active in the reduction of NO_x with *iso*-C₄H₁₀ and other alkanes, even in the presence of a high partial pressure of water [6]. The exchange data for these catalysts are compared with those for supported Fe₂O₃. The results are discussed in the context of oxygen desorption data of the same catalysts.

2. Experimental

2.1. Catalyst preparation

The Fe/ZSM-5 catalysts were prepared by sublimation as described previously [12]. ZSM-5 zeolites with different Si/Al ratios, synthesized by the template method, were kindly provided by Degussa. Another catalyst was prepared with ZSM-5, provided by UOP (Si/Al = 14.2). Prior to sublimation of FeCl₃ onto H-ZSM-5, the zeolites were calcined in flowing O₂ at 550°C for 4 h. After sublimation at 320°C, the catalysts were washed in DDI water, to remove the chlo-

Table 1
Chemical composition of catalysts

Catalyst	Si/Al	Fe (wt.%)	Code
Fe/ZSM-5 (UOP)	14.2	5.0	U14
Fe/ZSM-5 (Degussa), M = 40 ^a	20.1	4.1	D20
Fe/ZSM-5 (Degussa), M = 120 ^a	61.5	2.9	D60
Fe ₂ O ₃ /ZSM-5, by impregnation	14.2	5.0	
Fe ₂ O ₃ /SiO ₂ , by impregnation		5.0	

^aM = SiO₂/Al₂O₃, provided by manufacturer.

rine, dried and calcined in pure O₂ at 550°C. The chemical composition determined by ICP analysis is listed in Table 1.

Iron containing ZSM-5 and SiO₂ catalysts containing mostly Fe₂O₃ particles and having a total iron load close to that of the materials prepared by sublimation, were synthesized by impregnating H-ZSM-5 (Si/Al = 14.2, provided by UOP) or SiO₂ with an aqueous solution of Fe(NO₃)₃, followed by drying and calcination at 550°C.

2.2. Isotopic-exchange technique

Isotopic-exchange experiments were performed in a vacuum setup (total volume 450 ± 5 ml) with an on-line mass spectrometer. To avoid mass-transfer effects, a shallow catalyst bed was used, exposed to the gas phase on two sides, and wide tubes were used. A nonequilibrated O₂ mixture containing about 80 at.% ¹⁸O was used. Pressure was monitored by a TC gauge in the range 0.1–2 Torr and by an ionization gauge in the 10⁻⁶ to 10⁻² Torr range. A membrane pressure gauge was used for readings above 2 Torr. To dose the oxygen into the MS chamber, a leak valve was used. The decrease of total pressure owing to removal of oxygen was less than 5% during a 24-h run at 0.5 Torr and negligible at higher pressures. A calibration curve was plotted by step-by-step dilution of pure oxygen with nitrogen, passed through an Mn/Al₂O₃ trap.

To minimize the contribution of oxygen desorption at elevated temperature, the samples were evacuated at $P < 10^{-4}$ Torr at 400–500°C,

followed by preconditioning in ¹⁶O₂ overnight at the same temperature and pressure as in the exchange reaction. Two sets of conditions were used for the exchange experiments: either 0.2 g solid and 0.5 Torr ¹⁸O₂, or 0.035 g solid and 2 Torr, these conditions correspond to an O^{gas}/O^{solid} ratio of ~ 0.004 and 0.1 respectively, where O^{solid} refers to the total number of oxygen atoms in the solid, including the zeolite.

2.3. Temperature programmed desorption (TPD)

TPD experiments were performed under flow conditions with ultra-high purity He as a carrier (ca. 60 ml/min). An Mn/Al₂O₃ trap lowered the O₂ impurity in the He to 0.1 ppm. Typically, after an isotopic-exchange experiment the sample was closed inside the reactor, transferred to the TPD system and thoroughly purged with He before a TPD run was started. The temperature was increased to 600°C with a ramp of 8°C/min and held there for 1 h. For details see Ref. [13].

2.4. Reaction studies

Catalytic tests were carried out in a continuous downflow microreactor with on-line GC analysis of products. Typically, 0.2 g of Fe/ZSM-5 (60–80 mesh) and reaction mixture of 0.2% NO, 0.2% isobutane, 3% O₂ and balance He with a total flow of 280 ml/min were used. Other details are as in Ref. [12].

2.5. Evaluation of kinetic data

The following definitions will be used:

numbers of molecules: ¹⁸O₂: x ; ¹⁶O¹⁸O: y ; ¹⁶O₂: z ; their sum is $a = x + y + z$. It follows for the ¹⁸O atomic fraction in the gas phase: $w = (2x + y)/2a$;

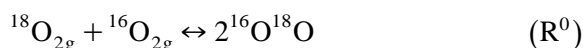
number of exchangeable O atoms in the solid: m , of which u atoms are ¹⁸O and v atoms are ¹⁶O. It follows that $m = u + v$ and the ¹⁸O atomic fraction in the solid $w_s = u/m$

First we will consider all m atoms kinetically equivalent, in a subsequent refinement we will distinguish a ‘pool’ of easily exchangeable (with the gas phase) O atoms from its environment of O atoms that may exchange with the ‘pool’ via a solid-state exchange process.

In writing the kinetic equations one must consider statistical factors. For instance, in the exchange of an $^{16}\text{O}^{18}\text{O}$ molecule with $^{16}\text{O}_s$ atoms two possibilities exist: either an $^{16}\text{O}_2$ is formed by exchange of the ^{18}O atom of the gas molecule, or a new $^{16}\text{O}^{18}\text{O}$ molecule is formed by exchange of the ^{16}O atom in the original molecule against an $^{16}\text{O}_s$ atom. Both exchange probabilities are equal but only the former is observed.

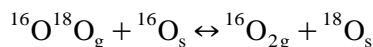
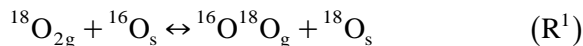
As outlined in the Introduction, three types of exchange have to be considered.

(1) No participation of atoms from the solid is observable:

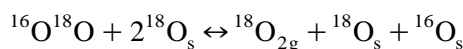
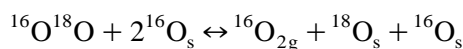
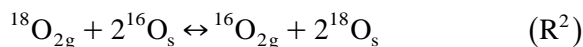


In this R^0 process $dw/dt = 0$

(2) In a given exchange event only one O atom in an O_2 molecule is exchanged against an O_s atom:



(3) In a given exchange event both atoms of an O_2 molecule are exchanged against two O_s atoms:



For the three isotopic molecules in the gas phase the following kinetic equations result:

$$\begin{aligned} dx/dt = & R^0/a^2[y^2/4 - xz] + R^1/am \\ & \times [(yu)/2 - xv] + R^2/am^2 \\ & \times [(y+z)u^2 - x(v^2 + 2uw)] \end{aligned} \quad (1)$$

$$\begin{aligned} dy/dt = & R^0/a^2[2xz - y^2/2] + R^1/am \\ & \times [xv + zu - yv/2] + R^2/am^2 \\ & \times [(x+y)v^2 - 2zvu] \end{aligned} \quad (2)$$

$$\begin{aligned} dz/dt = & R^0/a^2[y^2/4 - xz] + R^1/am \\ & \times [(yv)/2 - zu] + R^2/am^2 \\ & \times [(x+y)v^2 - 2zvu] \end{aligned} \quad (3)$$

Klier et al. [14] developed an algorithm, based on Eqs. (1)–(3) in integrated form, to calculate the rate constants R^0 , R^1 and R^2 . In a previous paper, this was applied to the exchange of hydrogen isotopes between the gas phase and EDA complexes of anthracene with Na or K [15]. The number of ^{18}O atoms in the gas phase w is given by:

$$\begin{aligned} w = & w_\infty + (w_0 - w_\infty)\exp[-(2R^2 + R^1) \\ & \times (1/m + 1/(2a))t] \end{aligned} \quad (4)$$

or, in empirical form, better suitable for numerical curve fitting:

$$w = w_\infty + (w_0 - w_\infty)\exp[-At] \quad (4')$$

If oxygen of the pool that exchanges rapidly with the gas phase, is leaking slowly from the pool to other parts of the solid, w_∞ is not constant. The time dependence of w_∞ is introduced into the model by putting:

$$w_\infty = w_{\infty 0}\exp[-k_w t] \quad (5)$$

The main advantage of Klier’s approach is that all three constants can be calculated simultaneously from experimental curves. Any gas-phase composition can be used; however, a high enrichment with ^{18}O is desired to minimize experimental error.

It is easy to see that for $R^2 = 0$ a pre-equilibrated gas phase with $\Psi = y^2/xz = 4$ will stay in equilibrium while exchange with the solid proceeds, but when the R^2 process dominates, this value will decrease even for a pre-equilibrated gas and return to the value $\Psi = 4$ only when w and w_s approach each other. Based on this approach, Tsuchiya et al. [15] developed

another algorithm for R^2 to evaluate experiments in which pre-equilibrated mixture of $^{18}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}_2$ were used at the start of the exchange with the solid. From the slopes of the measured curves the values of the rate constants were derived. The same strategy will be used in the present work. Experimental curves are fitted to exponential functions with empirical parameters. This appears physically meaningful since hetero-exchange reactions are considered as first-order. The slope of the curve (reaction rate) can be easily derived using a trivial calculus procedure and can be determined accurately at any time of the run. Good coincidence between the rate with decreasing and increasing concentrations ($dx/dt + dy/dt + dz/dt = 0$) verifies internal consistency.

When the same initial composition of oxygen is used for all experiments, the rate at $t \rightarrow 0$ can be used as a measure of the activity for a set of catalysts. A lack of accuracy, caused by the presence of $^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ impurities, is proportional to the partial pressure of these impurities and is not very high (less than 20%). In this way, $dz/dt|_{t=0}$ and $dy/dt|_{t=0}$ can be used for an estimate of R^2 and R^1 . Note that y will not simply increase because of R^1 , but it simultaneously decreases by the R^2 process converting $^{16}\text{O}^{18}\text{O}$ to $^{16}\text{O}_2$. Since $z/y \sim 10|_{t=0}$ this affects the value of $dy/dt|_{t=0}$ by about 10%, provided that R^1 and R^2 are of the same order. Similarly, the apparent (measured) value of $dz/dt|_{t=0}$ will be about 10% higher than the true value.

Under the conditions chosen here, the gas phase composition remained far from equilibrium during the first hour of the experiment; indicating that a homomolecular exchange may be disregarded. ($R^0 \sim 0$). Under these conditions the number of variables is equal to the number of equations, and the parameters R^1 , R^2 and m can be derived. The procedure chosen in this work is to pump off gas-phase oxygen after a certain reaction time and then to admit a fresh portion of $^{18}\text{O}_2$. Since the solid-state exchange proceeds much slower than the exchange with the gas phase, the state of the solid (w_s) is

nearly the same at the beginning of the $(N+1)$ th run as at the end of the N th run, i.e., $(w_s)_{N+1} \sim (w_s)_N$, while x , y , z and dx/dt , dy/dt , dz/dt are different. This provides a path for deriving R^1 and R^2 directly from Eqs. (1)–(3). They can be transformed, for instance, to the following:

$$R^2 = (dx/dt + 1/2dy/dt - ((2A+B)/C)(dz/dt + 1/2dy/dt)) / (2A+B+C) \quad (1')$$

$$R^1 = (2dz/dt + dy/dt)/C - 2R^2 \quad (3')$$

where $A = y/2 - x(1 - w_s)$; $B = zw_s + x(1 - w_s) - y/2$; $C = x + y/2 - w_s$.

For convenience, we will further substitute x , y and z by their normalized values, i.e., x/a . By Eqs. (1') and (3') refers, actually, to x/a . By varying w_s , we can minimize $\Sigma = |R_{N+1}^2 - R_N^2| + |R_{N+1}^1 - R_N^1| + |R_{N+1}^0 - R_N^0|$, where R_{i+1}^i refers to values obtained with (1') and (3') for the very beginning of the $(N+1)$ th run, R_N^i — for the end of the N th run. Actually, the values of dx/dt , dy/dt and dz/dt were obtained by fitting the whole kinetic curves, i.e., including all experimental points. The experimental scatter is small; although u/m increases with each run, the values of the rare constants depend little on the run number.

In the present work the value of m is of particular interest; it represents the number of readily exchangeable oxygen atoms in the solid. It can be calculated using the material balance equation, i.e., the number of ^{18}O atoms at $t = 0$ is equal to $[2pV/(RT)]w_0$; and at $t = \infty$ it is equal to $[2pV/(RT)]w_\infty + mw_\infty$. Both numbers should be equal (the natural abundance of ^{18}O is neglected). This leads to:

$$m = 2pV/(RT)(w_0/w_\infty - 1) \quad (6)$$

w_∞ is calculated using Eqs. (4') and (5).

3. Results

3.1. Diatomic versus monoatomic exchange

The composition of the catalysts and the codes used are listed in Table 1. As expected, samples with a low Si/Al ratio result in a low-iron loading. Isotopic exchange over Fe/ZSM-5 was studied in the range 375°C–500°C. Typical kinetic curves are shown in Fig. 1A. An interesting feature is a well-defined maximum of P_{34} , observed for all catalysts studied at or above 450°C. In the case of Fe₂O₃/ZSM-5 it also exists at 400°C, while this is not the case for the catalysts U14 prepared by sublimation at the same temperature (Fig 1B). Whenever this maximum was ob-

Table 2

Exchange rate at $P_{O_2} = 0.5$ Torr (in $\mu\text{mol min}^{-1} \text{g}_{\text{Fe}}^{-1}$)

Catalyst	Temperature (°C)	$-dx/dt$	dy/dt	dz/dt	$(dz/dt)/(dy/dt)$
U14	375	0.35	0.33	0.02	0.06
U14	400	0.76	0.57	0.19	0.33
U14	450	4.92	2.89	2.03	0.70
U14	500	18.87	6.57	12.29	1.87
D60	400	~0.04	n.d.	n.d.	
D60	450	0.94	0.68	0.26	0.38
D60	500	4.23	1.96	2.27	1.16
D20	450	2.51	1.25	1.26	1.01
Fe ₂ O ₃ /ZSM-5	400	1.71	0.36	1.34	3.72
Fe ₂ O ₃ /ZSM-5	450	14.38	3.45	10.93	3.17
Fe ₂ O ₃ /ZSM-5	500	21.54	4.26	17.28	4.06
Fe ₂ O ₃ /SiO ₂	450	1.42	0.66	0.76	1.15

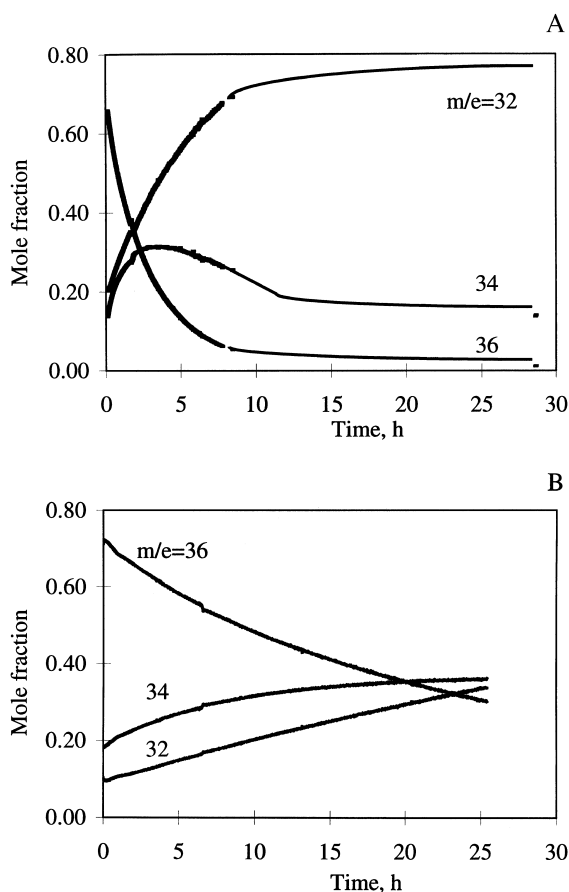


Fig. 1. Isotopic ¹⁸O₂ exchange over catalyst U14 at $P_{O_2} = 0.5$ Torr: 450°C (A) and 400°C (B).

served, $P_{34\text{max}}$ was always less than 0.33 (Fig 1A).

Reaction rates at $P_{O_2} = 0.5$ Torr, calculated from the slope of the kinetic curves at $t = 0$ are listed in Table 2. The first obvious conclusion is that at any temperature, the exchange rate is higher for Fe₂O₃/ZSM-5 than for any Fe/ZSM-5 prepared by sublimation. However, most of the latter catalysts are more active than Fe₂O₃/SiO₂; only for the zeolite with Si/Al = 60 is the exchange rate very low. Since Fe₂O₃/ZSM-5 and Fe₂O₃/SiO₂ have the same loading (5 wt.%), the difference in exchange rate is likely caused by different sizes of the Fe₂O₃ particles. The implication is that the surface of these particles is the locus of the exchange with the gas phase; secondary isotope exchange between surface and interior of Fe₂O₃ particles appears to be significantly slower.

The Arrhenius plot for samples U14, D60 and Fe₂O₃/ZSM-5 is shown on Fig. 2. For the U14 catalyst all measured rate points, dx/dt , can be fit with a straight line with an apparent activation energy of 133 kJ/mol. As mentioned, the exchange rate with D60 is very low at 400°C, no reliable activation energy can be determined. In the case of Fe₂O₃/ZSM-5 the

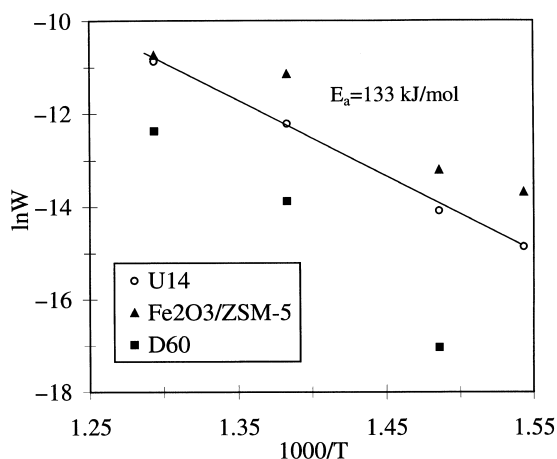


Fig. 2. Arrhenius plot of the overall reaction rates.

deviations from the Arrhenius line are significant. Two explanations can be considered: either at 500°C, the intrinsic reaction rate is very high and pore diffusion is no longer negligible; or the reaction rate over Fe_2O_3 particles might be sensitive to the number of oxygen vacancies which will depend on the activation temperature and the evacuation time before admission of $^{18}\text{O}_2$. Pretreatment at various temperatures, even for the same evacuation time (1 min for all runs) can result in a different number of vacancies.

The feature which puts all sublimation catalysts apart from Fe_2O_3 on either support is that in the low-temperature region ($\sim 450^\circ\text{C}$) dy/dt is always higher than dz/dt . This indicates a higher activity of the sublimation catalyst for the monoatomic exchange R^1 at low temperature. At 500°C the diatomic exchange appears to overtake the monoatomic exchange with both U14 and D60. In contrast, with $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ a temperature increase from 400 to 500°C hardly affects the ratios $(dz/dt)/(dy/dt)$ and R^2/R^1 . Within this temperature region $(dz/dt)/(dy/dt)$ remains almost constant at 3.6 ± 0.5 . Apparently, the activation energy for the R^2 reaction is higher with the sublimation catalysts than with $\text{Fe}_2\text{O}_3/\text{ZSM-5}$.

As a consequence of the intrinsic features of the R^1 and R^2 mechanisms, revealed in our

earlier paper [13], the behavior of the ratio $\Psi = y^2/xz$ can help to discriminate between R^1 and R^2 mechanisms. In case of R^1 $d(\ln \Psi)/dt = 0$ while for $R^2 \gg R^1$, $R^0 d(\ln \Psi)/dt < 0$. Although no pre-equilibrated mixtures were used in the present work the behavior of Ψ can be compared for different catalysts and temperatures.

In the first few hours of the exchange the value of Ψ is very far from its equilibrium value of $\Psi_\infty = 4$ in all cases. It slowly approaches ~ 3 over time. However, as Ψ is a quotient of measured data, its relative error will be larger than that of each individual value. The difference between the calculated value of $\Psi \sim 3$ and the theoretical value $\Psi = 4$ is not necessarily significant.

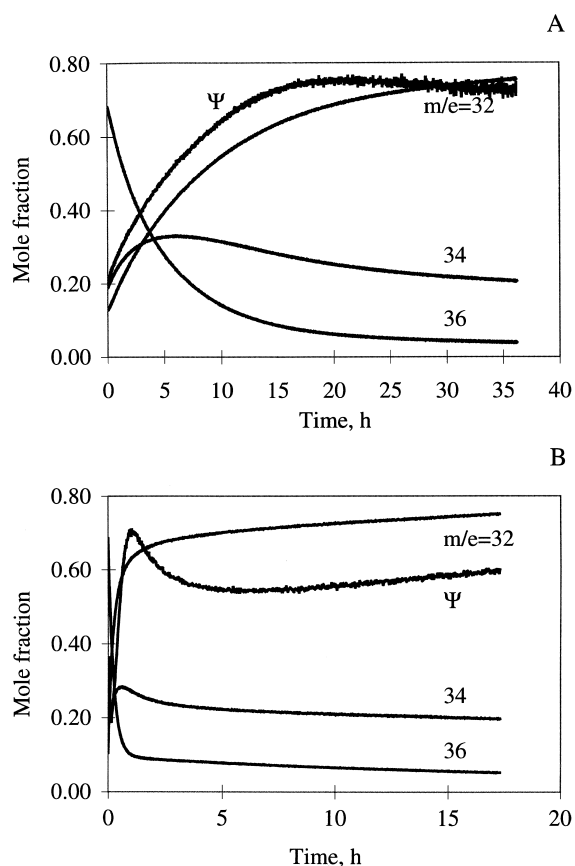


Fig. 3. Isotopic $^{18}\text{O}_2$ exchange at $P_{\text{O}_2} = 0.5$ Torr: D2O, 450°C (A) and $\text{Fe}_2\text{O}_3/\text{ZSM-5}$, 500°C (B). Behavior of Ψ -function is shown.

The Ψ -function of the catalysts U14, D20 and $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ shows a rather peculiar behavior at temperatures up to 450°C . First, Ψ grows steeply, reaching a value of 2–3, then it starts to decrease (Fig. 3). After a certain time, it increases again. This behavior was observed for several catalysts. From Fig. 3 one can see that always, $d\Psi/dt < 0$ while $dy/dt < 0$. This is another consistency criterion, as $d\Psi/dt < 0$ while $dy/dt > 0$ would be physically impossible.

In view of the temperature dependence of Ψ (in particular near 500°C , compare Fig. 3A and B) and the values of $(dz/dt)/(dy/dt)$ (see Table 2) we conclude that an R^2 type of exchange is typical for $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ while for the sublimation catalysts the R^1 type of exchange is preferred. However, at high temperature the contribution of the R^2 mechanism increases for the $\text{Fe}/\text{ZSM-5}$ prepared by sublimation.

3.2. Effect of oxygen pressure

Isotopic-exchange experiments were performed under different total oxygen pressures, they were varied from 0.5 to 100 Torr (Table 3). This pressure effect was studied in more detail for the catalyst U14. The overall reaction rate ($R^0 + R^1 + R^2$), measured as dx/dt , increases with rising O_2 pressure from 0.5 to 20 Torr for both U14 and $\text{Fe}_2\text{O}_3/\text{ZSM-5}$; the apparent reaction orders are 0.9 and 1.2, respectively. However, above 100 Torr the apparent order decreases, possibly suggesting pore diffusion con-

Table 3
Exchange rate at different O_2 pressures and $T = 500^\circ\text{C}$ (in $\mu\text{mol min}^{-1} \text{g}_{\text{Fe}}^{-1}$)

Catalyst	P_{O_2} (Torr)	$-dx/dt$	dy/dt	dz/dt
U14	0.5	18.9	6.6	12.3
U14	2	65.0	35.1	29.9
U14	20	75.2	56.0	19.2
U14	100	71.0	60.3	10.7
$\text{Fe}_2\text{O}_3/\text{ZSM-5}$	0.5	21.5	4.2	17.3
$\text{Fe}_2\text{O}_3/\text{ZSM-5}$	2	117.7	47.5	70.2

Table 4
Exchange rate at $P_{\text{O}_2} = 2$ Torr and $T = 500^\circ\text{C}$ (in $\mu\text{mol min}^{-1} \text{g}_{\text{Fe}}^{-1}$)

Catalyst	$-dx/dt$	dy/dt	dz/dt	Equilibration rate, a.u.
U14, 1st run	65.0	35.1	29.9	4.71
2nd	17.2	13.2	4.0	3.76
3rd	10.3	8.6	1.6	3.05
4th	7.4	6.7	0.6	2.78
$\text{Fe}_2\text{O}_3/\text{ZSM-5}$, 1st run	117.7	47.5	70.2	4.58
2nd	70.0	42.0	28.0	6.07
3rd	60.5	44.7	15.8	7.79
4th	52.7	41.35	11.35	8.65

trol, and the R^1 mechanism prevails. For U14 and $\text{Fe}_2\text{O}_3/\text{ZSM-5}$; the trend towards a higher contribution of R^1 becomes visible even below 20 Torr.

3.3. Extent of exchange

To obtain a high ^{18}O concentration in the solids, isotopic exchange was carried out at high O_2 pressure (20–100 Torr), and in multiple runs at 2 Torr. Run-to-run reaction rates are given in Table 4 and kinetic curves are shown on Fig. 4. As observed at 0.5 Torr, the reaction rate over $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ is higher than over the sublimation catalysts. Second and following runs result in an apparent rate decrease which is, however, a mere consequence of the growing ^{18}O content

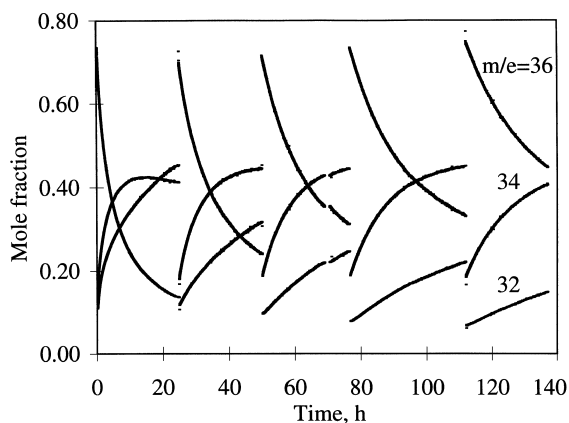


Fig. 4. Isotopic $^{18}\text{O}_2$ exchange over catalyst $\text{Fe}/\text{ZSM-5}$ at $P_{\text{O}_2} = 2$ Torr, 500°C . New portion of $^{18}\text{O}_2$ was added five times.

Table 5
Exchange degree of the solid at 500°C

Catalyst	20 Torr		100 Torr		4 runs at 2 Torr	
	O/O ^{solid}	O/Fe	O/O ^{solid}	O/Fe	O/O ^{solid}	O/Fe
U14	0.10	4.2	0.07	2.7	0.12	4.65
Fe ₂ O ₃ /ZSM-5	–	–	–	–	0.12	4.75

in the solid. Data in Table 4 show that dy/dt and dz/dt decrease more rapidly from run to run over Fe/ZSM-5 than over Fe₂O₃/ZSM-5, which suggests that the amount of ¹⁸O in the readily exchangeable pool is higher for the sublimation catalyst. Since experimental conditions are identical, this result indicates that either the size of the Fe ‘pool’ is smaller for Fe/ZSM-5, or exchange between the Fe pool and the rest of the solid is faster for Fe₂O₃/ZSM-5. The latter process moves ¹⁸O atoms from the small ‘pool’ to the larger ‘ocean’ of zeolite oxygen, thus decreasing w_s . Without knowledge about the size of the Fe pool we can not discriminate between these two possibilities.

Interestingly, the rate of gas-phase equilibration, measured as an initial slope of Ψ for the first run, is almost the same for both catalyst. The run-to-run behavior of it, however, is totally different (Table 4, last column). For the sublimation catalyst it decreases monotonously while for Fe₂O₃/ZSM-5 it increases. We can only speculate that this could be another indication of different pool sizes between these two catalysts.

Quantitatively, the number of ¹⁸O atoms introduced into the solid, is listed in Table 5. Up to 10% of all oxygen atoms, including the zeolite oxygen, could be replaced relatively easy. One can see that multiple runs when new por-

tions of ¹⁸O₂ were added are a more efficient way to achieve high extent of exchange, even though this exchange proceeds at a lower O^{gas}/O^{solid} ratio than the high-pressure experiments. Data in Table 5 refer to values calculated from experimental curves obtained at 20 and 100 Torr, at a time when the slopes of P₃₂, P₃₄ and P₃₆ became very low. Extrapolation to $t = \infty$ could be made using Eq. (4’); however, this extrapolation adds only about 5% to the last measured extent of exchange. Therefore, only the experimental values are listed in Table 5.

3.4. Simulated reaction rates and the size of the Fe pool

Where data were available, an estimate of R^0 , R^1 and R^2 was made on the basis of the approach, described in the previous section. The main assumption is that in successive runs the state of the solid does not change while the gas phase is replaced by fresh oxygen and the first rate is measured with it. Simulated values are given in Table 6 and compared with experiment. They confirm that in most cases, especially at 400°C, the rate of the homomolecular exchange is negligible ($R^0 \sim 0$). The only exception is U14 at 500°C. In general, the agreement between experiment and simulation is reasonable, though experimental values of dy/dt are lower than calculated R^1 values. Also the data of Doornkamp indicate absence of the R^0 mechanism [16].

For $R^0 = 0$ Eqs. 1–3 can be resolved and values of w_s , R^1 and R^2 can be derived. We believe that this assumption is correct at 450°C. The values of R^1 and R^2 , thus calculated are

Table 6
Calculated and experimental reaction rates ($\mu\text{mol min}^{-1} \text{g}_{\text{Fe}}^{-1}$)

Catalyst	R^1 (dy/dt)	R^2 (dz/dt)	R^0	$R^0 + R^1 + R^2$ (dz/dt)
U14, 400°C, 0.5 Torr	0.7 (0.6)	0.2 (0.2)	~ 0	0.9 (0.8)
Fe ₂ O ₃ /ZSM-5, 400°C, 0.5 Torr	0.8 (0.4)	1.7 (1.3)	~ 0	2.5 (1.7)
U14, 500°C, 2 Torr	4.3 (47.9)	26.4 (40.7)	62.9	93.7 (88.6)
Fe ₂ O ₃ /ZSM-5, 500°C, 2 Torr	60.3 (47.5)	82.8 (70.2)	~ 0	143.0 (117.7)

Table 7

Calculated and experimental reaction rates at 450°C and $P_{O_2} = 0.5$ Torr ($\mu\text{mol min}^{-1} \text{g}_{\text{Fe}}^{-1}$)

Catalyst	R^1	dy/dt	R^2	dz/dt	O/Fe, TPD
U14	6.0	2.9	1.9	2.0	0.108
D20	2.6	1.2	1.2	1.2	0.082
D60	0.7	0.7	0.2	0.3	0.042
$\text{Fe}_2\text{O}_3/\text{ZSM-5}$	9.3	3.5	15.9	10.9	0.02

presented in Table 7. Basically, data in Tables 6 and 7 agree with our previous conclusion that R^2 exchange is more typical for the impregnated catalyst while for all sublimation catalysts $R^1 > R^2$, regardless of the Si/Al ratio. Interestingly, the rates for the sublimation catalysts U14, D20 and D60 correlate qualitatively with the amount of oxygen released thermally, the data from Ref. [13] are included in the last column of Table 7. For the impregnated catalyst no such correlation exists.

The number of exchangeable oxygen atoms in the ‘active pool’ are listed in Table 8. This should, however, be read as a rough estimate only for the values marked with an asterisk, where the data processor did not find a global minimum of the parameters w_{O_2} , k_w and exponential coefficient in Eq. (4'). In the other cases the set of parameters remained unchanged upon iteration and independent of the choice of the initial parameters and a global minimum was found.

As expected, the size of the active ‘pool’ is directly related with the Fe load, which is determined by the Si/Al ratio. For the sublimation

Table 8

The size of Fe pool ($O^{\text{gas}}/O^{\text{solid}} = 0.004$)

Catalyst	t (°C)	Pool ($\times 10^{20}, \text{g}_{\text{cat}}^{-1}$)	O/Fe exchange	TPD
U14 ¹	450	2.6	0.54	0.108
D20 ²	450	1.7	0.39	0.082
D60 ³		0.6*	0.20	0.042
$\text{Fe}_2\text{O}_3/\text{ZSM-5}^1$	450	1.3	0.26	0.02
$\text{Fe}_2\text{O}_3/\text{SiO}_2$	450	0.15*	0.03	0.004
U14 ¹	400	0.45	0.09	
$\text{Fe}_2\text{O}_3/\text{ZSM-5}^1$	400	0.67	0.14	

* Determined with large inaccuracy due to ‘shapeless’ curve.

catalysts, the pool becomes larger at higher temperature. The pool size increases also for the $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ catalysts; however, this tendency is less pronounced.

3.5. Thermal release of oxygen

Thermal desorption of oxygen from Fe/ZSM-5 was measured following isotopic exchange at either 0.5 or 100 Torr. The TPD pattern at 0.5 Torr is shown on Fig. 5A. Two main features are observed: a low-temperature (LT) peak at around 150°C and high-temperature (HT) peak at 600°C. The LT peak corresponds to release of weakly bonded oxygen. The LT profile identifies only the masses 32

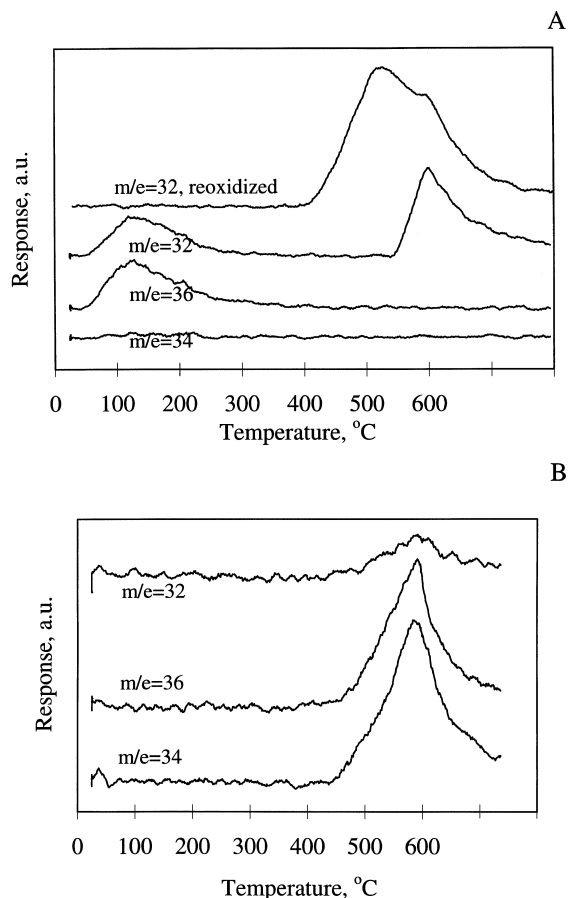


Fig. 5. TPD pattern of catalyst U14, subject to isotopic $^{18}\text{O}_2$ exchange at 0.5 Torr (A) and 100 Torr (B).

and 36 roughly in a 1:1 ratio, while only traces of mass 34 were detected.

At high temperature one sharp maximum is present near 600°C. Only mass 32 is observed in the released oxygen. Absence of mass 28 indicates the absence of a leak. A peak near 500°C, that was observed for Fe/ZSM-5 catalysts after treatment in O₂ at atmospheric pressure, is absent. As that feature is indicative for high coverage with adsorbed oxygen, the isotope exchange data correspond to ‘low coverage’. Indeed the HT peaks could be regenerated by heating the sample in flowing O₂ at 450°C. No LT peak at ~120°C was detected (Fig. 5A, upper curve). This experiment indicates that two types of Fe-oxocomplexes are present, both of which release molecular oxygen by heating, but only one type appears to participate in isotopic exchange at low O₂ pressure. The other type, that releases only O₂ of mass 32, does not participate in the exchange.

A TPD profile obtained after high-pressure exchange at 500°C is shown on Fig. 5B. The total absence of any peaks at 100°C–200°C is noteworthy, although the catalyst was cooled to room temperature in 100 Torr of O₂. The HT peak (or group of peaks) displays an isotopic composition, close to that of the gas phase at the end of isotopic exchange: roughly equal intensity of masses 34 and 36 and much less mass 32. This suggests that the state of the ‘pool’ of exchangeable oxygen in the solid and in the gas phase have reached isotopic equilibrium. In this stage further exchange is controlled by leakage of ¹⁸O from the ‘Fe pool’ to the zeolite oxygen.

3.6. Catalytic studies

Both U14 and Fe₂O₃/ZSM-5 catalysts were studied in NO SCR with isobutane as the reductant. The temperature dependence of the N₂, CO and CO₂ yields is shown on Fig. 6. The N₂ yield over the impregnated catalyst might be due to either the action of H-ZSM-5 or to the Fe oxide. Of greater relevance for the present topic

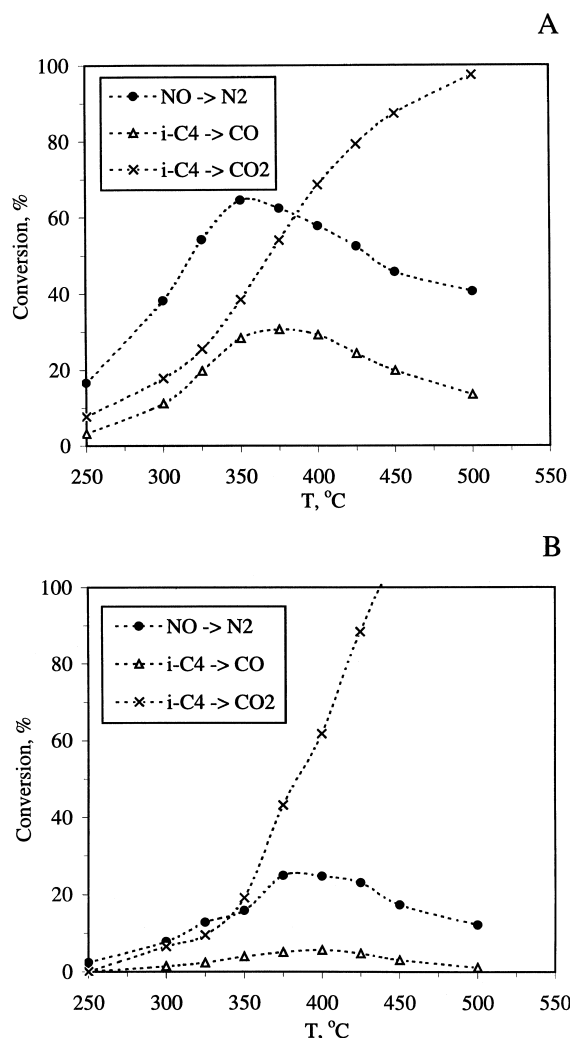


Fig. 6. NO SCR over U14 (A) and Fe₂O₃/ZSM-5 (B). Conditions: 0.2 g catalyst, 0.2% NO, 0.2% isobutane, 3% O₂ and balance He with a total flow of 280 ml/min.

is the CO/CO₂ ratio, which reflects the oxidizing ability of the catalysts. As one can easily see, the impregnated catalyst is much more selective towards complete oxidation of the hydrocarbon to CO₂ than the Fe/ZSM-5 catalyst prepared by sublimation.

4. Discussion

Homomolecular equilibration over Fe/ZSM-5 is negligible in most cases, except at tempera-

tures above 450°C. This makes $^{18}\text{O}_2$ exchange a sensitive probe reaction to characterization of active sites, able to activate oxygen. A major conclusion from the present study is that the nature of the Fe sites in the sublimation catalyst is different from that of Fe_2O_3 particles in ZSM-5 or on SiO_2 . Since the former is an active and selective catalyst for NO_x SCR in the excess of oxygen and water, it was proposed that this propensity is due to the lower catalytic oxidation power of the sublimation catalyst in comparison to iron oxide [12]. This is confirmed by the present catalytic data: the CO_2/CO ratio is much higher, under identical conditions, with $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ than with the Fe/ZSM-5 prepared by sublimation. The isotope-exchange data in Table 2 underscore the qualitative difference of the sites in these classes of Fe/zeolite catalysts. Irrespective of the temperature, the overall reaction rate is always higher over $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ than over the sublimation catalyst. This higher rate is not due to a higher dispersion of the active phase, in all likelihood the Fe_2O_3 particles in $\text{Fe}_2\text{O}_3/\text{ZSM-5}$ are larger than the clusters in the sublimation catalyst. Clearly, the high selectivity of the sublimation catalyst is due to the absence of sites which catalyze the deep oxidation of the alkanes.

A significant difference between both types of Fe catalysts is that, for all Fe_2O_3 containing catalysts the R^2 exchange mechanism prevails, but the sublimation catalyst displays an R^1 mechanism, especially at low temperature. Moreover, the contribution of either mechanism changes differently with temperature for both classes of catalysts: only over the sublimation catalysts does the contribution of the R^2 mechanism markedly increase with temperature. Apparently, there are only negligible amounts of Fe_2O_3 particles in the sublimation catalyst. The sites operating in the sublimation catalyst seem to be able to rupture the O–O bond of an adsorbed or impinging O_2 molecule, but they send it back to the gas phase with only one new O atom from the solid. In contrast, the surface of Fe_2O_3 acts as a stronger oxidizer, it retains

both O atoms of a trapped O_2 molecule and easily releases another pair of O atoms.

The nature of the R^2 mechanism is still subject to considerable speculation. A statistical model assumes a dynamic equilibrium between oxygen vacancies in an oxide and O_2 molecules in the gas phase. Once vacancies disappear by trapping O_2 , new vacancies are created by releasing O_2 elsewhere. Che and Tench assumed that strongly adsorbed $^{16}\text{O}_2$ molecules are displaced by impinging $^{18}\text{O}_2$ molecules [17]. We hesitate to accept that chemisorption of O_2 molecules can be strong enough to require 600°C for desorption, but we can imagine that at high temperature diatomic precursor states are formed; they might have the chemical characteristics of peroxide or superoxide ions. Displacement of such diatomic entities by O_2 molecules could be at the root of the R^2 mechanism. These precursors could be formed at elevated temperature from the normal surface O^{2-} ions or by interaction with the atmosphere. The presence of the low temperature TPD peak for samples exposed to $^{18}\text{O}_2$ at 0.5 Torr and the absence of oxygen molecules with mass 34 in the released gas suggest that adsorption can be involved in the formation of the diatomic units. Remarkably, this desorption is absent for Fe/ZSM-5 samples that were equilibrated at higher oxygen pressure.

The formation of diatomic $^{16}\text{O}-^{16}\text{O}$ units, capable of becoming displaced by $^{18}\text{O}_2$ molecules, is likely to be easier at the surface of an iron oxide particle than for spatially separated oxo complexes such as $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$ or $[\text{HO}-\text{Fe}-\text{O}-\text{Fe}-\text{OH}]^{2+}$, each having only one bridging oxygen atom. However, such complexes might communicate with each other via the O^{2-} ions of the zeolite. Indeed, the present work underscores the participation of zeolite oxygen in the isotope exchange process. One can imagine that two $\text{M}-\text{O}-\text{M}$ complexes, separated by a limited number of $\text{O}_{\text{zeol}}^{2-}$ ions, disproportionate into one $\text{M}-\text{O}-\text{O}-\text{M}$ and one $\text{M}-\square-\text{M}$ complex, where \square stands for an oxygen vacancy. Such disproportionation will require a higher

activation energy than the analogous process at the surface of iron oxide. Therefore, the sublimation catalysts will not catalyze the R^2 mechanism at low temperature.

In this view, the observation of Valyon and Hall of a fast R^2 exchange over Cu/Y [9] could indicate that ‘communication’ between two $[\text{Cu-O-Cu}]^{2+}$ complexes is much easier in the supercages of the Y zeolite with higher concentration of Al centered tetrahedra than in the cavities of MFI.

The present study also addresses the question of how much oxygen of the zeolite participates in isotope exchange. The highest extent of exchange observed in this work shows a ratio of exchangeable oxygen to iron equal to $\text{O}/\text{Fe} = 4.7$. Clearly, this is much higher than the number of oxygen atoms present in bridging positions or in Fe_2O_3 particles. The results thus confirm previous findings by Valyon and Hall [9] and by Brabec et al. [10]. However, the isotope-exchange rate appears to drop to zero long before all oxygen atoms in the zeolite are exchanged. With $\text{Fe}/\text{Al} \approx 1$ and $\text{Si}/\text{Al} = 14$, the ratio of total oxygen to Fe would be around 31/1, which is much higher than the extrapolated value of 4.7 in the present work. This number is, however, consistent with another geometric model. Upon assuming that the majority of the Fe complexes has a structure similar to the $[\text{HO-Fe-O-Fe-OH}]^{2+}$ ion, each Fe has 1.5 oxygen atoms attached to iron only. If each of the Fe atoms occupies a ‘hollow site’ of the zeolite wall, i.e., a position between three $\text{O}_{\text{zeol}}^{2-}$, the total number of oxygen atoms in contact with Fe will be 4.5, which is close to the number found experimentally. Previously, it was shown that the $[\text{HO-Fe-O-Fe-OH}]^{2+}$ model is in agreement with the observed Fe/Al ratio and the CO-TPR data [12,13]. Recent unpublished work showing a non-Curie-law temperature dependence of the EPR signal seems to indicate antiferromagnetic coupling between Fe ions by a bridging oxygen atom [18].

Part of the exchangeable oxygen is in the ‘active pool’ whereas the remainder communi-

cates with the gas phase more slowly, namely via that pool. The number of ‘active pool’ oxygen atoms has been estimated in Table 8. The estimate has a very high experimental error, the numbers given for the $\text{O}_{\text{act}}/\text{Fe}$ ratio are between 0.2 and 0.5 for the sublimation catalysts, which is consistent with the model.

For Fe/ZSM-5 catalysts with zeolites of various Al/Si ratios we had previously found that the amount of oxygen that could be released thermally decreases with decreasing Al/Si ratio [13]. This is consistent with the fact that a bipositive entity, such as the $[\text{HO-Fe-O-Fe-OH}]^{2+}$ ion, requires a pair of Al centered tetrahedra in close proximity for charge compensation. For thermal release of O_2 from such groups two such ions should be positioned close enough that they can ‘communicate’ with each other. At low Al/Si ratio of the zeolite, this condition will be fulfilled by only a small number of the Fe complexes.

5. Conclusions

Kinetic analysis of the isotope exchange kinetics reveals qualitative differences between two types of supported iron catalysts: (1) Fe/ZSM-5 prepared via sublimation and capable to catalyze NO_x reduction with some alkanes, (2) supported Fe_2O_3 on ZSM-5 or SiO_2 and displaying high activity but poor selectivity in NO_x reduction. The supported Fe_2O_3 catalysts show a prevailing R^2 exchange mechanism, analogous to other transition metal oxides, but the active Fe/ZSM-5 catalyst display a lower exchange rate and a prevailing R^1 mechanism. at low temperature. The activation energy for the R^2 mechanism is higher.

Exchange is not limited to oxygen atoms that are bonded to Fe ions only, but the extrapolated atomic ratio of exchangeable oxygen to iron is near 4.7/1. Part of this oxygen is exchanged readily, the remainder exchanges more slowly.

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