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The Isotopic Exchange Reaction of Oxygen on Metal Oxides

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Two methods have been used to determine the individual rate constants of the isotopic exchange reaction of oxygen on metal oxides. The best way to determine the three rate constants is to use the kinetic model of Klier and co-workers and fit the equations to the experimental data. The method of Tsuchiya and co-workers can be used to check the results obtained by the method of Klier and co-workers. The three rate constants, R^0, R^1, and R^2, of the three different exchange mechanisms are determined for the period IV metal oxides at various temperatures. The rate constants are correlated with parameters characterising the oxide, i.e. the position of the metal element in the periodic table and the average metal–oxygen bond strength. © 1999 Academic Press

Key Words: **oxygen isotopic exchange; metal oxides; activity pattern; metal–oxygen bond strength; Tammann temperature.**

INTRODUCTION

One of the essential functions of the catalyst in oxidation reactions is the activation of oxygen. The way in which oxygen is activated is a crucial problem in oxidation catalysis. It is generally accepted that lattice oxygen plays an important role in selective oxidation reactions. However, there is still a debate about the role of various adsorbed oxygen species in oxidation reactions (1, 2).

The interaction of molecular oxygen with a metal oxide can be investigated with the oxygen isotopic exchange reaction. From the course of the oxygen exchange reaction, conclusions can be drawn about the way in which oxygen takes part in the catalytic processes.

In the presence of an oxide there are three possible ways for an oxygen molecule to exchange its atoms:

—the oxygen molecule exchanges one of its atoms with another oxygen molecule from the gas phase, without the participation of the oxide's oxygen (R^0-mechanism).

$$^{18}O_2(g) + {}^{16}O_2(g) \rightarrow 2\ {}^{18}O^{16}O(g)$$

—the oxygen molecule exchanges one of its atoms with the surface oxygen of the metal oxide (R^1-mechanism).

$$^{18}O_2(g) + {}^{16}O_s \rightarrow {}^{18}O^{16}O(g) + {}^{18}O_s$$

—the oxygen molecule exchanges both its atoms with the surface oxygen of the metal oxide (R^2-mechanism).

$$^{18}O_2(g) + 2\ {}^{16}O_s \rightarrow {}^{16}O_2(g) + 2\ {}^{18}O_s$$

The isotopic exchange reaction was extensively studied in the 1960s by Klier and co-workers (3–8), Winter (9, 10), and Boreskov and co-workers (11–18). These authors used different methods to determine the rate constants of the different mechanisms of the exchange reaction. Klier and co-workers showed that it was possible to determine the three different rate constants by fitting their kinetic model (integral equations) to the experimental data. However, since the ^{18}O concentration in these experiments was low (approximately 18%), these fits were not very accurate (3–8). Winter, who also used kinetic equations to derive the rate of exchange, determined only the exchange rate of the main mechanism (9, 10). Boreskov and co-workers determined the exchange rates by following the $^{16}O^{18}O$ concentration with time over an oxide whose oxygen had been enriched to the same concentration of ^{18}O as the gas phase. In this case the overall rate constant K, being the sum of the three individual rate constants R^0, R^1 and R^2, was determined. Boreskov and co-workers also determined the exchange rate of ^{18}O with the oxide's oxygen starting with the natural isotopic composition of the oxide. This rate constant R is the sum of the individual rate constants R^1 and R^2 (11–18).

Another method to determine the rate constant of the R^2 mechanism was shown by Tsuchiya *et al.* (19) in the hydrogen–deuterium exchange reaction, since with the hydrogen–deuterium exchange reaction on hydrides or hydrogen containing catalysts in general, the same three types of mechanisms as described above can take place. Therefore, this method can also be used for determination of the R^2 rate constant of the isotopic oxygen exchange reaction.

To summarise, the rate constants of the isotopic oxygen exchange reaction published so far are either the overall

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rate constants as determined by Boreskov (18) or some individual rate constants which were determined with a limited accuracy (9).

Since it is very interesting to establish the exact contribution of the three exchange mechanisms, a good method is desirable to determine all the individual rate constants. In the first part of this paper, we have used the methods of Klier *et al.* (3) and Tsuchiya *et al.* (19) and made an attempt to determine all three rate constants with higher accuracy than achieved earlier. In the second part we determined the individual rate constants for the period IV metal oxides at various temperatures and correlated these values with parameters characterising the oxide, i.e., the position of the metal element in the periodic table and the average metal–oxygen bond strength. This will be done having in mind the potential impact of this correlation on the theory of activity and selectivity of metal oxides in oxidation reactions.

EXPERIMENTAL

Testing the Method of Klier et al. and Tsuchiya et al.

The isotopic exchange reactions were carried out in a static apparatus at low pressures (in the range of mbar). The concentration of all three isotopes in the gas phase was followed in time by a mass spectrometer (VG instruments 8–80 mm) connected with the apparatus via a continuous leak. The pressure decrease was negligible during the experiment. The reactor was made of quartz and had a volume of 912 ml. All experiments have been performed at a total pressure lower than 1 mbar to minimise mass transport problems.

Two types of exchange experiments were performed. Either the exchange reaction was started with an equilibrium mixture of all the dioxygen isotopes or with a nonequilibrium mixture of only $^{16}O_2$ (Messer Griesheim) and $^{18}O_2$ (Isotec Inc. 99.1% ^{18}O). The equilibrium mixture of all the dioxygen isotopes was prepared by introducing a 1 : 1 mixture of $^{16}O_2$ and $^{18}O_2$ into a vessel with a sealed-in platinum wire, which was heated to approximately 1300 K. In both types of experiments, the $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ concentration was followed with time and the total dioxygen pressure was in both cases 0.9 mbar.

Before each experiment the oxides were treated in a vacuum (10^{-3} mbar) at the temperature of the exchange reaction for 3 h. After treatment in a vacuum, the oxides were equilibrated for 3 h with $^{16}O_2$ at a pressure of 0.9 mbar and at the temperature of the reaction.

Since water and CO_2 can have an influence on the oxygen isotopic exchange reaction, the water vapour and CO_2 pressure have been monitored by the mass spectrometry during the standard treatment of the oxides. At the end of this treatment these pressures were at the noise level and do not have any influence on the exchange reaction.

To test the methods of Klier and co-workers and Tsuchiya and co-workers to determine the individual rate constants in the isotopic exchange reaction, two different oxides were used, V_2O_5 and Fe_2O_3. Because of large differences in the activity of these oxides in the exchange reaction, the exchange reaction on Fe_2O_3 was investigated in a different temperature range than on V_2O_5. For Fe_2O_3 the temperature range under investigation was between 623 and 823 K and for V_2O_5 between 743 and 823 K.

Commercially available V_2O_5 (BDH) was used. Fe_2O_3 was prepared by thermal decomposition of $Fe(OH)_2$, obtained by precipitation of the corresponding metal nitrate at pH 9. The hydroxide was decomposed in air at 773 K. X-ray diffraction was used to check the structure of Fe_2O_3.

Isotopic Exchange Reaction on the Period IV Metal Oxides

The exchange reaction on the period IV metal oxides was carried out at various temperatures. The temperature range was dependent on the activity of the oxide under investigation. Since the difference in activities of the oxides in the exchange reaction is quite large, the temperature ranges varied with the metal oxide. The amount of oxide which was used for an experiment was also chosen according to the activity of the metal oxide. The temperature and amount of oxide were chosen in such a way that within 1–10 h, equilibrium between gas phase and oxide had been reached. The total oxygen pressure was always 0.9 mbar.

The characteristics of the period IV metal oxides are shown in Table 1. NiO was prepared by thermal decomposition of $Ni(NO_3)_2$ at 773 K for 18 h. For the other period IV metal oxides commercially available oxides have been used as supplied.

The heat of formation, ΔH_f, of the oxide has been used as a measure for the average M–O bond strength (20). The M–O bond strength is defined hereby as the heat of formation of the metal oxide divided by the number of oxygen atoms contained in the oxide (ΔH_f/O atom).

TABLE 1

Characteristics of the Period IV Metal Oxides

Oxide	Precursor	Supplier	Surface area (m^2/g)	M–O bond strength (kcal/mol)	Melting point (K)
V_2O_5		BDH	5.1	74.1	963
Cr_2O_3		BDH	2.6	90.8	2539
MnO_2		Merck	2.9	62.2	808[a]
Fe_2O_3	$Fe(NO_3)$	Baker	22.9	65.7	1838
Co_3O_4		BDH	7.3	53.3	1223
NiO	$Ni(NO_3)$	Baker	7.0	57.3	2257
CuO		Merck	5.3	36.6	1599
ZnO		AZL	5.1	83.2	2248

[a] Decomposition at 808 K.

RESULTS

Two methods have been used for determining the rate constants of the three mechanisms of the isotopic exchange reaction. These methods depend on the initial composition of the gas phase. The first method (the method of Tsuchiya *et al.* (19)) can be used if the experiment is started with an equilibrium composition of the gas phase. The second method (the method of Klier *et al.* (3)) can be used with any kind of initial composition of the gas phase (equilibrium and nonequilibrium composition). With the first method only one rate constant (R^2) can be determined, while with the second method all three rate constants can be determined.

Method of Tsuchiya et al.: Starting with an Equilibrium Composition of the Gas Phase

If the quantity Ψ is defined as $\Psi = [^{16}O^{18}O]^2/[^{16}O_2][^{18}O_2]$ and the gas phase composition is at equilibrium, the quantity Ψ is equal to the equilibrium constant Ψ_{eq}, which is 4. When the exchange reaction is started with this equilibrium composition and only the R^0 or R^1 mechanisms operate then $d\Psi/dt = 0$. However if the R^2 mechanism operates as well, then $d\Psi/dt \neq 0$. In the case that the oxide only consists of ^{16}O and when $R^2 \gg R^1$ or R^0, the initial decrease of Ψ is given by

$$\left(\frac{d\ln\Psi}{dt}\right)_{t=0} = -R^2\frac{1}{z}, \quad [1]$$

with z the amount of $^{16}O_2$ molecules in the system at $t=0$ or

$$R^2 = -(^{16}O_2)\left[\frac{d\ln\Psi}{dt}\right]_{t=0}. \quad [2]$$

Thus, if the R^2 mechanism is large enough, it will always change the equilibrium composition. This means that the rate constant for the R^2 mechanism can be determined from the slope of $\ln\Psi$ with time. An example of the decrease of Ψ versus time is shown in Fig. 1a for V_2O_5 at 823 K.

Figure 1b shows the dependence of Ψ versus time for Fe_2O_3 at 743 K. The quantity Ψ decreases with time and reaches 4 again after 200 min. The return of Ψ to the equilibrium value is much faster for Fe_2O_3 than for V_2O_5.

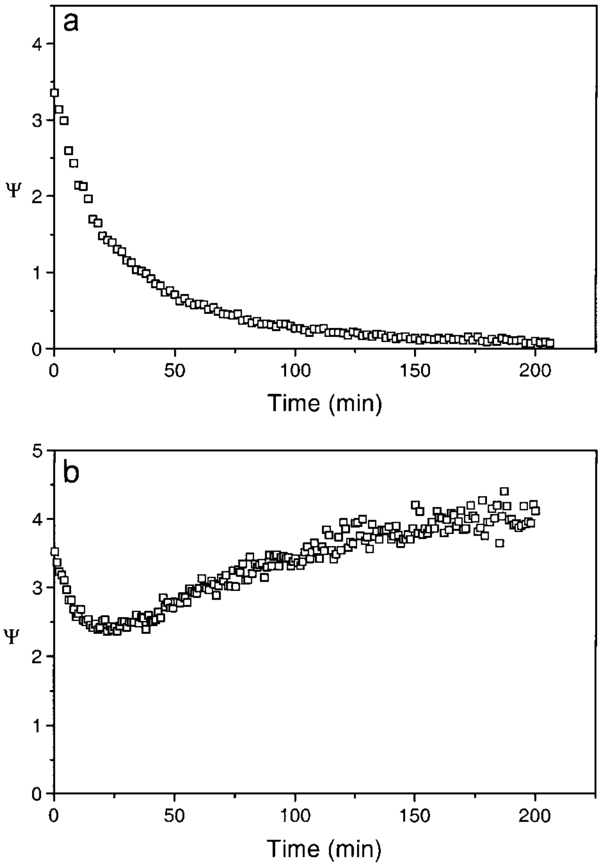

FIG. 1. The dependence of Ψ versus time on (a) V_2O_5 at 823 K and (b) Fe_2O_3 at 743 K.

Method of Klier et al.: Starting with a Nonequilibrium Composition of the Gas Phase

The second method to determine the individual rate constants is by fitting the kinetic equations as described by Klier and co-workers to the experimental data. The model of Klier is based on six different reactions in which the exchange leads to a change in the isotopic composition:

$$^{18}O_2(g) + {}^{16}O_2(g) \rightarrow 2\,{}^{18}O^{16}O(g) \qquad R^0$$

$$\left.\begin{array}{l} ^{18}O_2(g) + {}^{16}Os \rightarrow {}^{18}O^{16}O(g) + {}^{18}O_s \\ ^{18}O^{16}O(g) + {}^{16}Os \rightarrow {}^{16}O_2(g) + {}^{18}O_s \end{array}\right. \qquad R^1$$

$$\left.\begin{array}{l} ^{18}O_2(g) + 2\,{}^{16}O_s \rightarrow {}^{16}O_2(g) + 2\,{}^{18}O_s \\ ^{18}O^{16}O(g) + 2\,{}^{18}Os \rightarrow {}^{18}O_2(g) + {}^{18}O_s + {}^{16}O_s \\ ^{18}O^{16}O(g) + 2\,{}^{18}Os \rightarrow {}^{16}O_2(g) + {}^{18}O_s + {}^{16}O_s \end{array}\right. \qquad R^2$$

Klier and co-workers showed that the number of ^{18}O atoms (w) in the gas phase is given by

$$w = w_\infty + (w_0 - w_\infty)\exp\left[-(2R^2 + R^1)\left(\frac{2a+m}{2am}\right)t\right]. \quad [3]$$

The symbols used here are the same as used by Klier *et al.* (3), whereby m is the total number of exchangeable oxygen atoms in the oxide, a the total number of oxygen molecules, and R^1 and R^2 the rate constant for the R^1 and R^2 mechanism, respectively. By fitting this equation to the time dependence of the concentration of ^{18}O in the gas phase, the total exchange rate ($2R^2 + R^1$) with the oxide can be determined. The program used for fitting Eq. [3] to the experimental data performed a least square fitting using a modified Powell algorithm.

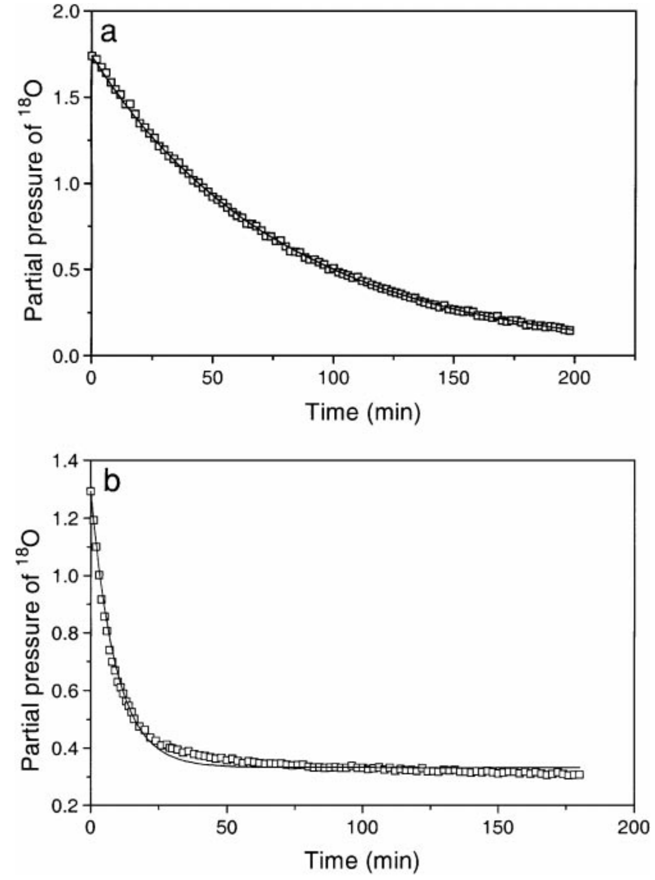

FIG. 2. Best fit of Eq. [3] to the time dependence of the partial pressure of ^{18}O on (a) V_2O_5 at 773 K and (b) Fe_2O_3 at 743 K.

In Figs. 2a and 2b the best fit of Eq. [3] for the ^{18}O concentration over, respectively, V_2O_5 and Fe_2O_3 is shown. The best fit is represented by the continuous line. In the case of V_2O_5 Eq. [3] fits the data very well, but this is not the case for Fe_2O_3.

According to the model of Klier *et al.* the concentration of ^{18}O in the gas phase (w) should be constant after equilibrium between the gas phase and the oxide has been reached. With Fe_2O_3 the ^{18}O concentration still decreases, also when equilibrium ($\Psi = 4$) has been reached. The apparent equilibrium concentration of ^{18}O (w_∞) is dependent on time. Therefore, a time dependence of w_∞ was introduced into the model of Klier *et al.* in the form of

$$w_\infty = w_{\infty 0} \exp(-k_w t). \qquad [4]$$

In Fig. 3 the best fit is shown by combining Eqs. [3] and [4] for the ^{18}O concentration over Fe_2O_3. In this case the kinetic equations fit the data very well.

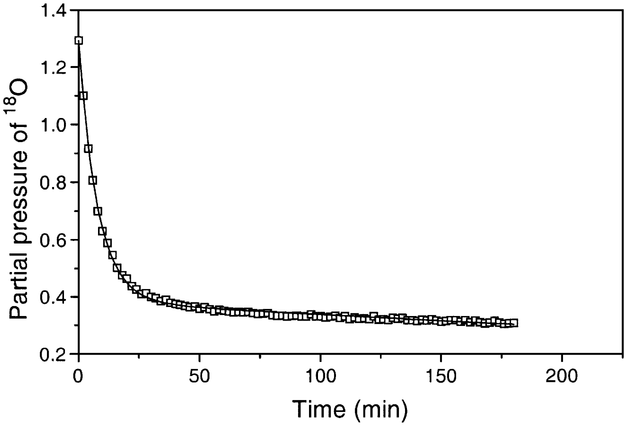

FIG. 3. Best fit of Eqs. [3] and [4] to the time dependence of the partial pressure of ^{18}O on Fe_2O_3 at 743 K.

With the kinetic equations as described by Klier and coworkers, fitting the time dependence of $^{18}O_2$ and ^{18}O should be sufficient to determine the three rate constants R^0, R^1 and R^2 of the exchange reaction. However, the kinetic equations which describe the $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$, and ^{18}O concentration versus time were used to fit the time dependence of all oxygen isotopes. Fitting only the time dependence of $^{18}O_2$ and ^{18}O gives more then one solution for the best-fit parameters, depending on the input parameters. Thus, in this way only local minima were found with the least square fitting. By using all kinetic equations the global minimum could be found resulting in one solution for R^0, R^1, and R^2 independent of the input parameters.

In Tables 2 and 3 the rate constants of the exchange reaction on Fe_2O_3 and V_2O_5 at various temperatures, determined by the two described methods, are shown. Both tables show that the R^2 rate constants determined by the method of Klier *et al.* and Tsuchiya *et al.* agree reasonably well.

Oxygen Exchange Reaction on the Period IV Metal Oxides

The three rate constants of the oxygen exchange reaction on the period IV metal oxides were determined by using the modified method of Klier *et al.* The results are shown in Fig. 4. In Fig. 4a an Arrhenius plot of the exchange

TABLE 2

Rate Constant for the Oxygen Exchange Reaction on V_2O_5 Determined by the Method of Klier *et al.* and Tsuchiya *et al.* at Various Temperatures

	V_2O_5		
	Equilibrium		Nonequilibrium
Temp. (K)	Tsuchiya R^2 (mol/min/m^2)	Klier R^2 (mol/min/m^2)	Klier R^2 (mol/min/m^2)
823	$5.6\ 10^{-8}$	$6.8\ 10^{-8}$	$5.9\ 10^{-8}$
803	$2.6\ 10^{-8}$	$2.2\ 10^{-8}$	$2.2\ 10^{-8}$
743	$2.5\ 10^{-9}$	$2.5\ 10^{-9}$	$1.6\ 10^{-9}$

Note. The use of initial equilibrated or nonequilibrated dioxygen mixtures is indicated.

TABLE 3

Rate Constants for the Oxygen Exchange Reaction on Fe_2O_3 Determined by the Method of Klier *et al*. and Tsuchiya *et al*. at Various Temperatures

	Fe_2O_3					
	Equilibrium				Nonequilibrium	
	Tsuchiya mol/min/m^2		Klier mol/min/m^2		Klier mol/min/m^2	
Temp. (K)	R^1	R^2	R^1	R^2	R^1	R^2
773	—	$5.9\ 10^{-7}$	$1.2\ 10^{-6}$	$7.9\ 10^{-7}$	—	—
743	—	$2.0\ 10^{-7}$	$2.0\ 10^{-7}$	$2.0\ 10^{-7}$	$2.3\ 10^{-7}$	$1.8\ 10^{-7}$
743	—	$4.3\ 10^{-7}$	$2.9\ 10^{-7}$	$3.6\ 10^{-7}$	$1.4\ 10^{-7}$	$2.9\ 10^{-7}$
673	—	$7.3\ 10^{-8}$	$2.8\ 10^{-8}$	$9.7\ 10^{-8}$	$1.7\ 10^{-8}$	$1.1\ 10^{-7}$

Note. The use of initial equilibrated or nonequilibrated dioxygen mixtures is indicated.

reaction on V_2O_5 is shown. In the case of V_2O_5 the exchange reaction only proceeds via the R^2 mechanism. In Fig. 4b the isotopic exchange reaction on Cr_2O_3, is shown. On this oxide, oxygen is exchanged via the R^1 and the R^2 exchange mechanisms. The oxides which show activity in all three exchange mechanisms are MnO_2, Fe_2O_3, Co_3O_4, CuO, NiO, and ZnO. Their activities as functions of temperature are shown in Figs. 4c to 4h, respectively.

Figure 4 also shows that with increasing temperature the increase in activity is steeper for the R^1 exchange mechanism than for the R^2 mechanism. In other words, the activation energy for the R^1 exchange reaction is higher than for the R^2 reaction. The only exception to this rule is ZnO. The activation energies for the exchange reaction for the period IV metal oxides are shown in Table 4.

In the case of Co_3O_4, NiO, and CuO a decrease in exchange rate for the R^1 an R^2 mechanisms is observed from a certain temperature onwards. This decrease in activity starts for the R^1 exchange reaction at a higher temperature than for the R^2 exchange reaction. In the temperature region where a decrease of exchange with the oxygen of the oxide is observed, the R^0 mechanism starts to become the main mechanism.

The maximum temperature possible to measure the exchange activity of MnO_2 is 673 K. Above 673 K MnO_2 starts to decompose and an increase of dioxygen pressure is observed during the measurement.

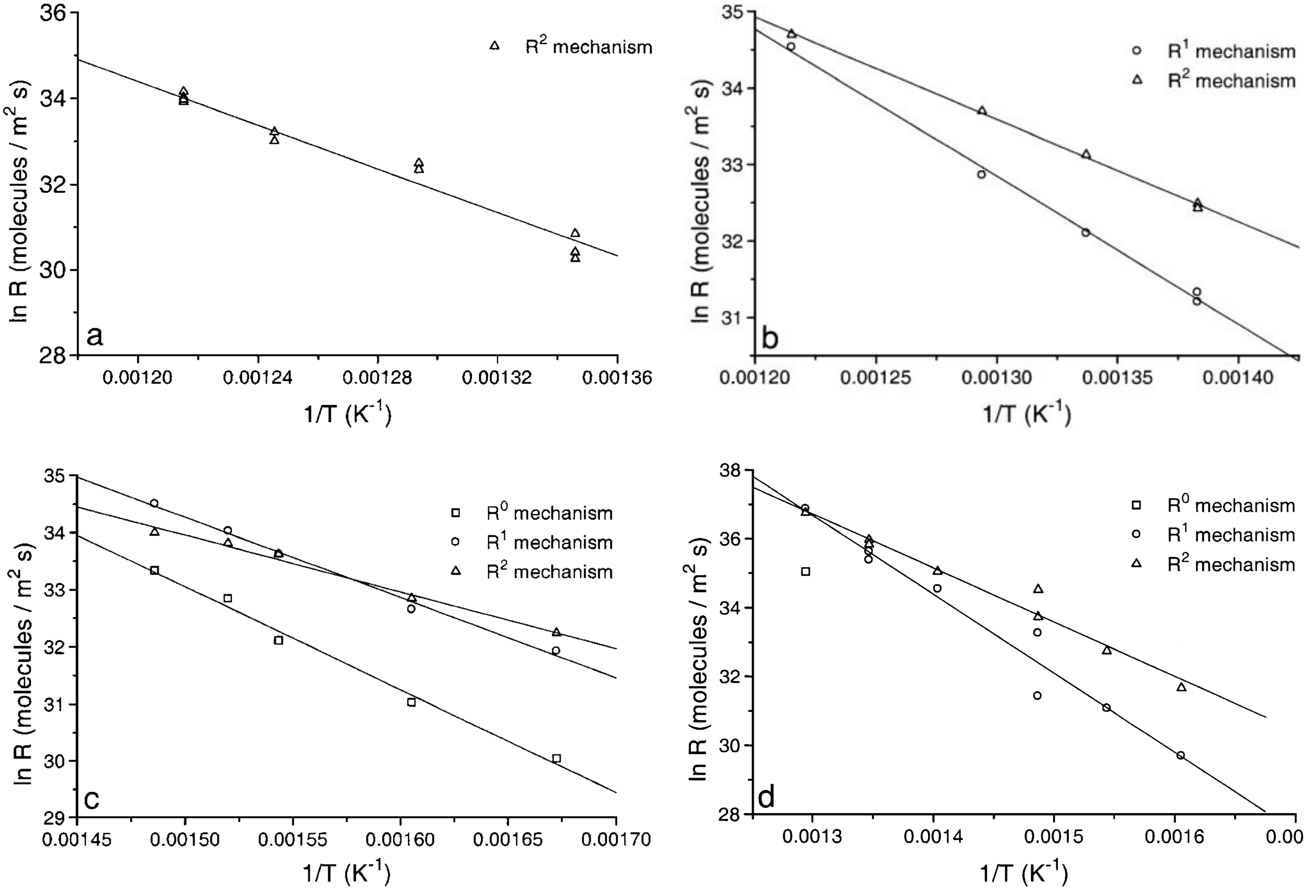

FIG. 4. Arrhenius plot of the isotopic oxygen exchange reaction on (a) V_2O_5, (b) Cr_2O_3, (c) MnO_2, (d) Fe_2O_3, (e) Co_3O_4, (f) NiO, (g) CuO, and (h) ZnO.

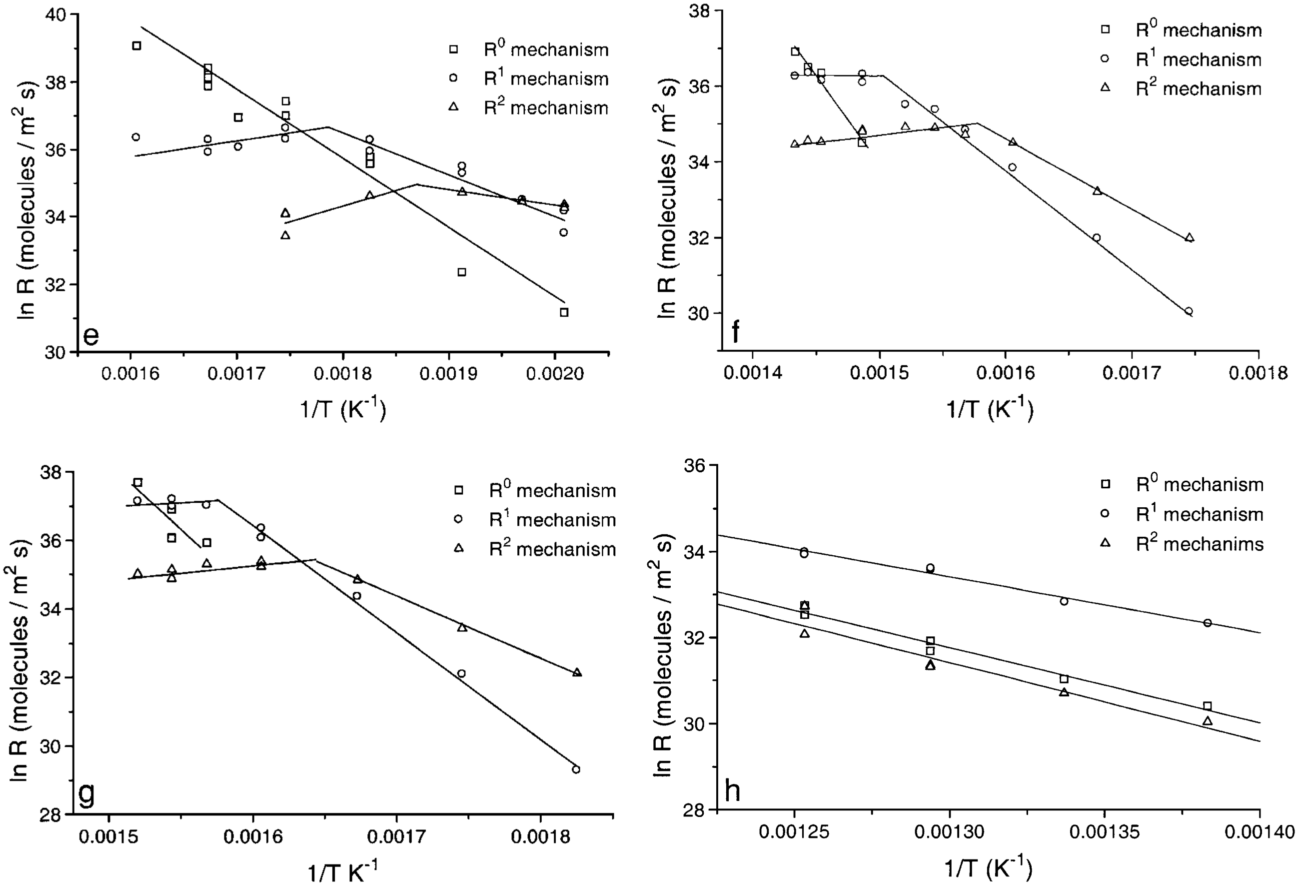

FIG. 4—*Continued*

In the previous paragraph it was shown that the model of Klier *et al.* had to be completed by an additional term, which takes into account diffusion of labelled oxygen from the surface into the bulk of the oxide, since this took place during the exchange measurements. By fitting the corrected model to the experimental data not only the rate constants for the three exchange mechanisms could be determined, but also an apparent diffusion parameter k. The apparent diffusion parameters for the period IV metal oxides at various temperatures are shown in Fig. 5. From these Arrhenius plots an apparent activation energy for diffusion in the oxide can be calculated. The results are shown in Table 5. However, in the case of V_2O_5 no diffusion rate could be detected. The apparent diffusion parameters can only be determined

TABLE 4

Activation Energies of the Isotopic Exchange Reaction

Oxide	R^0 mechanism (kJ/mol)	R^1 mechanism (kJ/mol)	R^2 mechanism (kJ/mol)
V_2O_5	—	—	211
Cr_2O_3	—	160	111
MnO_2	150	117	83
Fe_2O_3	—	190	130
Co_3O_4	170	103	36
NiO	389	210	149
CuO	307	258	148
ZnO	145	108	151

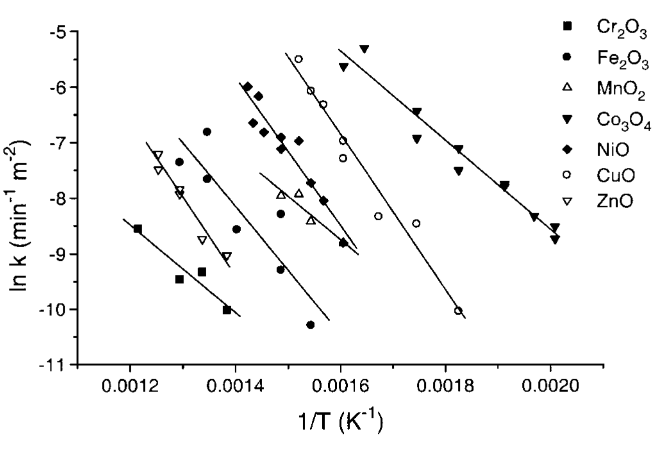

FIG. 5. Apparent diffusion rates as a function of temperature determined by fitting the corrected model of Klier *et al.* to the experimental data.

TABLE 5

Apparent Activation Energies for Diffusion

Oxide	Apparent activation energy for diffusion (kJ/mol)
Cr_2O_3	66
MnO_2	65
Fe_2O_3	95
Co_3O_4	66
NiO	107
CuO	116
ZnO	114

TABLE 6

Oxygen Exchange Activtiy of Some Period IV Oxides after Two Different Pretreatments

		Pretreatment A[a]			Pretreatment B[b]		
Oxide	T (K)	R^0	R^1	R^2	R^0	R^1	R^2
V_2O_5	773	0	0	0.78	0	0	0.84
Cr_2O_3	773	0	1.1	2.6	0.39	2.3	3.0
Fe_2O_3	713	0	6.3	9.9	0.32	16	15
Co_3O_4	548	21	3.5	0	74	33	3.6
CuO	598	0	5.1	8.2	2.3	16	14

[a] Evacuating for 3 h and equilibrating for 3 h at T_{reaction}.

[b] Evacuating for 3 h at T_{reaction} (rate constants in 10^{16} mol/m^2 min).

after equilibrium between the gas phase and the first two layers of the oxide has been reached. In the case of V_2O_5 no equilibrium was reached during the time of the experiment, since with this oxide it takes a very long time before the equilibration is accomplished.

In Fig. 6 the exchange activities of the period IV metal oxides at one temperature (573 K) are shown. Almost all oxides of the period IV metal oxides show activity in the R^1 and the R^2 exchange reaction at 573 K. The only exception is V_2O_5 as was already shown by Fig. 4a. At 573 K most oxides show a higher activity in the R^2 mechanism than in the R^1 mechanism. The only oxides which show a higher activity in the R^1 compared to the R^2 mechanism are Co_3O_4 and ZnO. The oxides which show the highest activity in the exchange reaction are MnO_2, Co_3O_4, and CuO. Figure 6 also shows that the activity pattern for the R^1 exchange mechanism and for the R^2 exchange mechanism are quite similar.

To test the influence of the pretreatment of the oxides on the exchange activity of the three mechanisms, the exchange reaction was performed on V_2O_5, Fe_2O_3, CuO, and NiO after evacuating these oxides only at the reaction temperature for 3 h. Thus, before the exchange experiment was started, these oxides were not equilibrated with $^{16}O_2$. The exchange activity of these oxides compared with the exchange activity after standard pretreatment are shown in Table 6.

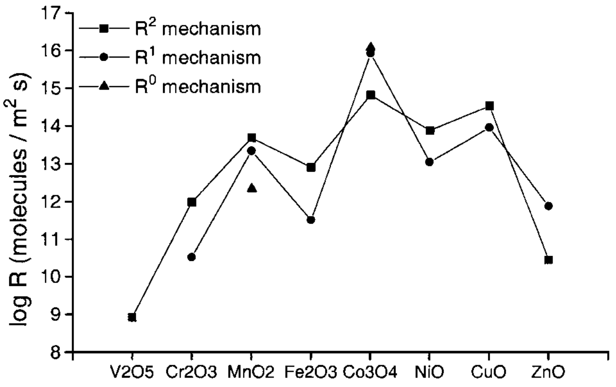

FIG. 6. Activities for the period IV metal oxides in the oxygen isotopic exchange reaction at 573 K.

If the oxides are not equilibrated with $^{16}O_2$, a higher exchange activity is observed for all three exchange mechanisms. When only pretreatment in a vacuum was carried out, oxides which had no exchange activity in the R^0 mechanism at a certain temperature showed some R^0 exchange activity at this temperature.

DISCUSSION

Method to Determine the Rate Constants of the Isotopic Exchange Reaction

The two methods suggested by Klier *et al.* (3) and Tsuchiya *et al.* (19) were used to determine the rate constants in the oxygen exchange reaction on metal oxides. With the method of Tsuchiya *et al.* only the rate constant for the R^2 mechanism can be determined, while with the method of Klier *et al.* three rate constants (R^0, R^1, and R^2) are accessible. In Tables 2 and 3 the rate constants of the exchange reaction over Fe_2O_3 and V_2O_5 determined by both methods are shown and compared, and the values for the R^2 mechanism agree reasonably well. Since both methods differ substantially, the method of Klier *et al.* is an integral technique, while the method of Tsuchiya *et al.* is a differential technique; this agreement shows that the theory of Klier *et al.* is a good method to determine the three different rate constants in the exchange reaction. An additional advantage of the method of Klier *et al.* is that one gets all three rate constants in one experiment. The method of Tsuchiya *et al.* can be used to check the results obtained by the method of Klier *et al.*

However, the kinetic equations of Klier *et al.* did not fit our data exactly. While according to their model the concentration of ^{18}O established after equilibrium had been reached should be constant, our experimental data showed a continuous decrease in time. This is because equilibrium has been reached first only between the gas phase and the first one or two layers of the oxides, and thereafter a slow diffusion of ^{18}O into the bulk of the oxide takes place. In the literature a more complete description of both oxygen exchange and diffusion can be found (21). Using the equations of Klier and Kucera, the exchange rates and diffusion coefficient can be determined simultaneously. However, we have chosen a more empirical approach and added an extra term to Eq. [3]. The reader should notice that this is only a small correction as can be seen from Figs. 2b and 3. When higher oxygen pressures are used in the oxygen exchange reaction, such as by Klier *et al.*, a contribution of this size is not visible.

The diffusion of ^{18}O into the bulk of the oxide is temperature dependent and increases with increasing temperature. This temperature dependence suggests a real relationship between the real diffusion coefficient and this apparent diffusion constant. The rate constants of Eq. [4], characterising the diffusion of ^{18}O into the bulk of oxide at different temperatures, are shown in Fig. 5. In the case of V_2O_5 no diffusion of ^{18}O into the bulk could be monitored, because no equilibrium between the gas phase and the first one or two layers of the oxide has been reached, which has been the case with the other oxides. In the case of V_2O_5 all oxygen layers take part in the exchange reaction simultaneously, as was already mentioned by Jíru and Nováková (4). This oxide behaves as a well-mixed liquid.

R^1 and R^2 Mechanisms

The Arrhenius plots of the exchange reaction on the period IV metal oxides show that at low temperatures the exchange reaction basically proceeds via the R^2 mechanism. This means that at low temperatures it is easier for an oxide to activate molecular oxygen via the R^2 mechanism. At high temperatures on the other hand, the R^0 mechanism is the most important mechanism. This is in contrast to our expectations since it is generally accepted that with oxidation reactions a Langmuir–Hinshelwood-type mechanism (i.e., a mechanism without participation of lattice oxygen) proceeds at low temperatures, while at higher temperatures the Mars–van Krevelen mechanism should prevail. Looking at oxidation reactions over metal oxides, different mechanisms or forms of O_2 activation are distinguished, depending on the temperature of the reaction. At low temperature the oxidation reaction can takes place by the Langmuir–Hinshelwood mechanism. At a temperature between about 473 and 873 K almost all oxidation reactions take place via the Mars–van Krevelen mechanism (also called a redox mechanism). This is the case not only of total oxidation reactions, but also of selective oxidation reactions. At higher temperatures a combination of surface reaction with radical formation at the surface occurs, with radicals reacting further in the gas phase (22).

Figures 4b to 4h show a relationship between the R^1 and the R^2 mechanisms. For all the period IV metal oxides the difference in exchange rate between those two mechanisms is not more then one order of magnitude. At low temperatures the exchange activity of the R^2 mechanism is higher and at higher temperatures the R^1 mechanism shows the highest activity. An exception to this rule is V_2O_5, since no R^1 exchange activity is observed. This lack of activity can be addressed to a difference in the degree of participation of lattice oxygen. In the case of V_2O_5 all oxygen layers of the oxide take part in the exchange reaction while in the case of the other oxides only one to two layers do so. All the layers can take part because diffusion of oxygen in V_2O_5 is much faster compared to other oxides. This was already mentioned by Jíru and Boreskov (4, 18).

The literature suggests that there are two kinds of R^2 exchange mechanisms: an exchange with oxygen from the lattice and the so-called place exchange (23). The place exchange is just a displacement of a preadsorbed O_2 molecule by another gas molecule. This mechanism does not involve scission of any O-O bond. With place exchange an increase in exchange rate is expected with a higher concentration of adsorbed oxygen molecules. However, Table 6 shows a higher activity in the R^2 exchange reaction if the oxides are pretreated in a vacuum and not in oxygen. Since after pretreatment in a vacuum less $^{16}O_2$ is adsorbed on the surface of the metal oxide compared to the situation after a pretreatment in oxygen, such an increase in exchange rate suggests that the prevailing mechanism for the R^2 exchange cannot be a place exchange but is a real exchange with oxygen of the lattice.

R^0 Mechanism

At elevated temperatures almost all oxides show a high exchange rate by the R^0 mechanism. In this mechanism oxygen is probably activated by metal ions at the surface of the oxides. At elevated temperatures the steady state of the surface of the oxides after pretreatment in oxygen is more reduced than at lower temperature. Apart from a higher number of vacancies, which leads to a higher activity in the R^1 and R^2 exchange reaction, reduced metal atoms could also appear at the surface. If the exchange reaction is performed on a metal surface, as on Pt(18), then only the R^0 mechanism can be observed. From the literature it is also known that CuO and NiO can be reduced or decomposed to Cu(0) and Ni(0) at conditions used here (24). This is in agreement with Table 6. When the oxides are only pretreated in a vacuum the surface of the oxide is on average more deeply reduced compared to pretreatment in oxygen. A higher degree of reduction results in more vacancies and a higher exchange rate.

Boreskov compared the activities of the so-called homo-exchange and hetero-exchange (12). It turned out that for almost all oxides which had been heated in oxygen before the exchange experiment, the rates of homo- and hetero-exchange were very similar. The results represented here show that most oxides show the R^0 activity only at elevated temperatures. Since the homo-exchange rate is the sum of all three exchange mechanisms and the hetero-exchange rate the sum of R^1 and R^2 activity, this agreement in exchange rates is not very surprising.

Correlation with Parameters Characterising the Oxide

In Figs. 6 to 9 the rate constants of the R^1 and R^2 mechanisms are correlated with the position of the metal element in the periodic table, the average metal–oxygen bond strength, and the Tammann temperature.

Figure 6 shows the same activity pattern for the R^2 and R^1 mechanism. Thus, the individual rates have the same sawtooth-like pattern as the total exchange activity, determined earlier by Boreskov. Although in the case of the R^1 mechanism one oxygen vacancy is needed and in the case of the R^2 mechanism two oxygen vacancies are required there is no difference between those two mechanisms in the sense suggested by Maltha and Ponec (25). As previously mentioned, the mechanisms R^1 and R^2 are related with each other, whereby the difference in activity is not much more than one or two orders of magnitude. This explains probably why both mechanisms depend in the same way on the average metal–oxygen bond strength as shown in Fig. 7.

In this graph the right *y*-axis represents the reciprocal of the mean M–O bond strength (notice the higher the M–O bond strength the lower the activity). A similar pattern for the reciprocal M–O bond strength is observed as for the R^1 and R^2 mechanisms, which suggests that both exchange mechanisms strongly and similarly depend on the average metal–oxygen bond strength.

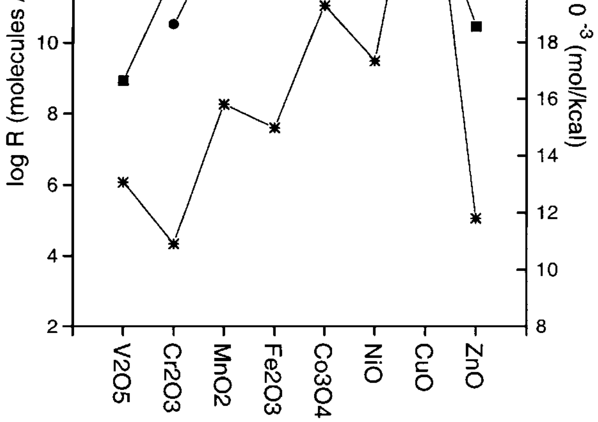

FIG. 7. Oxygen exchange rates of the R^1 and R^2 mechanism compared to the M–O bond strength for the period IV metal oxides.

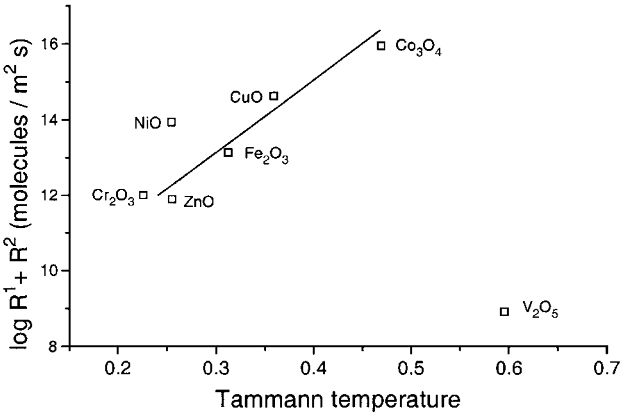

FIG. 8. Logarithm of the total activity of the R^1 and R^2 exchange reaction at 573 K as a function of the Tammann temperature.

Since diffusion is an additional factor in the exchange reaction, as can be concluded from Fig. 5, a correlation between activity in the exchange reaction and the Tammann temperature can be expected. The Tammann temperature is defined as the temperature of reaction divided by the melting temperature of the oxide. The temperature of reaction is 573 K and the melting temperatures of the oxides are shown in Table 1. Figure 8 shows the logarithm of the sum of the exchange rates of the R^1 and R^2 mechanisms plotted versus the Tammann temperature of the reaction.

A Tammann temperature between 0.2–0.5 means that surface diffusion already takes place. Above 0.5, bulk diffusion occurs as well. This is the case for vanadium oxide. When surface diffusion takes place, which is the case of the other oxides, the plot as in Fig. 8 shows a higher exchange rate for a higher Tammann temperature of the reaction. A similar relationship is observed if the apparent diffusion rates at 573 K is compared with Tammann temperature, which is shown in Fig. 9.

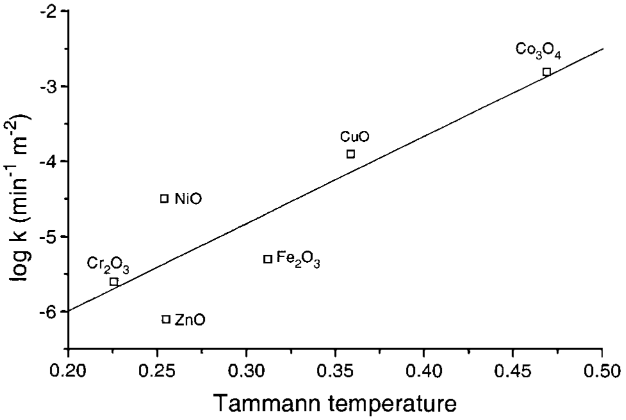

FIG. 9. Apparent diffusion rate *k* at 573 K as a function of the Tammann temperature.

This study has been performed to correlate the results of the oxygen isotopic exchange reaction with those on the oxidation reactions in a more convincing way than in the paper of Maltha and Ponec (25). A detailed comparison of this kind will be presented in the next paper (26). This paper will show that the same activity pattern as in Figs. 6 and 7 is observed with a great number of oxidation reactions. This activity pattern is not only observed for total oxidation reactions, but also for the selective oxidation of allyl iodide to acrolein.

CONCLUSION

The methods of Klier *et al.* and Tsuchiya *et al.* have been used to determine the individual rate constants of the isotopic exchange reaction of oxygen on metal oxides. The best way to determine the three rate constants is by using the kinetic model of Klier *et al.* and fit all the equations to the experimental data. The method of Tsuchiya *et al.* can be used to check the results obtained by the method of Klier *et al.*

Since diffusion of labelled oxygen into the bulk of the oxide also takes place during the exchange reaction, the kinetic model of Klier *et al.* had to be adjusted. An empirical term was added to this model. By fitting the modified model to the experimental data, not only the three different rate constants could be determined, but also the apparent diffusion parameter.

The rate constants for the oxygen exchange reaction were determined for the period IV metal oxides at different temperatures. The results show that with the exception of V_2O_5 the exchange reaction always proceeds with the R^1 and R^2 mechanisms operating or with all three exchange mechanisms. On V_2O_5 only the R^2 mechanism occurs. At low temperatures the most important mechanism is the R^2 mechanism, while at elevated temperatures the R^0 mechanism becomes the prevailing one. On V_2O_5 and Cr_2O_3, no exchange activity by the R^0 exchange mechanism is observed.

It seems that the R^1 and R^2 exchange mechanisms are closely related to each other. The difference in activity between those two mechanisms at a certain temperature is not more than one or two orders of magnitude. They both show the same activity pattern for the period IV metal oxides and are both in the same way dependent on the average M–O bond strength.

A linear relationship between the total exchange activity ($R^1 + R^2$) with the oxide and the Tammann temperature shows that the surface diffusion of oxygen is somehow related to the exchange activities by these two exchange mechanisms. The exchange rate and surface diffusion depend on the same features of the solid state.

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