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Catalytic Oxygen Transfer between CO and CO_2 on TiO_2

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The rate of the exchange reaction: $*CO_2 + CO \rightarrow *CO + CO_2$ was measured at atmospheric pressure in a flow reactor containing different TiO_2 catalysts. The variables investigated and their range were as follows: ratio (p_{CO_2}/p_{CO}), 0.2 to 5.0; temperature, 450° to 575°C; flow rate, 10 to 50 cc min^{-1}; additions of Fe, Cr, Nb, and P to TiO_2. From the results, the influence of the (p_{CO_2}/p_{CO}) ratio on the rate of reaction was determined and compared to that of p_{O_2} on the electronic conductivity of TiO_2 as gathered in previous investigations. From this information suggestions are advanced for the nature of the defect equilibrium reaction at the surface, the controlling step of the reaction rate, the nature of the adsorbed oxygen, and the influence of alterions upon the reactivity of TiO_2. The results on TiO_2 + Cr indicated that a space-charge layer at the surface governed the reactivity of TiO_2. In this instance, the thermodynamic derivations were modified to take into account the influence of the surface space charge on the defect equilibrium. The values of the reaction rate constants were compared with those calculated with the help of the absolute rate theory and the experimental activation energies. Order of magnitude agreement was obtained assuming that the adsorption of CO_2 was the controlling step of the isotope exchange reaction. On TiO_2 with low impurity levels a mobile configuration of the adsorption complex is in best accord with the results. At higher impurity levels an immobile complex gives better agreement. The significance of the present results for the oxidation of CO on TiO_2 is pointed out. Finally, the diverse yet complementary, roles of electron and ion defects in governing surface reactivity and catalytic activity of TiO_2 and metal oxides in general is pointed out.

The reactivity of solid surfaces towards gaseous phases is dependent upon the concentration or activity of the chemical components of the solid and of the gas. For a reacting solid surface, the concentration of adsorbed species becomes an important variable of the system. Since the adatom concentration is controlled by equilibria with the gas phase, studies of surface reactivity under conditions of physicochemical equilibrium between surface and gas phases permit to observe the rate of surface reactions at constant concentration of intermediates. In the case of the reactivity of metal oxide surfaces for molecular O_2, studies on the rate of equilibration between oxygen isotopes have proven of great value (*1*). In oxide compounds isotope equilibration between gaseous molecules often occurs concurrently with the exchange of O_2 between gas and solid phases. To eliminate this complication, reactivity studies using the exchange reaction between CO and CO_2, namely;

$$CO(g) + *CO_2(g) \rightarrow *CO(g) + CO_2(g) \quad (1)$$

where $*CO_2$, $*CO$ represent species containing radioactive carbon, seemed advantageous. In fact, recent work has shown that reaction (1) may be conveniently used to gain information on oxygen transfer processes at solid surfaces (*2*). Because of the interest in TiO_2 as adsorbent and catalyst we have investigated the surface reactivity of TiO_2 toward O_2 by means of reaction (1). Our effort was guided by the desire to seek out the diverse but complementary roles of ionic and electronic imperfections, as centers responsible for the chemical reactivity of TiO_2 surfaces. The theoretical development

underlying the application of reaction (1), does in fact permit elucidation of this role (*2*, *3*) and contribute to the development of the thermodynamics of defect solid surfaces. The results of this study are summarized in this paper.

Experimental

Premixed compositions of research grade CO + He and CO_2 + He (~90% He) were purified by passage over hot Cu and Ascarite. The O_2 content of the gases was < 5 ppm. $*CO_2$, from a commercial source, was mixed with He by high-vacuum techniques and stored under pressure in a stainless steel cylinder. TiO_2 samples were prepared by hot hydrolysis of purified tetraisopropyl titanate solutions. The precipitate was filtered, and dried at 105°C for 48 hr in air followed by 24 hr under vacuum. It was subsequently heated under He at 700°C for 16 hr. This treatment produced complete rutilization, as shown by X-ray analysis, and stable and reproducible surface activity. The impurities detected by wet chemical analysis were Fe (1 ppm) and Cr (<0.5 ppm). TiO_2 samples containing Cr and Nb were prepared in a similar manner from tetraisopropyl titanate, Cr_2O_3, and Nb_2O_5, while samples containing P and Fe were obtained from titanic sulfate, phosphoric acid, and Fe sulfate. The hydrolyzates were dissolved by heating, H_2O_2 added to remove traces of organic materials, followed by a second hydrolysis, drying, and calcining through a time–temperature program similar to that used for pure TiO_2. X-Ray analysis showed that no second crystalline phase was present in any of the samples and that rutilization was not as complete as for pure TiO_2 preparations, mostly for samples containing P and Fe. BET surface area and chemical analyses of the samples investigated are reported in Table 1.

Freshly prepared TiO_2 surfaces are known to contain OH^- groups (*4*), which yield H_2 when contacted with a CO + CO_2 at low temperatures. Mass spectrometric analysis of the reacted CO + CO_2 mixture failed to indicate the presence of H_2.

To obtain a qualitative indication of the effect of the addition upon the defect structure and nonstoichiometry of the TiO_2 preparations, measurements of the dc electrical conductivity, were carried out on pressed pellets at 570°C in an atmosphere of CO + CO_2. The values obtained are reported in Table 2.

TABLE 1
Surface Area of TiO_2 Samples

Sample	Surface area (m^2g^{-1})	Addition (mole %)
TiO_2	0.651	—
TiO_2 + Nb	8.8	1.0
TiO_2 + Cr	13.6	1.0
TiO_2 + P	25.6	3.9×10^{-2}
TiO_2 + Fe	16.6	8.5×10^{-4}

The rate of reaction (1) was measured in a conventional flow apparatus (Fig. 1). Provision was made to equilibrate the samples with a nonradioactive mixture of CO + CO_2 of desired composition, prior to introduction of $*CO_2$. The ratios (p_{CO_2}/p_{CO}) used ranged between 0.2 to 5.0. They corresponded to a virtual $p_{O_2} \cong 10^{-20}$ torr at

TABLE 2
Ratio. σ_R. between the dc Electrical Conductivity of TiO_2 Samples Containing Solid Additions to the Conductivity of Pure TiO_2, 570°C, (p_{CO_2}/p_{CO}) = 0.213

Addition	σ_R
Cr	6.4×10^{-2}
Nb	15.7
P	1.3
Fe	4.2

500°C. This value is several orders of magnitude larger than that of the estimated equilibrium p_{O_2} of TiO_2 and the next reduced phase at the same temperature. A fixed-bed, Vycor glass reactor, electrically heated, was used. Temperature was held constant to ±2°C. The extent of the exchange reaction was followed by measuring the total radioactivity in CO + CO_2 and that in CO. The measurements were carried out in a flow-type Geiger counter with Mylar window. Steady counting rates and reproducible catalytic activity were obtained after 1–1.5 hr from the starting time. The overall experimental error was estimated to be 10%.

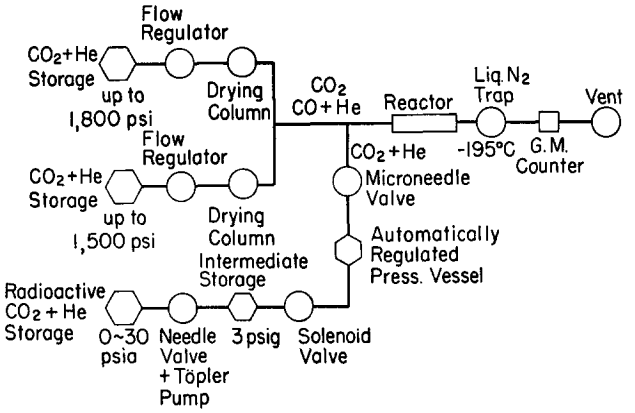

FIG. 1. Experimental setup for studying exchange reaction (1).

RESULTS

The derivation of the rate coefficient for the exchange reaction (1) has been reported previously (*2*). It is assumed that reaction (1) takes place in a two-step sequence:

$$*CO_2(g) \rightarrow *CO(g) + O(s) \qquad (1a)$$

$$CO(g) + O(s) \rightarrow CO_2(g) \qquad (1b)$$

where (g) and (s) refer to gas and adsorbed phases, respectively. Since the transfer of oxygen between CO_2 and CO occurs at equilibrium, the rates of steps (1a) and (1b) are equal. The rate of reaction step (1a) is given by

$$\frac{1}{A}\frac{dn_{*CO}}{dt} = k_{ca}p_{*CO_2} - k'_{ca}p_{*CO} \qquad (2)$$

where A, n_{*CO}, k_{ca}, k'_{ca} are the catalyst surface area, moles of *CO, and rate coefficients of forward and backward reactions of step (1a).

The reaction rate expression (2) may be rearranged by introducing the gas flow rate v, integrating, and solving to give the reaction rate coefficient, k_{ca}

$$k_{ca} = \frac{v}{ART(1+\beta)} \ln \frac{1}{1-(1+\beta)[p_{*CO}/(p_{*CO_2})_0]} \qquad (3)$$

where the subscript $_0$ refers to initial conditions, and $\beta = p_{CO_2}/p_{CO}$.

Within the range of flow rates employed no influence of the latter on the rate of reaction (1) was detected (Table 3).

The influence of β upon k_{ca} for pure TiO_2 samples, at 520° and 578°C is shown in Fig. 2, while in Figs. 3, 4, 5, and 6 similar results are presented for TiO_2 samples containing Cr, Nb, Fe, P, respectively. No

TABLE 3

RATE COEFFICIENT, k_{ca}, OF REACTION (1) ON TiO_2 + Cr AT VARIOUS GAS FLOW RATES, 500°C, AND $(p_{CO_2}/p_{CO}) = 0.923$

Flow rate (cc min^{-1})	k_{ca} (mole cm^{-2} sec^{-1} atm^{-1}) $\times 10^{12}$
14.5	2.6
28.4	3.0
29.5	2.7
32.5	2.9

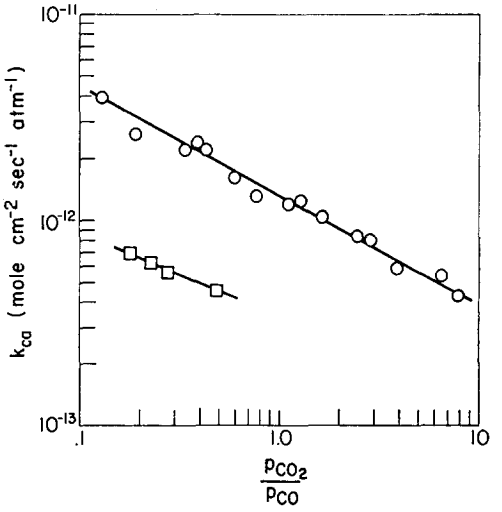

FIG. 2. Rate coefficient, k_{ca}, for reaction step (a) versus p_{CO_2}/p_{CO} for pure TiO_2; temperature: □, 520°C; ○, 578°C.

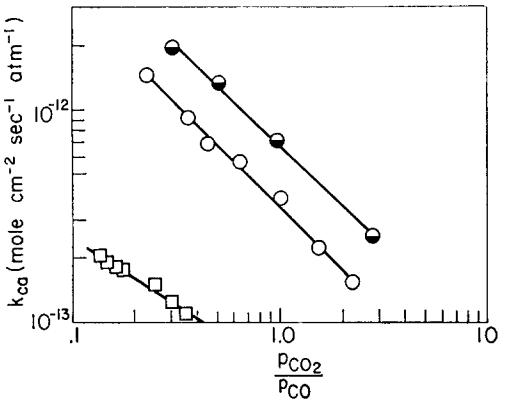

FIG. 3. Rate coefficient, k_{ca}, for reaction step (a) versus p_{CO_2}/p_{CO} for TiO_2 + Cr; temperature: □, 452°C; ○, 520°C; ◒, 575°C.

detectable exchange was found with the empty reactor up to temperatures of 650°C.

Known amounts of O_2 were added to the reacting CO + CO_2 mixture and the effect on the rate of exchange was noted. It was found that O_2 had a strong inhibition. For instance, at 578°C, with the introduction of 8 vol % of O_2 reaction (1) was totally suppressed.

DISCUSSION

The significant experimental results reported in the previous section are the following:

(a) in the temperature interval 450° to 575°C the exchange reaction (1) is readily catalyzed by equilibrated TiO_2 surfaces. In the same temperature range previous studies

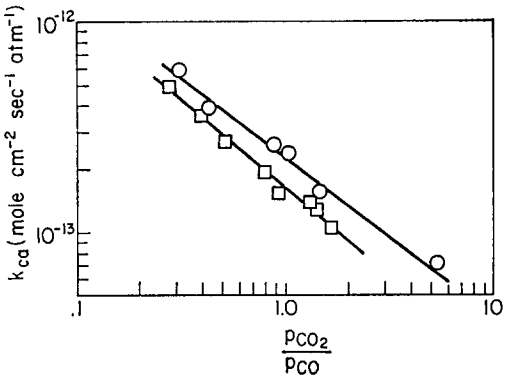

FIG. 4. Rate coefficient, k_{ca}, for reaction step (a) versus p_{CO_2}/p_{CO} for TiO_2 + Nb; temperature: □, 520°C; ○, 570°C.

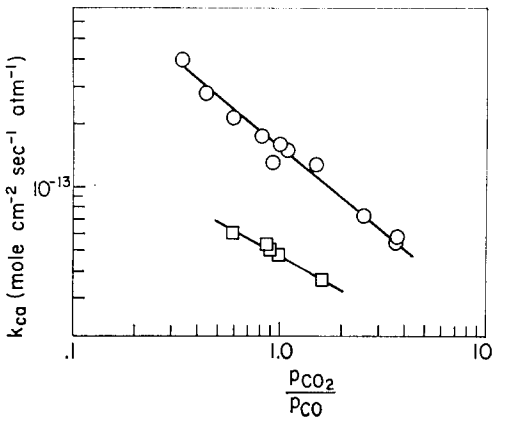

FIG. 5. Rate coefficient, k_{ca}, for reaction step (a) versus p_{CO_2}/p_{CO} for TiO_2 + Fe; temperature: □, 523°C; ○, 571°C.

have indicated that the equilibration of O_2 isotopes readily occurs on TiO_2(*1*b, *5*);

(b) the rate of reaction is influenced by the presence of alterions in TiO_2 and by the composition of the gas mixture

(c) the introduction of molecular O_2 into the reacting mixture inhibits reaction (1).

As previous studies have indicated (*6*), the present investigation has shown that the free electron concentration of TiO_2 is influenced by the presence of foreign ions in the bulk of the solid. Assuming that Cr was present in TiO_2 as a cation with a fixed charge $<+4$, and Nb, P, Fe with a fixed charge $>+4$, the results of Table 2 are

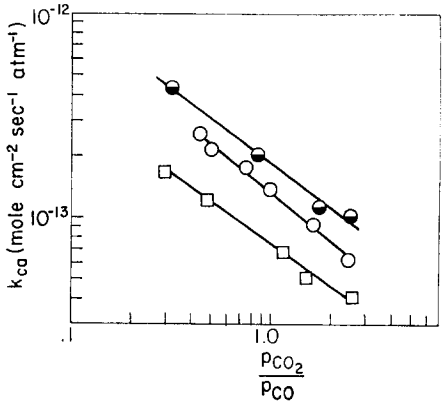

FIG. 6. Rate coefficient, k_{ca}, for reaction step (a) versus p_{CO}/p_{CO_2} for TiO_2 + P; temperature: □, 520°C; ○, 548°C, ◒, 575°C.

consistent with a simple mechanism of controlled valency. Previous results on this system did not always bear this out (*6*), conceivably whenever the charge of the dissolved alterion was influenced by the gas-phase equilibrium.

The rate expression (2) was written as a first order equation in p_{CO_2} and p_{CO}. Surface effects which may modify the first order relation are included in k_{ca}, k'_{ca} which are consequently dependent upon p_{CO_2} and p_{CO}. The relation between the rate coeffcient, k_{ca}, and the true constant k_a is expressed as (*2*),

$$k_{ca} = k_a\beta^{-m} \qquad (4)$$

where m is a constant. The values of m computed with the aid of Eq. (4) from the experimental results (Figs. 2 to 6) are collected in Table 4.

TABLE 4
VALUES OF m [EQ. (4)] FOR REACTION (1) CATALYZED BY TiO_2

Catalyst	Temperature (°C)	m
Pure TiO_2	520	0.40
	572	0.52
TiO_2 + Cr	452	0.96
	520	0.96
TiO_2 + Nb	520	0.83
	570	0.76
TiO_2 + Fe	520	0.55
	571	0.81
TiO_2 + P	520	0.67
	548	0.78
	575	0.71

The value of m provides a measure of the degree of control of the extrinsic activity of the TiO_2 surfaces; namely, the extent to which gas-phase composition influences surface activity. Table 4 shows that for all of the solid additions investigated the value of m increased from 0.5 for pure TiO_2 to ~ 1, except for the low-temperature runs (520°C) of TiO_2 + Fe. This indicates a higher susceptibility of TiO_2 to reaction conditions whenever foreign ions are incorporated into the solid. It does not imply a beneficial or detrimental effect of the addition on the rate of reaction (1). As a matter of fact, the experiments show that the influence of the solid addition to TiO_2 on the rate of reaction (1) is practically negligible. Taking Cr and Nb additions, which were present at the same concentration level but produced drastically opposite effects on the electrical conductivity, it is found that at 575°C and $\beta = 1$, the values of k_{ca} are 1.1×10^{-13} (pure TiO_2), 9×10^{-14} (TiO_2 + Cr), 6×10^{-14} (TiO_2 + Nb) (mole cm^{-2} sec^{-1} atm^{-1}).

We shall analyze first the results from samples of TiO_2 with additions of Nb, Fe, and P and, subsequently, those from samples of TiO_2 + Cr.

TiO_2 with Additions of Nb, Fe, and P

Previous measurements on the electronic conductivity of TiO_2 (*6*) have shown a wide range of numerical values for the relation between $[e^-]$ and p_{O_2}, namely $-0.16 \leq \partial \ln [e^-]/\partial \ln p_{O_2} \leq -0.5$ where $[e^-]$ represents the concentration of excess electrons of the solid. Values ≈ -0.25 were found to be more preponderant, especially at temperatures close to those employed in the present experiments. If it is assumed that under a CO_2 + CO atmosphere the defect conditions at the TiO_2 surface are similar to those prevailing under O_2, and that the rate-controlling step of reaction (1) on pure TiO_2 is

$$CO_2(g) + e^-(s) \rightarrow CO(g) + O^-(s) \qquad (5)$$

the rate coefficient of the forward step of reaction (1) is given by $k_{ca} = k'_a[e^-] = k_a\beta^{-0.5}$. This is consistent with the experimental results obtained on pure TiO_2 [Table 4 and Eq. (4)]. On the other end, a surface rate-controlling step

$$CO_2(g) + 2e^-(s) \rightarrow CO(g) + O^{2-}(s) \qquad (6)$$

requires a rate coefficient $k_{ca} = k_a\beta^{-1}$. Conceivably, whenever the free electron population of the solid is increased, reaction step (6) will be more likely to occur. Additions of Nb, P, and Fe were found to increase the electrical conductivity, and hence the free electron concentration, of TiO_2. For these samples, it should therefore be expected that reaction step (6) would gradually replace reaction step (5) as a reaction-controlling stage, with a corresponding increase in the value of m. This is in agreement with the experimental results (Table 4).

This conclusion might, at first, be taken as an indication of a paramount, indeed preponderant, role of the electronic disorder of the solid in the reactivity of its surface and an indication that the so-called electronic factor is the key parameter that governs the oxidation activity of TiO_2. This point of view has been emphasized often in past studies in this field and correlations based only on the electronic disorder of the solid have been advanced (*7*). However, it must be realized that the satisfactory agreement between the experimental and the theoretical m values from reaction steps (5) and (6), implies that a definite set of conditions for the ionic disorder of TiO_2 be present. Indeed, ionic and electronic disorders of the solid are closely interrelated and, in general, it is neither possible nor valid to neglect one type of disorder to stress the other.

Since this point has been often neglected in past studies on the catalytic activity of metal oxides, we shall briefly analyze it in more detail. To do so a model for ionic defects in TiO_2 is needed. It is known that bulk TiO_2 contains an excess of metal over the stoichiometric amount but the exact nature of the incorporation of the excess, interstitial cations and/or anionic vacancies, is yet unsettled, and it is probably dependent upon experimental variables: temperature, p_{O_2}, and purity.

Let us consider the general case of a metal oxide, MO, containing only ionic Schottky disorder:

$$sV_M^{r-} + rV_O^{s+} = 0 \qquad (7)$$

$$e^+ + e^- = 0 \qquad (8)$$

In reaction equations (7) and (8) V_M^{r-}, V_O^{s+} represent ionized lattice defects, $r = 1, 2,3 \ldots$, and $s = 1,2$. The defect equilibria of the metal, M, and of O_2 may be written as

$$\tfrac{1}{2}O_2(g) = V_M^{r-} + re^+ \qquad (9)$$

$$M(g) = V_O^{s+} + se^- \qquad (10)$$

For a metal excess oxide the condition of electrical neutrality is approximated by

$$[e^-] = s[V_O^{s+}] \qquad (11)$$

Assuming that ideal mass action expressions can be applied to reactions equilibria (7) and (10) and taking into account Eq. (11) it is found that

$$\frac{\partial \ln[e^-]}{\partial \ln p_{O_2}} = -\frac{s}{2r(s+1)} \qquad (12)$$

Expression (12) will yield the value of ~ 0.25 needed to fit the results from most of the measurements on the electonic conductivity and from those on the catalytic activity [reactions (5) and (6)], for well-defined degrees of ionization of V_O^{s+} and V_M^{r-} only. Either one or both V_O^{s+} and V_M^{r-} may contribute to the reactivity of the TiO_2 surface toward O_2. Since $[V_M^{r-}] \propto 1/[M^{r+}]$ where M^{2+} represents a surface adsorbed cation (interstitial cation), and V_O^{s+} is an anionic vacancy, it is clear that V_M^{r-} and V_O^{s+} are important for surface defect equilibria involving oxygen. The presence on the surface of TiO_2 anatase of anion vacancies with trapped electrons, similar to F centers, has been demonstrated by ESR measurements (*8*).

The successful combination of values of r and s in Eq. (12) is not unique, but the choice is not wide. Thus, it is clear that the results from the catalytic experiments can be successfully interpreted by means of defect reactions (5) and (6), which formally stress the electronic disorder of the solid, if the conditions of the ionic defect equilibria at the TiO_2 surface bring forth values of s and r, satisfying the relation $s/2r(s+1) \cong 0.25$. A view emphasizing the electronic disorder equilibrium only may be accepted under limiting conditions and in special cases with a high degree of ionic disorder (whenever the electroneutrality expression is approximated by $r[V_M^{r-}] = s[V_O^{s+}]$).

In the present instance, in view of the results on the electronic conductivity, it seems reasonable to retain reaction steps (5) and (6) as the rate-controlling stages of reaction (1) on TiO_2. If it is found that $\partial \ln \sigma / \partial \ln \beta \neq \partial \ln k_{ca} / \partial \ln \beta$, it is clear that the electronic disorder of the solid is not of paramount importance for the controlling stage of the catalytic reaction.

TiO_2 with Cr Addition

The effect of additions of Cr requires special consideration, since in this instance

the electrical conductivity was found to be about one order of magnitude lower than that of pure TiO_2 and $m \approx 1$. A decrease in free electron concentration of the solid is generally associated with an increase in the thickness of the space-charge layer at the surface, δ. A simple calculation shows that this effect was indeed present in TiO_2 + Cr samples. By means of the Debye expression, $\delta = (\epsilon \bar{k} T N_a / 8\pi[e^-]e^2)^{\frac{1}{2}}$, where ϵ, $\bar{k}$, N_a, e are the dielectric, Boltzman, and Avogadro constants, and electron charge, respectively, and taking $\epsilon = 100$, $[e^-] = 3 \times 10^{20} cc^{-1}$, and $T = 800°K$ it is found that $\delta = 8$ Å for pure TiO_2. Addition of Cr decreased the conductivity of pure TiO_2 by a factor of 6.4×10^{-2} (Table 2) with a corresponding increase of $\delta \cong 40$ Å. As a result, the application of the ideal mass action expression to defect equilibria as performed in the derivations of the previous section, is not valid. To determine the correction needed for the condition of a thick δ and its influence on the value of m, we shall follow a treatment first proposed several years ago (*9*).

The distribution of charges in the surface layer is represented by the well-known expression

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi[e^-]e}{\epsilon} \times \left\{\exp\left(-\frac{e\varphi}{\bar{k}T}\right) - \exp\left(\frac{e\varphi}{\bar{k}T}\right)\right\} \quad (13)$$

where φ, is the local electrical potential in relation to that prevailing in the bulk of the solid and x, the distance from the surface.

The boundary conditions are

$$\left(\frac{d\varphi}{dx}\right)_{x=\infty} = 0 \quad (14)$$

and

$$\left(\frac{d\varphi}{dx}\right)_{x=0} = -\frac{4\pi\eta}{\epsilon} \quad (15)$$

where $\eta = -je[O^{j-}]$ is the electrical charge per cm^3 at the surface resulting from the presence of O^{j-} adsorbed oxygens, $j = 1,2$. Because of the formation of a space charge at the surface, reaction equilibria (9) and (10) should be modified and the equilibrium of O_2 incorporation with a CO–CO_2 mixture becomes

$$CO_2(g) + e^-(s) = CO(g) + O^-(s) \quad (16)$$

whose equilibrium condition is written as

$$[O^{j-}] = \frac{[e^-]\exp\{e\varphi_0/\bar{k}T\}^j}{K_{16}}\beta \quad (17)$$

where the subscript $_0$ refers to surface conditions and K_{16} is the equilibrium constant of reaction (16). Substitution of Eq. (17) into Eq. (15) yields

$$\frac{d\varphi_0}{dx} = \frac{4\pi je}{\epsilon}\frac{\beta}{K_{16}}\left\{[e^-]\exp\left(\frac{e\varphi_0}{\bar{k}T}\right)\right\} j \quad (18)$$

Introducing the dimensionless quantities

$$\Psi = \frac{e\varphi}{\bar{k}T} \quad (19) \text{ and } \xi = \left(\frac{8\pi[e^-]e^2}{\epsilon\bar{k}T}\right)^{1/2} x \quad (20)$$

Eq. (13) is recast into

$$d^2\Psi/d\xi^2 = -\tfrac{1}{2}\{\exp(-\Psi) - \exp(\Psi)\} = \sinh\Psi \quad (21)$$

Integration of Eq. (21) with the boundary conditions (14) and (15) gives

$$\sinh\left(\frac{\Psi_0}{2}\right) = -\frac{1}{2}\left(\frac{4j\pi e^2}{\epsilon\bar{k}T}\right)^{1/2}\frac{[O^{j-}]}{[e^-]^{1/2}} \quad (22)$$

The bulk electronic equilibrium, similar to that of the surface in the absence of a space-charge effect [Eq. (12)], yields

$$[e^-] = K\beta^{-s/r(s+1)} = K\beta^{-0.5} \quad (23)$$

where K is a constant. Substitution of Eqs. (17) and (23) into Eq. (22) gives

$$2\sinh\left(\frac{\Psi_0}{2}\right) = -\frac{1}{2}\left(\frac{4\pi je^2}{\epsilon\bar{k}T}\right)^{1/2}\frac{K^{(j/2-1/4)}}{K_{16}} \times \beta^{(j/4-j/2)}\exp\{j\varphi_0\} \quad (24)$$

Equation (24) is the desired relation between Ψ_0 and β. Two limiting cases are noteworthy:

(a) $|\Psi_0| \to 0$
or $e\varphi < \bar{k}T$ (thin surface charge layer).

From Eq. (17)

$[O^{j-}] \propto \beta^{1-(j/2)}$, and, for $j = 1$, $[O^-] \propto \beta^{-1/2}$

which is the result for pure TiO_2 and TiO_2 with additions of Nb, Fe, and P.

(b) $|\Psi_0| \gg 1$
or $-e\varphi \ll \bar{k}T$ (thick surface layer)

Since in this instance

$$\exp\{\tfrac{1}{2}\Psi_0\} \cong 0$$
$$\text{and } -2\sinh(\tfrac{1}{2}\Psi_0) \cong \exp\{-\tfrac{1}{2}\Psi_0\} \quad (25)$$

Substitution of expression (25) into Eq. (24) and rearrangement yields

$$\exp\left\{-\left(j+\frac{1}{2}\Psi_0\right)\right\} = -\frac{1}{2}\left(\frac{\Psi j\pi e^2}{\epsilon \bar{k}T}\right)^{1/2}\frac{K^{(j/2-1/4)}}{K_{16}}\beta^{(5/4-j/2)}$$

or

$$\exp\{-(j+\tfrac{1}{2})\}\Psi_0 \propto \beta^{(5/4-j/2)} \quad (26)$$

For $j = 1$ expression (26) gives

$$\exp\{\Psi_0\}\beta^{-1/2} \quad (27)$$

Substitution of Eqs. (23) and (27) into Eq. (17) finally gives

$$[e] \propto \beta^{-1} \quad (28)$$

This result shows that the exponent m increases whenever the electrical space charge has a dominant influence upon the electrochemical equilibrium at the surface, and in particular, m changes from -0.5 to -1.0. This is in excellent agreement with the reported results on TiO_2 + Cr (Table 4). We conclude that interesting deductions on the origin of surface reactivity and reaction intermediates during the catalytic oxygen transfer between CO and CO_2 are still possible in the presence of a thick surface layer, provided that the necessary modifications in the mass action expression are carried out.

TiO_2 Surface during Catalytic Oxygen Transfer between CO and CO_2

The rate-controlling reaction (5) can be considered as the result of a sequence of three reaction steps, namely;

$$CO_2(g) \rightarrow CO_2(s) \quad (5a)$$
$$CO_2(s) + e^-(s) \rightarrow CO(s) + O^-(s) \quad (5b)$$
$$CO(s) \rightarrow CO(g) \quad (5c)$$

Reaction step (5a) represents the adsorption of CO_2 on the TiO_2 surface, reaction step (5b) the surface reaction, and reaction step (5c) the desorption of CO from the TiO_2 surface. To determine the rate-controlling step of reaction (5), it is helpful to carry out calculations based on absolute rate theory and on the experimentally observed activation energies. The following possibilities and related expressions were considered: (i) immobile adsorption:

$$v_{ia} = c_g c_s \frac{\sigma}{\sigma^\ddagger}\frac{h^4}{8\pi^2 I(2\pi M\bar{k}T)}\exp\left\{-\frac{E}{RT}\right\}$$

(ii) mobile adsorption:

$$v_{ma} = c_g \frac{\bar{k}T}{(2\pi M\bar{k}T)^{1/2}}\exp\left\{-\frac{E}{RT}\right\}$$

(iii) desorption

$$v_d = c_a \frac{\bar{k}T}{h}\exp\left\{-\frac{E}{RT}\right\}$$

In expressions (i), (ii), and (iii) c_g, c_s, c_a, σ, $\sigma^\ddagger$, h, I,M a re the concentration of gas-phase molecules, of empty surface sites, and of occupied sites, the symmetry numbers of CO_2 and adsorbed complex, the Planck constant, the moment of inertia, and the molecular mass of CO_2, respectively.

Using the following values: $T = 520°C$, $c_g = 9 \times 10^{18}\ p_{CO_2}$ molecules/cm^3, $I = 6096 \times 10^{-39}$ g cm^2, $c_s = 4.7 \times 10^{-14}$ cm^{-2}, $M = 7.67 \times 10^{-23}$ g, and taking $c_a = c_s$ it is possible to compute the results summarized in Table 5.

The values of the activation energies employed in the calculations were derived from rate experiments carried out at two temperatures only. From a calculation of the experimental error, the uncertainty in the value of the activation energies ($\sim$20%) was found to contribute to about one order of magnitude error in the calculation of the rate constants.

Inspection of Table 5 shows that for all the samples investigated the adsorption of CO_2 [step(5a)] is the controlling process. On TiO_2 with low impurity levels (pure TiO_2, TiO_2 + Fe) a mobile configuration of the adsorption complex is in best accord with the results. Upon increasing impurity level, the results show that the adsorption complex becomes immobile.

The general increase in the value of m upon dissolution of alterions in TiO_2, as found in this work is reminiscent of a similar effect, previously discovered during

TABLE 5

COMPARISON BETWEEN RATE CONSTANT, k_a CALCULATED FROM ABSOLUTE RATE THEORY AND OBSERVED ACTIVATION ENERGIES AND FROM RATE EXPERIMENTS FOR REACTION (5), 520°C, $\beta = 0.15$

	$k_a \left[\frac{\text{molecules}}{\text{cm}^2 \text{ sec atm}}\right]$			
		Calculated		
		Step (5a)		
Catalyst	Experimental	Immobile	Mobile	Step (5c)
TiO_2	4.58×10^{11}	8.3×10^{5}	1.5×10^{12}	1.8×10^{17}
TiO_2 + Cr	9.48×10^{11}	2.1×10^{13}	3.6×10^{19}	4.5×10^{24}
TiO_2 + Nb	3.04×10^{11}	9.1×10^{12}	1.6×10^{19}	2.0×10^{24}
TiO_2 + Fe	4.43×10^{11}	3.0×10^{6}	5.3×10^{12}	6.6×10^{17}
TiO_2 + P	1.14×10^{11}	2.1×10^{10}	3.7×10^{16}	4.5×10^{22}

studies on the rate of isotopic equilibration of molecular oxygen (*10*). In these studies, the dependence of the rate of reaction upon p_{O_2} was found to be higher that that expected from the application of the ideal mass action expression to surface defect equilibria. The effect was mostly noticeable for oxides of metals of the first group of the periodic system and it was related to the influence of the reaction activation energy on the concentration of defects.

The experimental results (Table 4) show that at 521°C, Fe additions did not modify the rate of reaction (1), the value of m, and the electrical conductivity in pure TiO_2. These findings indicate that under the conditions of the experiments the pertinent physicochemical characteristics of TiO_2 were not altered by the levels of Fe introduced.

The conclusions of this investigation are in good agreement with previous studies on the O_2–TiO_2 system. In an investigation on the chemisorption of O_2 on TiO_2 rutile, it was found that the rate and the maximum degree of surface coverage were increased by the dissolution of 0.5 mole % of WO_3 in TiO_2 (*11*). The suggestion was advanced that electrons trapped by surface acceptors were the centers responsible for the reactivity. Surface anion vacancies were also found important for the adsorption of N_2O on rutilized TiO_2 (*12*).

Catalytic Oxidation of CO on TiO_2

Results on the influence of the addition of molecular O_2 on the rate of reaction (1) have interesting implications for oxidation reactions catalyzed by TiO_2. In fact, assuming that the oxidation of CO on TiO_2 takes place in two steps, namely;

$$\tfrac{1}{2}O_2(g) \rightarrow O(s) \qquad (1c)$$

$$CO(g) + O(s) \rightarrow CO_2(g) \qquad (1d)$$

the inhibition of reaction (1) by O_2 shows that the stationary concentration of adsorbed O_2, $[O(s)_{ss}]$, on working TiO_2 catalyst for the CO oxidation is controlled by step (1c): $[O(s)_{ss}] \cong [O(s)_{(c)}]$. From studies on the influence of WO_3 additions and O_2 chemisorption, it was concluded previously that the oxidation reaction was not controlled by step (1c) (*13*). It was also found that additions of Fe in the temperature range 345–450°C had no effect on the rate and activation energy for the oxidation of CO.

CONCLUSIONS

Although the topological details of the surface defects in TiO_2 cannot be ascertained from our results, it is possible to conclude that adsorbed O_2, a key intermediate for the reactivity of TiO_2 toward molecular O_2, was preponderantly present in an ionized form. Solid additions, which increased the free electron population in TiO_2, also increased the extent of charge localization upon the adsorbed oxygen, possibly by promoting a more nonuniform distribution of the crystal field around the adatom. A similar influence of the catalyst compositon upon the extent of charge localization on the adsorbed oxygen was found in cobalt ferrite (*14*). In the present study, different reaction intermediates (O^-, O^{2-}) induce a different

reactivity pattern. This results from both thermodynamic and kinetic factors and include the possibility of thin or thick surface charge layers.

The important role of free electrons of the solid in the kinetically controlling reaction step was emphasized by this investigation. In TiO_2, with relatively low free electron population, the availability of the latter is an important factor in the kinetic aspects of surface reactivity, while ionic defects play a decisive role in the establishment of the gas–surface equilibrium. The latter fixes the energetic and the numerical aspects of surface active centers. Thus, both ionic and electronic defects contribute to the overall reactivity of TiO_2 surfaces. This conclusion implies that the oxygen of TiO_2 participates in the catalytic step of reaction (1). This is consistent with the fact that reaction (1) was found to occur readily on TiO_2 in the same temperature range in which the equilibration of oxygen isotopes on TiO_2 takes place. It is well known that at high temperatures this latter reaction occurs with the participation of surface oxygen (*1*b). The general accord between the results from reaction (1) and those from oxygen isotope equilibration stems from the common feature of the two reactions; namely, the establishment of a solid–gas equilibrium during isotope redistribution.

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