Competitive Reconfiguration of Adsorbed Species on Heterogeneous Solid Surfaces[*]

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Abstract

The competitive reconfiguration behavior of adsorbed species has been studied on the heterogeneous solid surfaces of Cr_2O_3, Ag and MgO by using the transient response method, and the characteristic anomalous transient behavior has been observed depending on the catalysts. On Cr_2O_3, in the temperature range 131~163°C, the reduction of surface removing surface oxygen works to increase the degree of coordinated unsaturation of the surface sites, and the adsorption of oxygen on the reduced surface decreases the degree of it inducing the rapid desorption of CO and CO_2 preadsorbed. On Ag, in the temperature range 80~120°C, the desorption of CO_2 adsorbed on the oxidized surface is accelerated when H_2 is adsorbed on the surface.

On MgO, the single gas adsorption of CO or CO_2 obeys a Langmuir isotherm on the same active sites such as coordinatively unsaturated surface O^{2-} ions or paired surface ions $Mg^{2+}O^{2-}$, in the temperature range 290–320°C. The desorption response of CO is extremely affected by the second component CO_2 mixed in the gas phase, while the desorption of CO_2 is not influenced by the ambient gas. The adsorbed CO is retained on the surface by the attraction force of adsorbed CO_2, and its amount decreases with increasing concentration of coexisting CO_2. The temperature programmed desorption spectra of the CO retained on the surface give a single peak and satisfy the first order desorption kinetics.

1. Introduction

As is well known, the adsorption of reaction components is necessary to initiate reactions progressing on solid catalyst surfaces. The adsorption and desorption rates are very important in heterogeneous catalysis sequences. Based on the Langmuir adsorption theory, it has been accepted with no doubt that the rate of adsorption is dependent on the surface coverage and pressure, and the rate of desorption is only a function of surface coverage. Recently, Tamaru[1~4] has proposed a new presentation "adsorption assisted desorption", using the desorption behavior of CO on Pd, Rh, Ru and Ni. The new concept demonstrates that the rate of desorption is sensitively affected by the ambient gas. In the present study, the dynamic behavior of adsorbed species affected by the attraction or repulsion force from the neighboring adsorbed species has been studied in

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detail on Cr_2O_3, Ag and MgO.

On the surface of Cr_2O_3, the fold number of coordination is easily changed by the amount of adsorbed oxygen, and it will effect the rate of desorption of the ambient gas components.

On the surface of Ag, generally speaking, oxygen is absorbed into bulk about ten layers from the surface to form Ag_2O, AgO_2 or Ag_2O_3.[5,6] The adsorption behavior is extremely affected by the degree of oxygen adsorption.

A large number of investigators have studied the surface nature of magnesium oxide, being especially interested in its bifunctional characteristic nature, having both base sites and acid sites.[7] Generally speaking, CO_2 adsorbs on the O^{2-} ion as the base sites which are distributed in broad degree of coordinated unsatura-tion, inducing the broad distribution of the strength of basidity.[8] The strength of the adsorption of CO_2 should therefore be distributed over a wide range.

For the adsorption of CO on MgO, Zecchina et al.[9] have recently studied eagerly to clarify the fine structure of the adsorbed state by using the spec-troscopic technique, IR and UV. They have demonstrated the population of the surface ions of MgO by classifying three groups : (1) five-fold coordination which is mainly located on [100] faces and occupies $95 \sim 98\%$ of the total surface ions, (2) four-fold coordination which is located on edges and steps and occupies $5 \sim 2\%$, and (3) three-fold coordination which is located on corners and other defects and occupies $\ll 1\%$.[10] Interestingly, at room temperature, CO adsorbs on only three-fold coordinated sites and four-fold coordinated sites to form polycarbonylic species and carbonates, respectively.[9] Furthermore, nitric oxide adsorbs only on the ions located on edges and steps, whereas the ions located on the [100] faces are not active for adsorption.[11] The adsorbed NO forms N_2O dimers on Mg^{2+} ions. From these results, one may recognize that the surface ions of MgO are extremely selective for adsorbates and the species adsorbed on the adjacent sites make a strong interaction forming some complexes consisting of more than two molecules.[12]

In the present study, our interest is focused on the competitive configuration of H_2, O_2, CO and CO_2 adsorbed on the heterogeneous active sites of Cr_2O_3, Ag and MgO. The configuration will shift depending on the adsorption and desorp-tion conditions, and the mobility of their molecules will strongly affect the tran-sient adsorption behavior of the adsorption components. For this study, the transient response method is conveniently employed with the temperature pro-gramed desorption technique.

2. Experimental Procedure

(1) Catalysts

Chromium sesquioxide and silver were prepared and pretreated using the procedures reported previously.[13,14] The catalyst weight and surface area were 55.2 g ($24 \sim 32$ mesh) and 21 m^2/g for Cr_2O_3 and 206.0 g–Ag, 1.13 g–K_2SO_4/53.5–α–Al_2O_3 ($20 \sim 42$ mesh) and 0.3 m^2/g for Ag, respectively.

The magnesium oxide used in this study was supplied by the Wako Pure Chemicals guaranteed reagent. The purity of the sample is guaranteed to be at least 99.5% and the metal impurities detected were Ba, Zn, As and Fe less than 0.03%. The fine white powder was pressed by 138 kg/cm^2 to make a disk and crashed by an agate mortar so as to form $20 \sim 42$ mesh. The catalyst (61.8 g) was preheated in a N$_2$ stream (10 cc (NTP/min)) at 300°C for 20 hr, prior to use. The BET surface area of the sample obtained thus was 27.5 m^2/g.

(2) **Gases**

The gases used in this study were prepared by Hokusan Co. with no further purification. The purities of the gases were guaranteed as carbon monoxide (99.9% CO), carbon dioxide (99.8% CO$_2$), oxygen (99.9% O$_2$), hydrogen (99.9% H$_2$) and helium (99.99% He).

(3) **Analysis**

Two gaschromatographs attached to a thermal conductivity detector were simultaneously employed to follow the transient response of the outlet gases as continuously as possible. A Hitachi 164 T and Shimadzu GC-3AH were commonly attached to a Porapak Q column for analysing CO$_2$ and to a Molecular Sieve 5A column for H$_2$, CO and O$_2$. The lengths of the columns were 1 m and 2 m depending on the separating conditions of the objective gases.

(4) **Procedures**

The catalyst was packed into a tubular flow reactor which was made of Pyrex glass (0.7 cm ID and 140 cm length for Cr$_2$O$_3$, 1.0 cm ID and 110 cm length for Ag, and 0.8 cm ID and 97 cm length for MgO). The total gas flow rate was 160($\pm$5) ml/min through all experiments. The reactor was immersed into an oil bath for Cr$_2$O$_3$ and Ag, and a fluidized sand bath (15 cm ID and 50 cm length) for MgO, the temperature was thereby well controlled within $\pm$0.5°C at desired temperatures. In these conditions, the longitudinal gas mixing effect in the reactor was negligibly small based on the data: the transient response of gases at the outlet caused by the switching between two different inlet gas streams (N$_2$ and He) was completed within $10 \sim 20$ sec, which was a very short period compared to the actual responses of more than ten min. The internal and external particle diffusion effects were also confirmed to be negligible by testing the catalytic activities for CO oxidation on two different particle sizes of catalyst ($80 \sim 100$ mesh and $20 \sim 42$ mesh), and at two different flow rates (160 and 320 cc/min) with the same W/F value at the respective reaction temperatures.

For the temperature programed desorption (TPD) experiments for MgO, a program temperature controller from CHINO Co. (Model JP-1131) was used, and special attention was paid to follow a given temperature schedule within $\pm$1.0°C.

Further detailed experimental apparatus and the procedures for the transient response method will be found elsewhere.[15]

3. Experimental Results and Discussion

3-1. Anomalous Acceleration of the Desorption of Adsorbed Species on Cr_2O_3 and Ag

(1) Cr_2O_3

The catalyst surface is reduced by the $CO-N_2$ mixture for 530 min until no formation of CO_2 at 131°C can be seen. The surface is then exposed to the O_2 (20%)-N_2 mixture and the response of CO_2 is followed as shown in Run 2 of Fig. 1. A large amount of CO_2 is desorbed for 450 min with the desorption of CO. Since the desorption of CO is completed within 3 min, the desorption of CO_2 in Run 2 results from the acceleration of its desorption due to the adsorption of O_2, when the CO_2 has irreversibly been adsorbed in Run 1. The strength of the CO_2 adsorption is weakened by the adsorption of O_2, because the number of the fold coordination of Cr ions is decreased.

(2) Ag

CO_2 is adsorbed on the oxidized surface not on the reduced surface in contrast to the surface of Cr_2O_3. H_2 reacts easily with surface oxygen higher than 50°C to form metallic silver. Fig. 2 illustrates the acceleration of CO_2 desorption. In Run 1, CO_2 is preadsorbed on the oxidized surface at 90°C, then the CO_2 (0.6%)-He mixture is switched over to the pure H_2 stream in Run 2. The rate

	P^o_{CO}	$P^o_{O_2}$	$P^o_{N_2}$
A	—	0.20	0.80
B	0.065	—	0.935

(atm)

T = 131°C
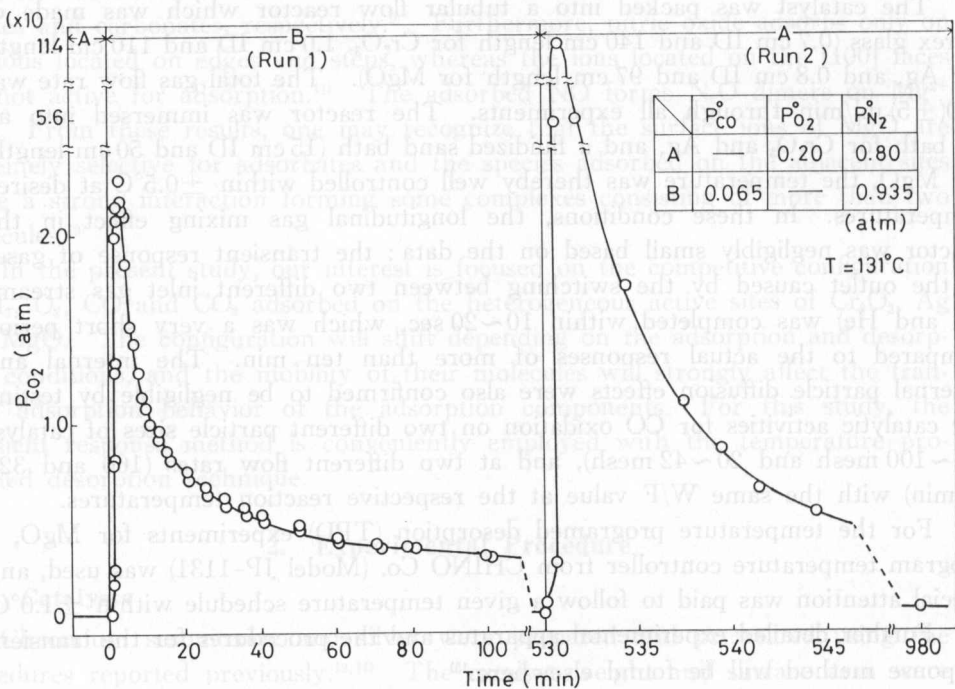
Fig. 1.   Acceleration behavior of CO_2-desorption due to the adsorption of O_2 on Cr_2O_3.
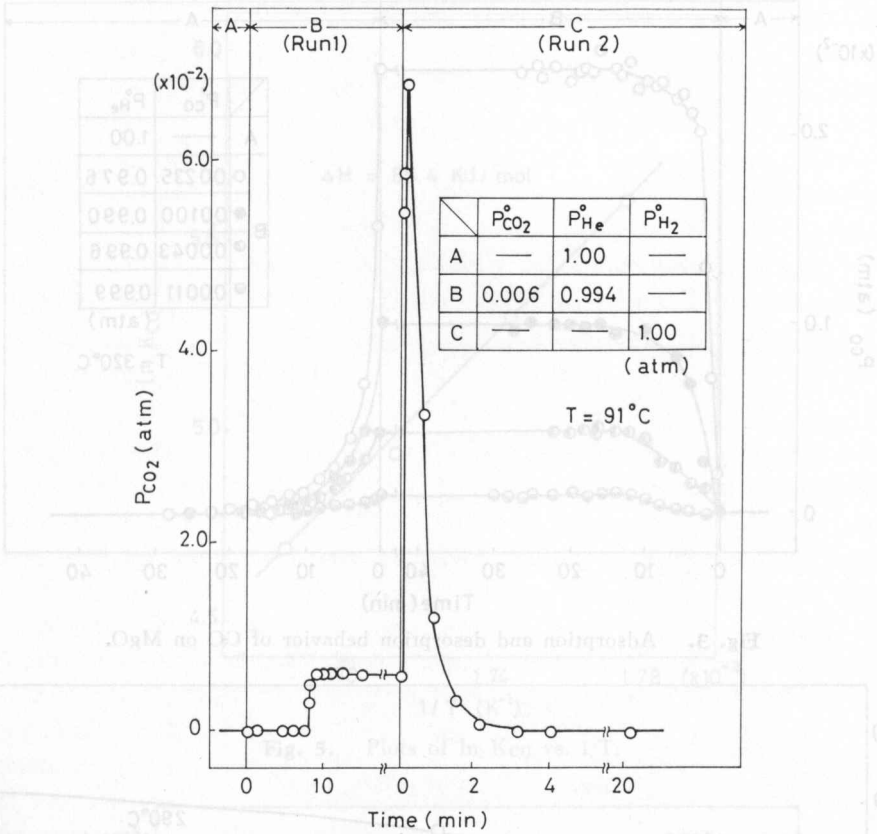
Fig. 2. Acceleration behavior of CO_2-desorption due to the adsorption of H_2 on AgO.

of desorption becomes about ten times higher than that in He. This enhancement is caused by the repulsion of the metallic silver surface against the adsorption of CO_2.

3-2. Adsorption Isotherms of CO and CO_2 on MgO

The adsorption and desorption behaviors of CO have been followed under atmospheric pressure by the transient response method using the step change in gas concentration between the pure He stream and the stream of CO–He mixture, in the temperature range 290°~320°C. The typical response curves obtained are presented in Fig. 3. The time to reach the steady state depends on the adsorption temperature, more than 60 min at 290°C and around 15 min at 320°C. The graphical integrations of the CO(inc., 0)–CO and CO(dec., 0)–CO response curves propose the adsorbed and desorbed amounts, respectively. The two amounts are in good agreement through all temperatures and CO-concentration regions. This suggests the reversible adsorption of CO on the surface.

Fig. 4 shows the adsorption isotherms for CO, and thereby one may recognize that they obey a Langmuir equation. Analysis of the equation evaluates
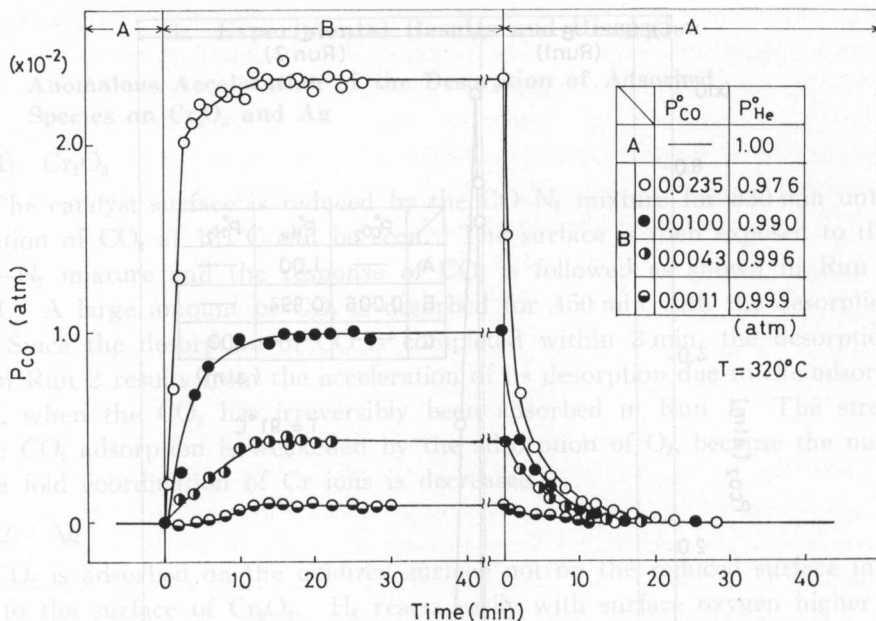
Fig. 3. Adsorption and desorption behavior of CO on MgO.
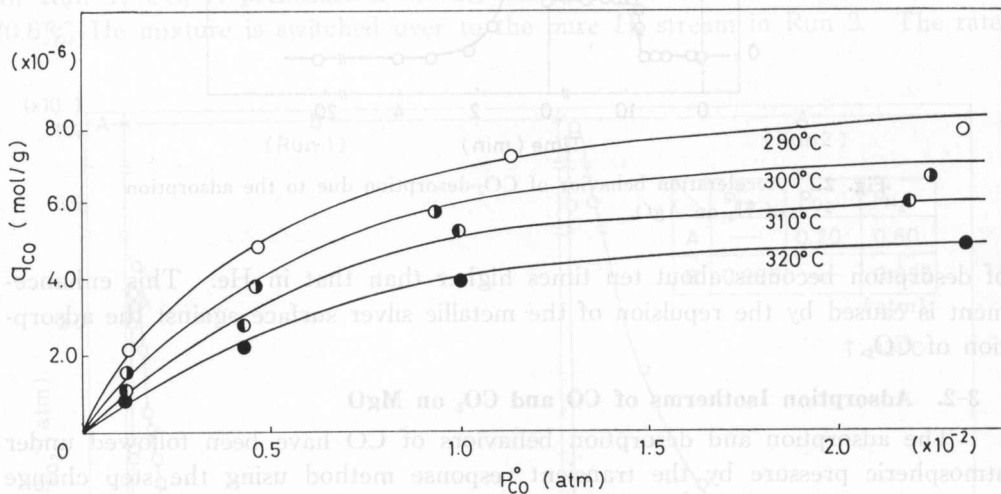
Fig. 4. Adsorption isotherms for CO on MgO.

the saturated amount to be 8.5×10^{-6} mol/g ($=1.9 \times 10^{13}$ molecules/cm²) with no dependence on the adsorption temperature. In addition, the plots of ln K_{CO} vs. 1/T give a good straight line as shown in Fig. 5. From the slope of the line, the adsorption heat is estimated to be 85.4 kJ/mol.

For the adsorption of CO_2, similar transient responses are carried out. The amounts of adsorbed and desorbed CO_2 obtained are in rough agreement suggesting a reversible adsorption. Fig. 6 illustrates the adsorption isotherm which again obeys the Langmuir equation. The saturated amount of adsorbed CO_2 is

$\Delta H = 85.4 \text{ KJ/ mol}$

ln K_{CO}

1.70   1.74   1.78 $(\times 10^{-3})$

$1/T \ (K^{-1})$

Fig. 5. Plots of ln K_{CO} vs. 1/T.

290°C
300°C
320°C

q_{CO_2} (mol/g)

$P^{\circ}_{CO_2}$ (atm)
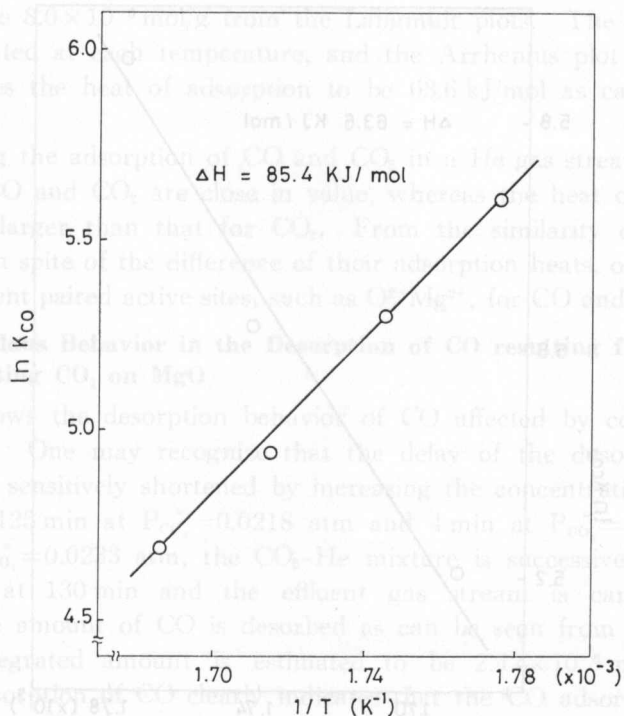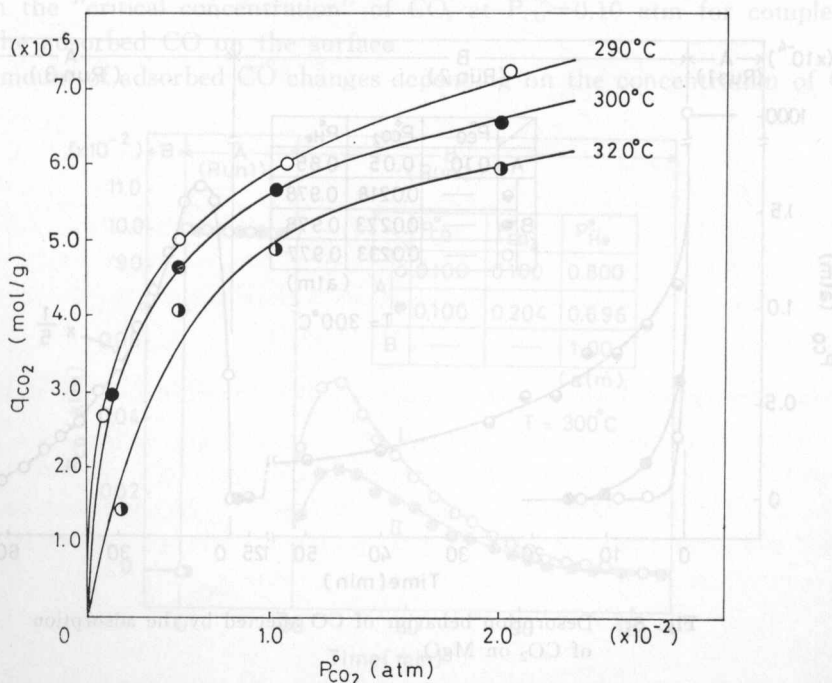
Fig. 6. Adsorption isotherms for CO_2 on MgO.
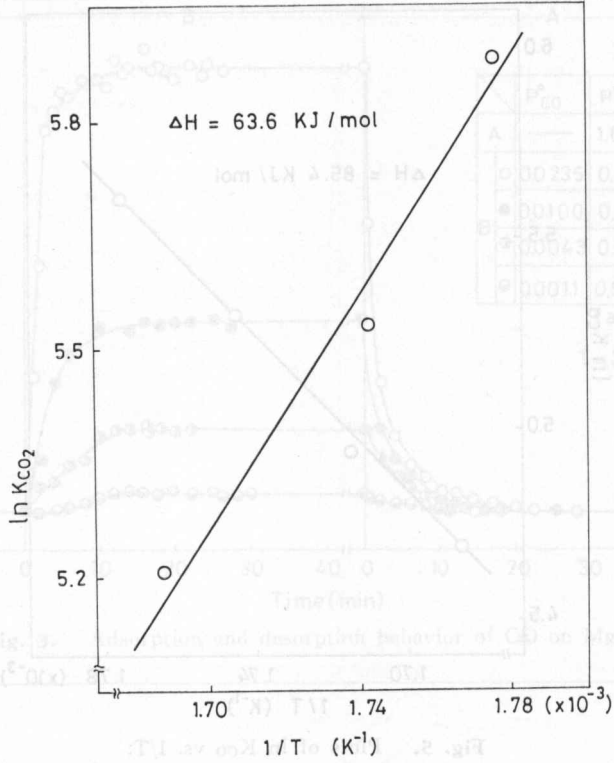
Fig. 7. Plots of $\ln K_{CO_2}$ vs. $1/T$.
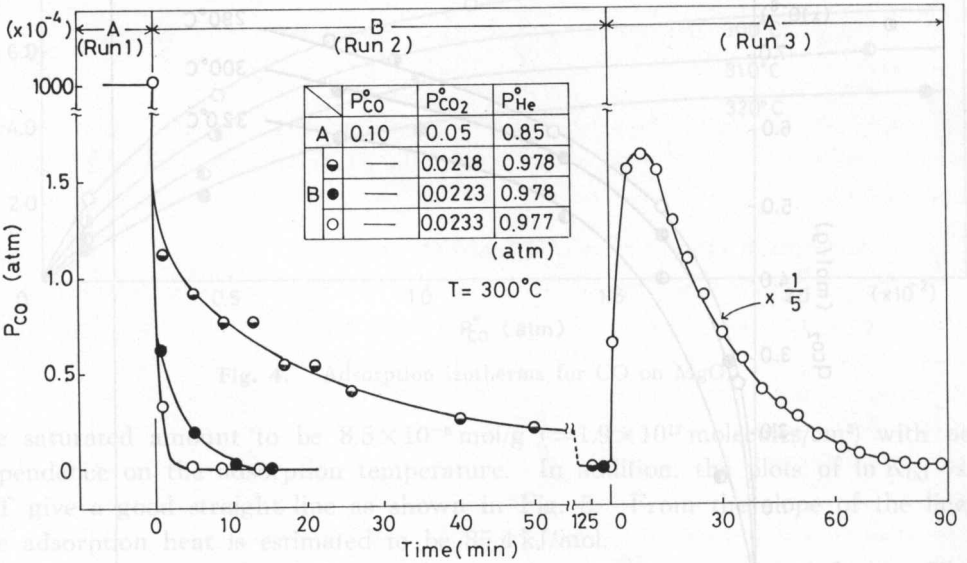
Fig. 8. Desorption behavior of CO affected by the adsorption of CO_2 on MgO.

estimated to be 8.0×10^{-6} mol/g from the Langmuir plots. The equilibrium constant is estimated at each temperature, and the Arrhenius plot of the obtained values evaluates the heat of adsorption to be 63.6 kJ/mol as can be seen from Fig. 7.

Comparing the adsorption of CO and CO_2 in a He gas stream, the saturated amounts for CO and CO_2 are close in value, whereas the heat of adsorption for CO is rather larger than that for CO_2. From the similarity of the saturated amounts and in spite of the difference of their adsorption heats, one may presume common adjacent paired active sites, such as $O^{2-}Mg^{2+}$, for CO and CO_2 adsorption.

3–3. Anomalous Behavior in the Desorption of CO resulting from the Coexisting CO_2 on MgO

Fig. 8 shows the desorption behavior of CO affected by coexisting CO_2 in the gas phase. One may recognize that the delay of the desorption curves is drastically and sensitively shortened by increasing the concentration of coexisting CO_2 (Run 2); 125 min at $P_{CO_2}^{\circ}=0.0218$ atm and 4 min at $P_{CO_2}^{\circ}=0.0233$ atm. In the case of $P_{CO_2}^{\circ}=0.0233$ atm, the CO_2–He mixture is successively changed into a He stream at 130 min and the effluent gas stream is carefully analysed. An appreciable amount of CO is desorbed as can be seen from Run 3, and the graphically integrated amount is estimated to be 2.42×10^{-6} mol-CO/g. This unexpected desorption of CO clearly indicates that the CO adsorbed during Run 1 is retained by the CO_2 adsorbed during Run 2, and its amount is sensitively dependent on the amount of CO_2 coexisting in Run 2. One may thus call $P_{CO_2}^{\circ}=0.0233$ atm the "critical concentration" of CO_2 at $P_{CO}^{\circ}=0.10$ atm for completely retaining the adsorbed CO on the surface.

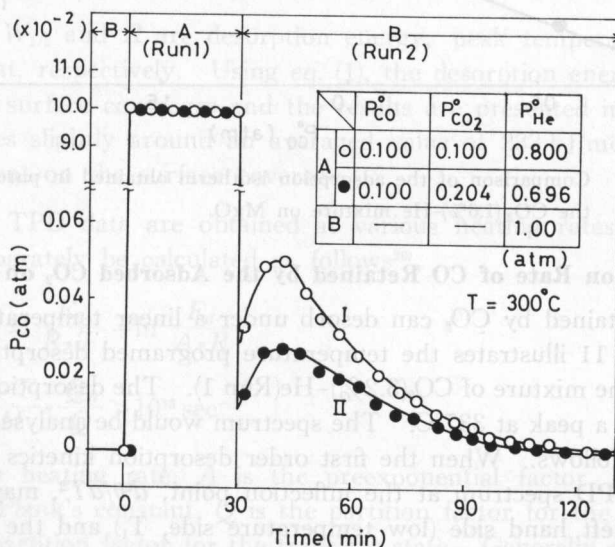The amount of adsorbed CO changes depending on the concentration of CO_2

Fig. 9.   Variation of the adsorption of CO depending on the concentration of CO_2 in the mixture on MgO.

during the coadsorption conditions in Run 1 of Fig. 8. Fig. 9 illustrates the effect of the concentration of CO_2 on the adsorption behavior of CO in the He stream. The graphically integrated amounts of Curves I and II in Run 2 propose 1.88×10^{-6} at $P_{CO_2}^{\circ} = 0.100$ and 1.14×10^{-6} mol/g at $P_{CO_2}^{\circ} = 0.204$ atm. From these results, one may recognize that CO and CO_2 are competitively adsorbed on the same active sites or on the adjacent sites of each adsorbed site. The adsorption isotherms for CO obtained in the pure He stream and in the $CO_2(1.6\%)$–He mixture are compared in Fig. 10. At a partial pressure of CO lower than $P_{CO}^{\circ} = 0.0165$ atm, the isotherm in He(Curve I) is clearly higher than that in the CO_2–He mixture (Curve II). In addition, Curve I clearly obeys the Langmuir equation whereas Curve II slightly follows a characteristic mode which belongs to a type III isotherm illustrated by Lennard-Jones.[11] The S-shape isotherm has qualitatively been explained by Fowler[17,18] as the adsorption of specified molecules with the interaction between adsorbed species.
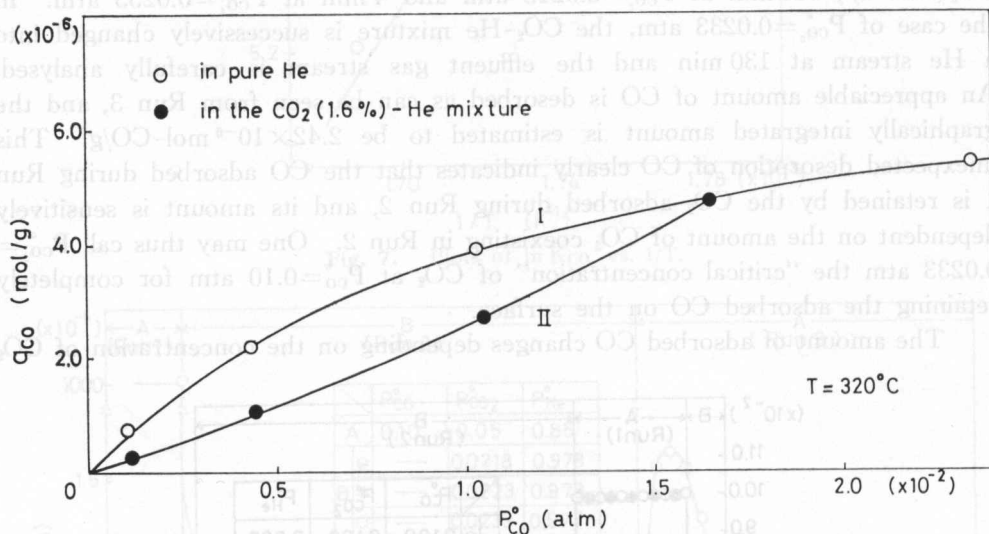
Fig. 10. Comparison of the adsorption isotherm obtained in pure He and the $CO_2(1.6\%)$–He mixture on MgO.

3–4. Desorption Rate of CO Retained by the Adsorbed CO_2 on MgO

The CO retained by CO_2 can desorb under a linear temperature increase up to 360°C. Fig. 11 illustrates the temperature programed desorption (TPD) spectrum of CO in the mixture of $CO_2(3.2\%)$–He(Run 1). The desorption begins around 295°C and gives a peak at 337°C. The spectrum would be analysed by Weinberg's procedure[11] as follows. When the first order desorption kinetics is accepted, the slopes of the TPD spectrum at the inflection point, $d^2\theta/dT^2$, may easily be estimated for the left hand side (low temperature side, T_1) and the right hand side (high temperature side, T_2) (see Run 1 in Fig. 11), expressing S_1 and S_2, respectively. The ratio, S_1/S_2, at all adsorption conditions falls in the range of 0.70~
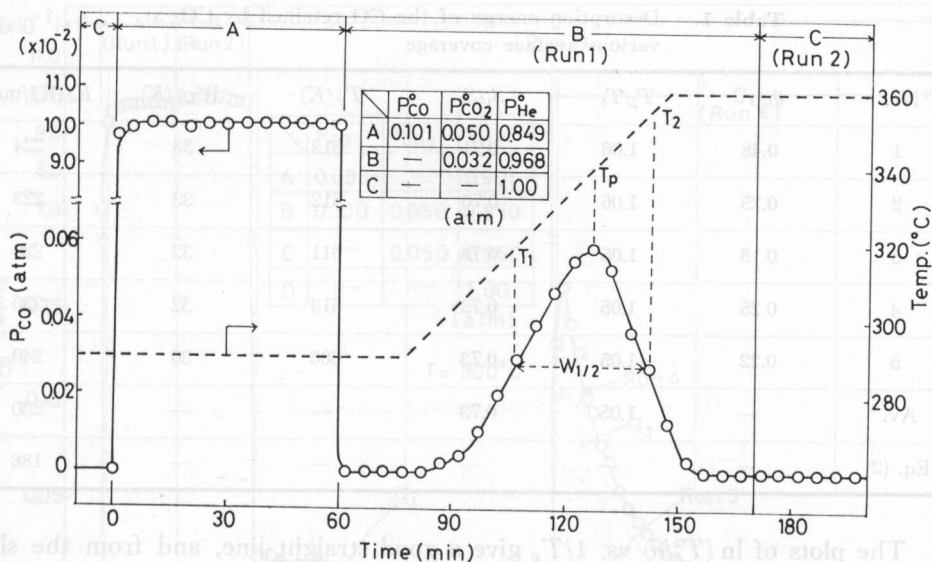
Fig. 11.   TPD spectra of CO in the $CO_2(3.2\%)$–He mixture on MgO.

0.78.   In addition, T_2/T_1 becomes 1.05.   These results satisfy Weinberg's nec-
cessities for the first order desorption kinetics of the retained CO with no re-
adsorption.

For the calculation of the desorption energy, a simplified equation for the
first order kinetics of TPD is proposed[19]

$$\frac{E_d}{R \cdot T_p} = -1 + \left(\frac{1 + 5.832\, T_p^2}{W_{1/2}^2}\right)^{1/2} \qquad (1)$$

where E_d, T_p, $W_{1/2}$ and R are desorption energy, peak temperature, half-width
and gas constant, respectively.   Using eq. (1), the desorption energy (E_d) is evalu-
ated at various surface coverages and the results are presented in Table 1.   The
energy fluctuates slightly around an averaged value of 233 kJ/mol, suggesting no
change dependent on the surface coverage.

When the TPD data are obtained at various heating rates, the desorption
energy may separately be calculated as follows[20].

$$\ln \frac{T_p}{\alpha} = \frac{E_d}{R \cdot T} + \ln \frac{E_d}{A \cdot R} \qquad (2)$$

$$A = \frac{k \cdot T}{H} \cdot \frac{Q_R}{Q} > 10^{13}\ \text{sec}^{-1} \qquad (3)$$

where α is the heating rate, A is the preexponential factor, k is Boltmann's
constant, H is Plank's constant, Q is the partition factor for the reactant system
and Q_R is the partition factor for the transient state.   Generally speaking,[21] Q_R is

$$1 < Q_R < 1000 \qquad (4)$$

Table 1. Desorption energy of the CO retained by CO_2 at various surface coverage

No.	θ_{CO}	T_2/T_1	S_1/S_2	$T_p(K)$	$W_{1/2}(K)$	E_d (KJ/mol)
1	0.48	1.06	0.71	613	33	224
2	0.25	1.06	0.70	612	33	223
3	0.13	1.05	0.78	611	32	229
4	0.25	1.05	0.73	613	32	230
5	0.22	1.05	0.73	606	30	240
Av.	—	1.05	0.73	—	—	230
Eq. (2)	—	—	—	—	—	186

The plots of $\ln(T_p^2/\alpha)$ vs. $1/T_p$ give a good straight line, and from the slope of the line E_d is calculated as 186 kJ/mol which is smaller than the 230 kJ/mol presented in Table 1. This deviation is caused by the rough estimation due to equation (1).

In Fig. 10, after the TPD experiments, the CO_2-He mixture is switched over to the pure He stream (see Run 2). No CO is desorbed exhibiting no existence of the adsorbed CO after Run 1.

3-5. Influence of the Order of the Addition of Adsorption Gases in the Mixture on MgO

The adsorption of CO is sensitively affected by the order of mixing the gases in the mixture, depending on whether CO is first then CO_2 second or the reverse procedure. Fig. 12 illustrates the case of first CO adsorption (Run 1) and then CO_2 adsorption (Run 2). The adsorption response of CO is successively followed under the existence of $CO_2(5\%)$ as shown in Runs 1∼3. One may be interesting to note that the response obtained in Run 3 clearly shows slight desorption of CO, even though the concentration of CO_2 is higher than the critical concentration of $CO_2(2.6\%)$ described in section 3-2. This strongly suggests that the pre-adsorption of CO proposes a difficulty for the adsorption of CO_2 onto the neighboring sites because of their competitive adsorption of the same sites. Therefore, to retain CO on the surface, it is necessary to have two or three vacant sites for the CO_2 adsorption. In other words, one may speculate that one CO molecule forms a cluster with two or three CO_2 species on the surface.

After Run 2 in Fig. 12, two different transient experiments are separately carried out : (1) the CO_2-CO-He mixture is changed into the $CO_2(5\%)$-He mixture and the response of CO is then followed for 13 hrs (Run 3), and (2) at 4 hrs, the CO_2-He mixture is changed into the pure He stream (Run 4). In Run 3, the desorption of CO is observed for 13 hours with very slow decay. This slow desorption will be caused by a little interaction of the CO_2 located on the close
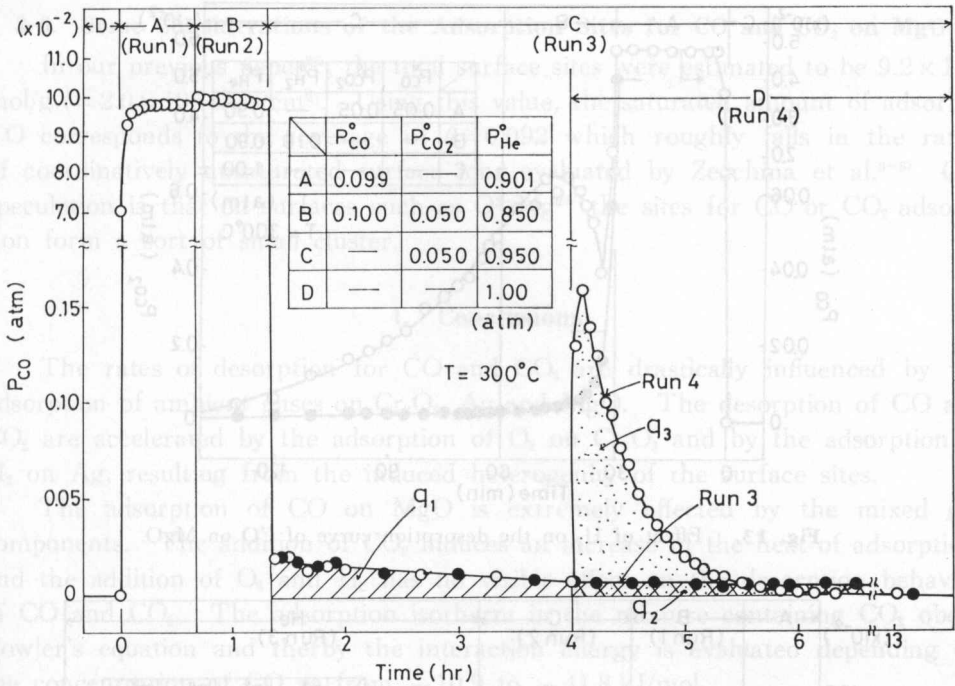
Fig. 12. Effect of the preadsorption of CO prior to introducing CO_2 on the desorption curve of CO on MgO.

sites and not on adjacent ones. The graphical integration of the curve gives the amount of desorbed CO (q_1 plus q_2, see Fig. 12) to be 7.2×10^{-6} mol/g. When the CO_2-He mixture is changed into the pure He stream at the period of 140 min in Run 4, the desorption of CO is accelerated and responds to zero within two hours. The desorption time is clearly shortened, resulting from the disappearance of the attraction force due to CO_2. The graphical integration of the curves in Run 4 proposes $q_1 + q_3$ to be 7.6×10^{-6} mol/g which is close to $q_1 + q_2$. This close agreement supports again the previous consideration for the retaining effect of CO_2 on CO. Furthermore, the amount is much higher than 2.6×10^{-6} mol/g which is the equilibrium amount for the CO(10%)-CO_2(5%)-He mixture. It seems that the replacement of the preadsorbed CO with CO_2 progresses very slowly, differing from the simultaneous adsorption of CO and CO_2.

Let us consider the effect of the third components of the ambient gas on the desorption of the CO retained on the surface. First of all, the effect of H_2 has been studied and the results are presented in Fig. 13. As can be seen from the figure, the desorption curves of CO and CO_2 are not affected by the addition and the removal of H_2. One may recognize that the adsorption of H_2 has no influence on the adsorption behavior of CO and CO_2, probably resulting from its weak adsorption.

On the adsorption of O_2, Fig. 14 illustrates the reactivity of the CO retained by CO_2. The CO is partly desorbed because of the concentration of CO_2(1.1%)
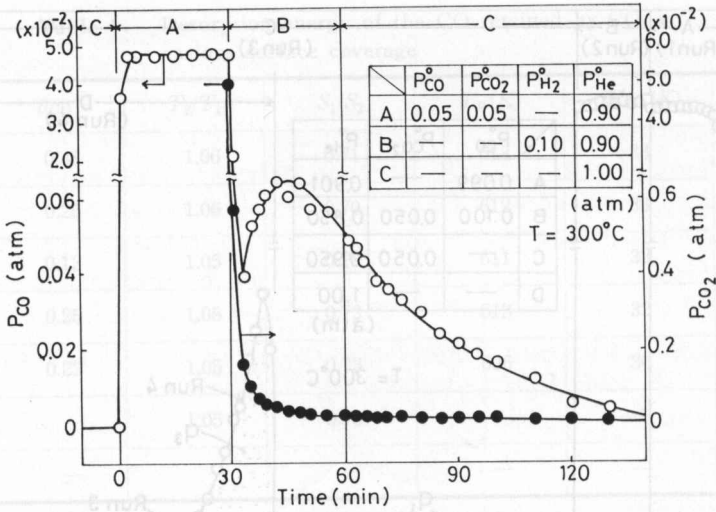
Fig. 13. Effect of H_2 on the desorption curve of CO on MgO.
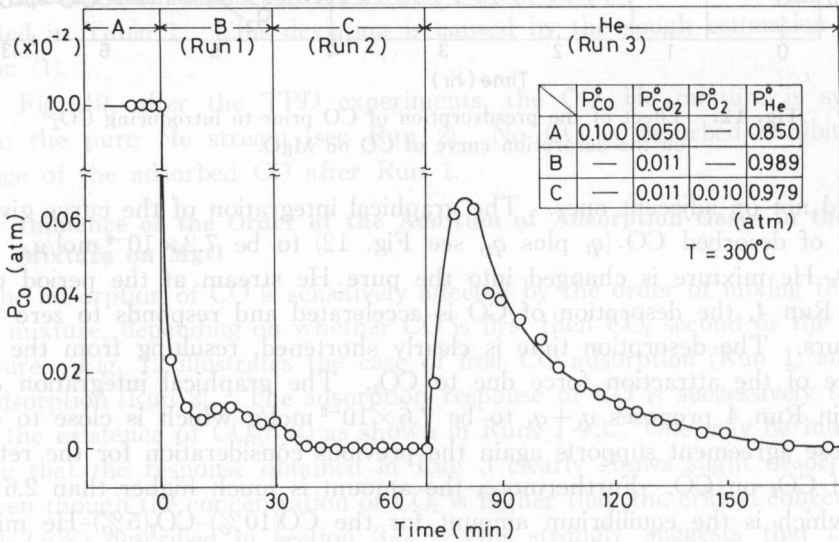
Fig. 14. Effect of O_2 on the desorption curve of CO on MgO.

in Run 1 which is lower than the critical concentration (2.6%), and then the
mixture is switched over to the mixture containing O_2 (Run 2). The desorption
curve of CO responds to nil at seven minutes because of the reaction with oxygen.
After this, when the mixture is changed into the pure He stream (Run 4), an
appreciable amount of CO is desorbed. The graphical integration of the curve
in Run 3 gives 2.4×10^{-6} mol/g. This is a little smaller than the equilibrium
amount resulting from consumption by reaction with oxygen.

3-6. Some Considerations of the Adsorption Sites for CO and CO_2 on MgO

In our previous paper[22], the total surface sites were estimated to be 9.2×10^{-5} mol/g ($= 2.0 \times 10^{15}$ sites/cm^2). Using this value, the saturated amount of adsorbed CO corresponds to the coverage of $\theta = 0.092$ which roughly falls in the range of coordinatively unsaturated surface ions evaluated by Zecchina et al.[3~6] Our speculation is that on surfaces such as $O^{2-}Mg^{2+}$ the sites for CO or CO_2 adsorption form a sort of small cluster.

4. Conclusions

The rates of desorption for CO and CO_2 are drastically influenced by the adsorption of ambient gases on Cr_2O_3, Ag and MgO. The desorption of CO and CO_2 are accelerated by the adsorption of O_2 on Cr_2O_3 and by the adsorption of H_2 on Ag, resulting from the induced heterogenity of the surface sites.

The adsorption of CO on MgO is extremely affected by the mixed gas components. The addition of CO_2 induces an increase of the heat of adsorption, and the addition of O_2 and H_2 has no visible effect on the desorption behavior of CO and CO_2. The adsorption isotherm in the mixture containing CO_2 obeys Fowler's equation and therby the interaction energy is evaluated depending on the concentration of CO as from -10.9 to -41.8 kJ/mol.

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