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Kinetic study of gas-surface molecular exchange between CO/CO* on metals

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Isotopic switching technique has been used to study the exchange of gaseous CO* with chemisorbed CO molecules on metal surface. The kinetic curves observed on Re(0001) exhibit a nonlinear dependence of desorption rate on the surface coverage of CO. However, the desorption rate for CO on Rh(111) in the same temperature range is strictly linear with the coverage of CO. A concerted adsorption-desorption mechanism is postulated which emphasizes that the desorption of CO in enhanced by the pressure of gas phase CO* on the one hand, and may be retarded by the screening effect of the CO* molecule chemisorbed on the surface on the other hand. It is pointed out that the adsorption of CO* (or CO) and the desorption of CO (or CO*) on a surface at high coverage, i.e. the molecular exchange processes, are primarily taking place simultaneously and concertedly.

Keywords: Kinetics of CO exchange; kinetics of CO desorption; CO desorption from metals

1. Introduction

The easy replacement of a chemisorbed molecule with a gas molecule has been studied by many authors since 1970 [1,2]. Tamaru and coworkers [3–6] systematically studied CO chemisorption on metals by means of the isotope switching technique and found that when desorption was taking place in parallel with the adsorption of ambient gas molecules, the specific rate was greatly increased. They coined a name of adsorption-assisted-desorption (AAD) for the P-enhanced desorption and proved that the initial desorption rate $-V_0$ of CO at coverage Θ under a CO* gas pressure P can be expressed as

$$-V_0 = (K_0 + K_p P)\Theta. \tag{1}$$

The P-dependent desorption phenomena were also observed on Pt by Shen et al. [7,8] and Yates et al. [9] using different experimental methods.

It is noted that first order kinetic interpretations have been usually adapted in the literature to obtain the calculated value of desorption rate from the experimental Θ vs. t curves. However, we reported in a previous work [10] that the P-dependent desorption of Co/Re could be well fitted by FOD (first order) + SOD (second order) kinetics, whereas simple first order kinetics are inadequate. In this work, we observed the desorption of CO/Re in a gas flux of different isotope CO/CO* ratios and found again that the desorption rate is nonlinear. It is found also that, in contrast to CO/Re, the desorption of CO/Rh is strictly first order. Based on these experimental results a novel mechanism, namely, the concerted adsorption-desorption mechanism is postulated and a general expression is deduced for kinetic interpretation of the Θ vs. t curves of CO desorption on different metals. The advantages and similarity of a concerted versus a precursor state mechanism are discussed in detail.

2. Experimental and results

The isotope switching technique was used to study of AAD on CO/Re. The change in surface coverage Θ of CO with time t was determined by recording the temperature-programmed desorption spectra (TDS) of CO after definite time intervals. The experimental details were given in the previous paper [10].

Except when otherwise stated, the clean Re(0001) or Rh(111) was at first equilibrated with CO by exposing it to CO gas flux at $P = 2.6 \times 10^{-6}$ Pa for a long time and then switched to a gas flux of CO* or (CO + CO*) mixtures at the same pressure to determine the gas-surface exchange of isotope molecules during a certain time interval. This means that the total surface coverage Θ_t in the course of AAD experiment was maintained at a constant of Θ_{eq} at the respective temperature (fig. 1). It should be noted that in the temperature range of the present work, CO is molecularly adsorbed and the scrambling reaction between CO and CO* could be presumably neglected. Data treatment for the correlation between desorption rate and Θ, P parameters was carried out by iteration computation to yield the best least squares approximation. Figs. 2–4 show the AAD experiments at different temperatures and mixed isotope gas fluxes of varying partial pressures. It is interesting to note that unlike the case

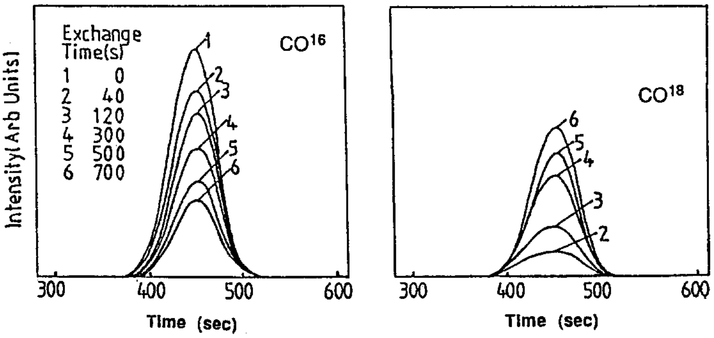

Fig. 1. The constant total coverage Θ_{eq} of CO + CO* during the AAD experiment.

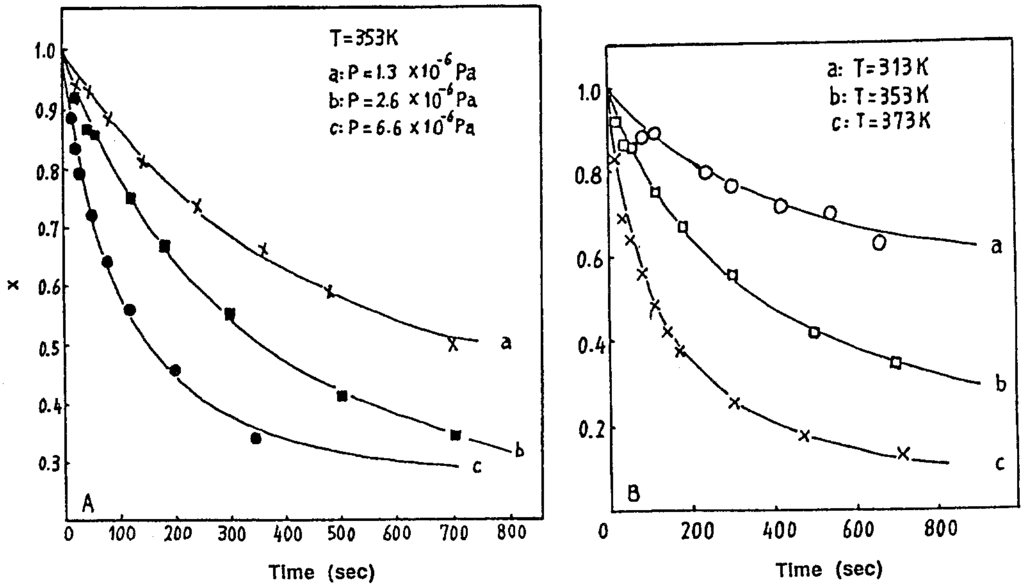

Fig. 2. Isothermal desorption of CO(16)/Re(0001) under an ambient pressure of CO(18) molecules at different pressures (a) and temperatures (b). The curves are obtained by fitting the (x, t) experimental data with the FOD + SOD expression (see text).

for CO/Rh, FOD + SOD kinetics were required to fit the desorption rate data of CO/Re rather than just FOD kinetics. Moreover, the ultimate mole fraction of CO on Re reaches a value of x_∞ at steady state, which was found to be either greater of smaller than its partial pressure fraction f_1 in the gas phase, depending on the surface temperature and partial pressures in AAD measurement (see table 1). This peculiarity of AAD processes on Re(0001) has not been disclosed in the literature.

To examine the effect of the initial coverage of CO on the AAD kinetics, a low coverage surface was prepared by first exposing the metal surface at 373 K to CO flux at 2.6×10^{-6} Pa, followed by cooling the surface to 353 K in vacuum. The cooled surface was then switched to CO* flux at the same pressure to measure the AAD rate of an initially non-equilibrated surface. The results of CO/Re are shown in fig. 5(a), which indicate that at the same coverage of CO, the surface with less total coverage of (CO + CO*) gave a greater specific rate compared with the equilibrated surface (i.e. $\tan t_1 < \tan t_2$). However, as shown in fig. 5(b), the specific rate on Rh was unchanged with initial coverage of CO and was substantially in conformity with the first order kinetics,

$$-\mathrm{d}x/\mathrm{d}t = K(x - f_1), \tag{2}$$

where $x = \Theta/\Theta_t$ $(= \Theta/\Theta_{eq})$ and $f_1 = P_1/P$ are the mole fraction of CO in the surface and gas phase respectively

3. Discussion

1. THE SOD+FOD RATE EXPRESSION

The pressure dependence of desorption rate is apparent for both Re and Rh surfaces. Fig. 6(b) shows that the specific rate for Rh increases linearly with pressure. For Re, as indicated in previous work [10,11], the initial specific rate at a given T is also linearly dependent on the partial pressure of CO (fig. 6(a)). This trend suggests that Tamaru's equation is also applicable to the initial rate of desorption for Re despite of the fact that the rate curve over a significant period follows a SOD + FOD instead of a FOD rate expression. We therefore use Tamarus expression as a boundary condition at the initial moment of $t = 0$ and $\Theta_2 = 0$ or $\Theta = \Theta_{eq}$, and try to elucidate a nonlinear rate expression for the experimental results of CO/Re.

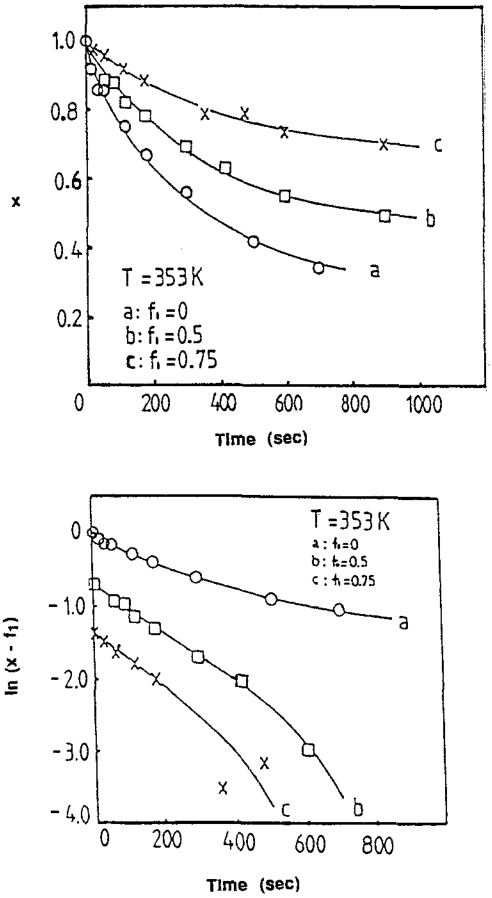

Fig. 3. Plots of (a). x vs. t and (b). $\ln(x - f_1)$ vs. t for isothermal desorption of CO(16)/Re(0001) under an ambient pressure of mixed isotope molecules at constant total pressure P (2.6×10^{-6} Pa) and temperature 353 K.

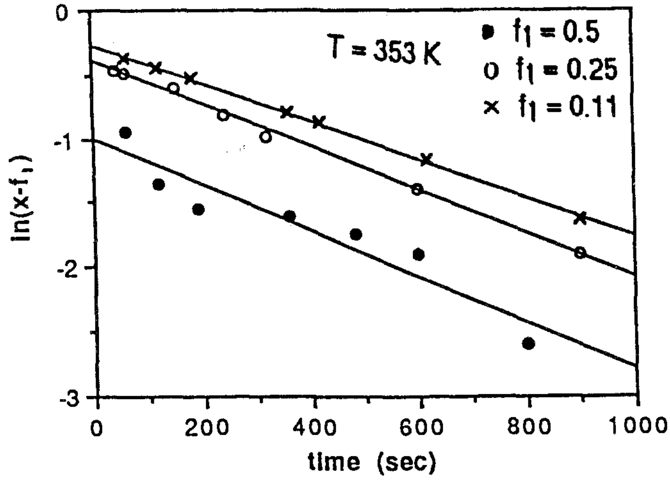

Fig. 4. Plots of $\ln(x - f_1)$ vs. t for isothermal desorption of CO/Rh under an ambient pressure of mixed CO isotope molecules at constant total pressure P.

Under a gas flux of isotope mixtures, Tamaru's expression can be transformed to

$$-\mathrm{d}x/\mathrm{d}t = (k_\mathrm{d} + k_\mathrm{E}P)(x - f_1), \tag{3}$$

where k_d and k_E are the rate constant for thermal and P-enhanced desorption respectively. To get a quadratic expression of x, a second term $k_\mathrm{E}P\beta x_2 x$ (where $x_2 = (1 - x)$) is introduced to eq. (3) and a SOD + FOD rate expression is obtained,

$$\begin{aligned} -\mathrm{d}x/\mathrm{d}t &= (k_\mathrm{d} + k_\mathrm{E}P)(x - f_1) - k_\mathrm{E}P\beta x(1 - x) \\ &= k_2 x^2 + (k_\mathrm{s} - k_2)x - k_\mathrm{s} f_1. \end{aligned} \tag{4}$$

β is the screening factor (a detailed derivation of eq. (4) is given in ref. [12]). The parametric values for k_2 and k_s obtained by least squares fitting are shown

Table 1
Calculated value of k_s, k_2 from general AAD rate equation $-\mathrm{d}x/\mathrm{d}t = k_2x^2 + (k_\mathrm{s} - k_2)x - f_1k_\mathrm{s}$

k_s (10^3 s^{-1})	k_2 (10^{-3} s^{-1})	x_∞	$f_1 = p_1/p$	T (K)
1.9	6.0	0.00	0.00	313
	3.0	0.78	0.50	
	1.7	0.86	0.75	
3.2	3.8	0.00	0.00	353
	−0.39	0.48	0.50	
	−1.4	0.67	0.75	
8.4	7.5	0.00	0.00	373
	0.37	0.26	0.25	
	−1.4	0.46	0.50	

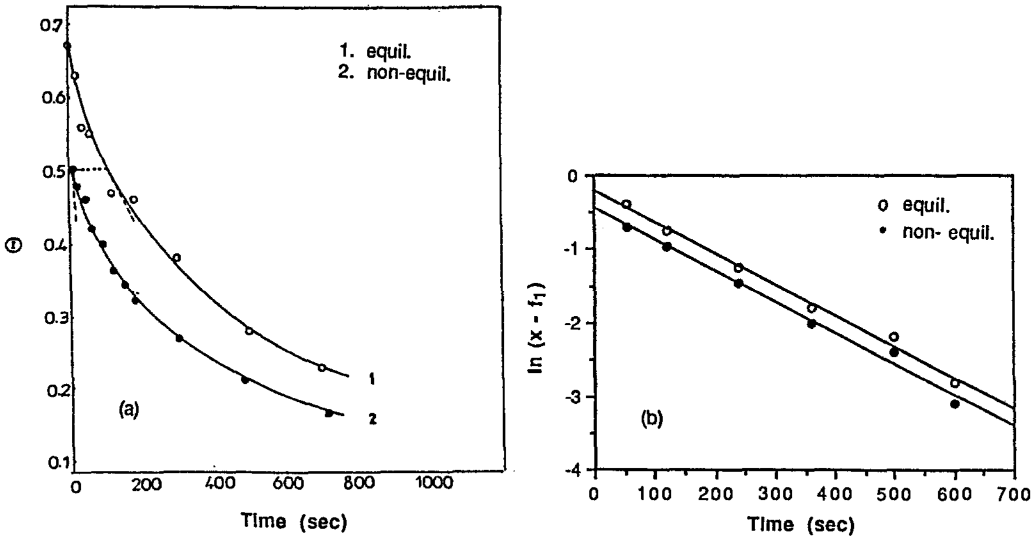

Fig. 5. Comparison of AAD rate for the non-equilibrated surface with that for the equilibrated surface at the same ambient pressure: (a). CO/Re(0001); (b). CO/Rh(111).

in table 1, and the corresponding curves plotted in figs. 2 and 3 fit the results of CO/Re well.

Yamada and Tamaru suggested that the desorption of chemisorbed CO could be facilitated by gas phase CO* via precursors formed in the surface. It is implied that the interaction between the weakly bound precursor and chemisorbed molecules leads to a pathway for the adsorption assisted desorption [4,6]. Along with this picture, it might be envisioned that the assisted desorption of CO would become less efficient after CO* molecules are chemisorbed in the course of AAD experiment. This is because when both CO

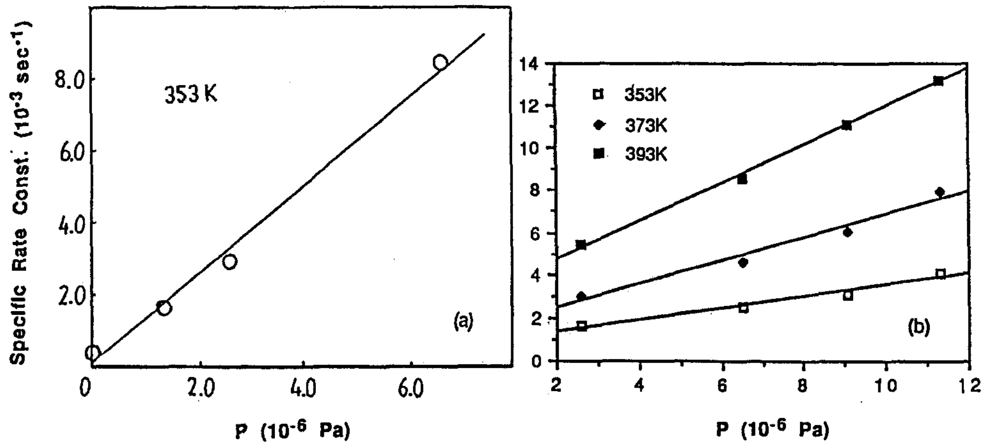

Fig. 6. The linear relation between initial rate constant and ambient pressure for AAD experiment. (a). CO/Re(0001); (b). CO/Rh(111).

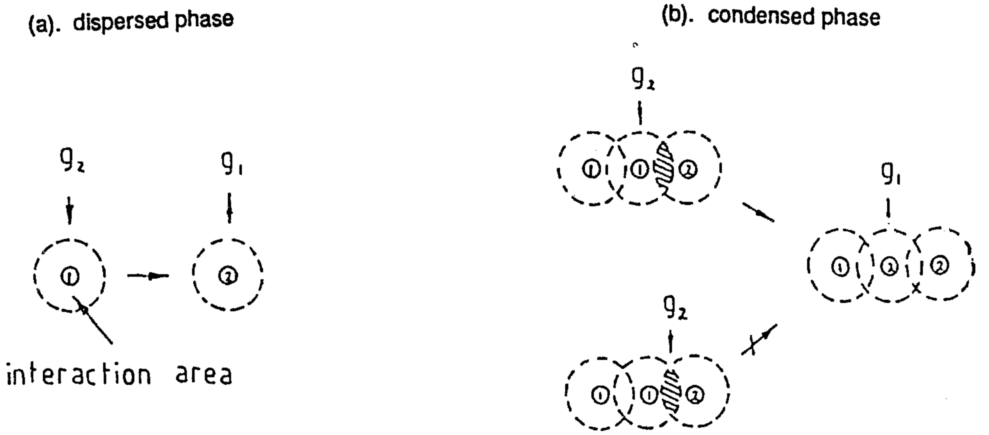

Fig. 7. The mechanistic feature of concerted adsorption and desorption in (a). the dispersed phase; (b). the ensemble phase with screening effect.

and CO* are present and migrate together to form the reconstructuring structures of micro-islands or ensemble states on the surface, the chemisorbed CO* will participate in or shield off the interaction of CO either with the CO* precursors or with the gas CO* molecules as demonstrated in fig. 7. Since such a screening effect is induced by the coadsorption of CO* in the course of exchange processes, a factor of βx_2 is used for it to indicate the increasing retarding effect with time of exchange process.

If the total coverage is small or the surface migration of admolecules is fast so that the adsorbed isotope molecules are uniformly distributed in the surface, the screening effect is negligible. In this case, k_2 in eq. (4) equals zero and the desorption rate is first order. When the surface coverage is high and the surface migration is low in comparison with the exchange rate, then the screening effect in the island region could be very significant and the isotope ratio of CO/CO* in the ensemble phase might be markedly different from the dispersed phase. That is to say, although the thermal desorption rate is constantly increased in the ensemble phase, the exchange rate of CO with gas CO* could be depressed by adsorbed CO* on the surface. This explains why the total desorption rate of a Re surface always increases with total coverage of (CO + CO*), but the desorption rate of CO at fixed coverage of CO is decreased rather than increased by the presence of the additional CO* coadsorbed on the surface (fig. 5). The reason is that the exchange between gaseous CO* and adsorbed CO can be shielded only by the coadsorbed CO* during the course of AAD process but not by the CO adsorbed on the surface. A concerted adsorption-desorption mechanism is therefore postulated which suggests a promotion effect or single step exchange of impinging gas or weak bonding precursors with the chemisorbed molecules but a retarding or screening effect of the coadsorbed molecules on the desorption rate of CO.

2. MOLECULAR INTERACTION AND DESORPTION MECHANISM

It can be seen from the exchange experiment that the P-enhanced desorption is always associated with a lower activation energy. This lowering of activation energy must be caused by the dynamic interaction between the precursor and chemisorbed molecules which is completely absent in vacuum condition. Tamaru [6] and Madix [13] reported that the relative sticking coefficient of carbon dioxide on metals is nearly independent of Θ_t even in the high coverage regime. According to precursor state theory [14] this is possible only when the physisorbed molecules tend to skitter around over the chemisorbed molecules. This is qualitatively consistent with the mechanism of fig. 7. That is to say, the essential picture of the concerted mechanism is similar to the concept of a precursor state theory. The important difference is that the activation energy is lowered mainly by the elementary action of simultaneous adsorption-desorption of two CO molecules rather than by the repulsive interaction between them. That the lower coverage CO/Re surface has a higher desorption rate as mentioned above seems to deny that the repulsive interaction is the only way to lower the activation energy. Moreover, adsorption and desorption are usually considered as two elementary and independent processes. They are not mutually coupled even though the precursors and chemisorbed molecules interact intimately. If this is always true, then the nonlinear desorption kinetics would hardly occur. In our concerted mechanism, it is argued that the interactions would make desorption and adsorption mutually coupled so that, at least in the island phase, the chemisorption is plausibly associated with simultaneous desorption.

Finally, it should be noted that in the presence of isotope gas mixtures, the net result of screening effects of coadsorbed CO and CO* molecules can be either a reduction or a promotion of CO-desorption and CO*-adsorption, i.e. β in eq. (4) can be positive or negative. As a consequence, the ultimate mole fraction x_∞ for the steady state $t = \infty$ may be greater or smaller than the partial pressure fraction f_1 in the gas phase depending on how the interactions between gas and the adsorbed isotope molecules and their distribution on the surface are affected by the surface temperature and gas partial pressures. Table 1 demonstrates that in conformity with the nonlinear kinetics, the isotope distributions of CO/CO* are nonuniform and x_∞ is not equal to f_1 on Re. However, in agreement with first order desorption kinetics, the calculated value of x_∞ for CO/Rh is equal to f_1 and the ultimate value can not be approached over a significant period of time.

In summary, we report for the first time a nonlinear dependence on coverage for the rate of CO desorption on Re(0001) or its replacement with the gaseous isotope CO*. The kinetic data of desorption in a gas flux of CO + CO* mixtures are well fitted with a FOD + SOD rate expression. However, the desorption of CO/Rh(111) is found to be strictly linear. A concerted adsorption-desorption mechanism is postulated which is anticipated to provide some understanding of the dynamic nature of gas-surface interaction in CO exchange process.

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