

## Interaction effect between adspecies on TPD spectra of methanol on SiO<sub>2</sub>-supported Pd-catalyst

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**Abstract** - Mutual interaction of coadspecies of CH<sub>3</sub>OH and D<sub>2</sub>O, CH<sub>3</sub>OH-13C and CO and CH<sub>3</sub>OH and CH<sub>3</sub>OH-13C molecules on Pd-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts was studied on the basis of TPD diagrams. The results substantiate that the surface migration of adspecies plays an important role in TPD performance, possibly by the formation of instantly interacting ensembles between the ad molecules. It was suggested that the interaction between adspecies is always favorable to the desorption of molecularly adsorbed species and it can either facilitate or delay the chemical reaction of adspecies depending on the electronic mechanism of the activation process on the active sites.

### INTRODUCTION

Heterogeneous catalysis is concerned with the reactivity of the adspecies attached or bonded on the coordinatively unsaturated sites (CUS) on the surface. As proposed by Mutttertities et al (ref. 1), cluster compound is of fundamental interest for the understanding of correlations between hetero- and homo-geneous catalysis in the aspect that the electronic configuration and hence, the catalytic performance of cluster compounds could be considered as the intermediate state for the "isolated" active centers in homogeneous catalysis on the one hand, and the multifunctional surface sites in heterogeneous catalysis on the other hand. Besides the difference in the complexity of active centers, the interaction between adspecies is one of influential factors affecting the dynamic behaviours of surface catalysis. Study of interaction effect between adspecies on the mechanism of surface reaction is, therefore, indispensable for communicating the basic information between hetero- and homo-geneous catalysis.

### EXPERIMENTAL

#### Materials

The catalysts used in this work were prepared by a conventional impregnating method. SiO<sub>2</sub> of 20-40 mesh size fraction was calcined at 873K for 4h before impregnation and its surface area was 323 m<sup>2</sup>/g (BET). A solution in the desired Pd/La atomic ratio was prepared by mixing PdCl<sub>2</sub> in 2N HCl with a solution of La(NO<sub>3</sub>)<sub>3</sub> 6H<sub>2</sub>O and was brought into contact with required amount of SiO<sub>2</sub>. The resulting mixture was held over at room temperature for 24h and then evaporated and dried over a steam bath. The sample was stored in a dessicator before use. The Pd dispersion was determined by H<sub>2</sub> chemisorption method (ref. 2). The results were given in Table 1.

Methanol-13C was obtained from Merck Frost Canada Inc. with the isotope enrichment of about 99.5%. A home-made reagent of D<sub>2</sub>O was used without further purification. The purity examined by mass spectrometer was better than 99.0 wt%.

Analytic grade methanol with the purity of 99.5 wt% was further treated with zeolite 5A to remove trace of water.

He gas of 99.99% purity was selected as carrier gas in TPD and/orTPDE experiment. It was passed through a cold trap before entering the reactor system.

H<sub>2</sub> and CO gases were purified by a conventional deoxidizing and dewatering system.

Table 1. The chemical composition and metal dispersion of Pd-catalysts

Sample	Composition wt %		Pretreatment	H <sub>2</sub> Chemisorption	
	Pd	La <sub>2</sub> O <sub>3</sub>		ml H <sub>2</sub> /g	H/Pd
Pd5S	4.8	--	Ar (873K)	0.1	0.02
			H <sub>2</sub> (673K)	1.8	0.34
Pd5La8S	5.2	8.2	Ar (873K)	0.1	0.01
			H <sub>2</sub> (673K)	1.3	0.24

TPD and TPDE of Methanol on SiO<sub>2</sub>-Supported Pd Catalysts

The setup for TPD/TPDE experiment is the same as mentioned in a previous work (ref. 3). The sample loading in the reactor was 100 mg. Two kinds of in situ treatments were imposed individually on the catalyst for each TPD/TPDE measurement.

## (1). Thermal treatment of the catalyst in He stream (He Treatment):

He stream with a flow rate of 56 SCC/min was passed through the evacuating reactor while the sample was heated at a heating rate of 16 K/min to 873K and kept at that temperature for 1h, then cooled down to room temperature in He stream.

(2). H<sub>2</sub>-Reduction:

H<sub>2</sub> stream with a flow rate of 56 SCC/min was passed through the reactor under vacuum and was heated up to 673K at a heating rate of 16 K/min and held for 0.5h, the system was then switched to He stream for 15 min and the sample was heated from 673K to 873K for 1h and was cooled down to room temperature in the He stream.

A microinjector was used for the adsorption of methanol and/or D<sub>2</sub>O in He carrier gas at room temperature. Each injection was 1  $\mu$ l and 4 injections of methanol were injected in a normal TPD/TPDE experiment. After adsorption, the catalyst was purged in He stream with the system continuously evacuated by a rotary pump for 10 min and then was TPD/TPDE performed.

The species desorbed from the surface were monitored by a multichannel mass spectrometer. The ultimate vacuum of the equipment was 1.0E-7 torr and the vacuum of the ionization chamber of the mass spectrometer was adjusted to 2.0E-6 torr during the experiment.

The same procedure as suggested by Ko (ref. 4) was used for treatment of the data recorded from mass spectrometer. At first, the area of each desorption spectrum was weighed to give, after correction, the area corresponding to the desorption and decomposition of methanol, then multiplied by the correction coefficient C<sub>i</sub>, to determine the mole percentage of each product. Such a procedure for data treatment, of course, only has its significance for the purpose of relative comparisons of the catalysts evaluated under the same experimental conditions.

## RESULTS AND DISCUSSION

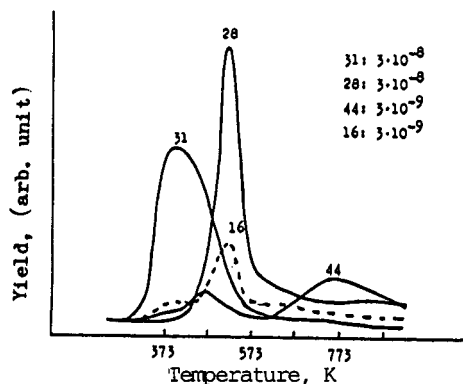
1. The TPD/TPDE bands of methanol on Pd-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts

Fig. 1a. Typical Thermal Spectra of Methanol on Pd<sub>5</sub>La<sub>8</sub>S(He) Catalyst.

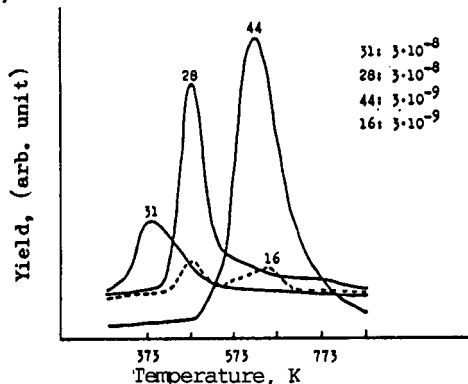


Fig. 1b. Typical Thermal Spectra of Methanol on Pd<sub>5</sub>La<sub>8</sub>S(H<sub>2</sub>) Catalyst.

Fig. 1a and 1b are typical examples of the TPD diagrams observed for methanol on the catalysts. It consists of a desorption band of molecular CH<sub>3</sub>OH in the temperature range of 373-393K, a decomposition band of CO at about (or above) 473K, and an additional small band of CO<sub>2</sub> at temperature of about (or above) 633K. The formation of CH<sub>4</sub> and H<sub>2</sub>CO has been detected in some case especially on the reduced catalysts. The amounts of both CH<sub>4</sub> and H<sub>2</sub>CO are much smaller than CO<sub>2</sub> and are not presented in Table 2. It is noted from Table 2 that the reduced catalysts are more active for methanol decomposition than the He treated catalysts. Since the La<sub>8</sub>S sample can appreciably adsorb methanol at room temperature, the adsorption amount on La-promoted catalysts is several times greater than that on the monometallic Pd-catalyst. On the other hand, it has been proved that La<sub>8</sub>S is itself inactive for CH<sub>3</sub>OH decomposition, therefore, it can be rationalized that Pd<sub>5</sub>La<sub>8</sub>S(H<sub>2</sub>) is less active than Pd<sub>5</sub>S(H<sub>2</sub>) of the same metal dispersion. However, the presence of La<sub>2</sub>O<sub>3</sub> is by no means simply to increase the molecular desorption band of the TPD spectra only. The molecular desorption of methanol on the Pd<sub>5</sub>La<sub>8</sub>S catalyst is increased to a far less extent than to account the increment gained in the total adsorption of methanol on the catalyst. This means that methanol molecules can migrate over the surface and can

Table 2. The molecular desorption and decomposition products of CH<sub>3</sub>OH-13C on supported Pd-catalysts

Catalyst	Adsorption Amount of CH <sub>3</sub> OH-13C	Product Distribution, mol%			
		CH <sub>3</sub> OH-13C (32)	CO-13C (29)	CO <sub>2</sub> -13C (45)	H <sub>2</sub> CO-13C (31)
SiO <sub>2</sub> (He)	373	100	--	--	--
Pd5S(He)	607	74	23	1	2
Pd5La8S(He)	2171	72	26	1	1
La8S(He)	1515	97	3	0	0
Pd5S(H <sub>2</sub> )	500	37	48	15	--
Pd5La8S(H <sub>2</sub> )	1496	54	37	6	4
La8S(H <sub>2</sub> )	1328	98	1	1	0

be activated by the Pd-sites so that in the presence of La-oxide, more methanol molecules are reacted on the Pd-sites. In other words, the surface migration of methanol molecules in the adlayer exerts certain effects on the kinetic behaviours of thermal spectra on supported catalyst.

The surface migration is, in certain cases, closely relevant to the rate process of heterogeneous catalysis and biocatalysis especially when the reaction mechanism involves the transference of and/or the mutual inter-

action between the intermediate species on different active sites. We are therefore interested in studying in more detail how the thermal spectra of methanol on supported Pd-catalysts are affected by the mutual interaction between adspecies caused by surface migration.

## 2. The influence of coadsorbed D<sub>2</sub>O

Tables 3 and 4 give the product distributions observed on Pd-catalysts(H<sub>2</sub>) in the presence of coadsorbed D<sub>2</sub>O. It can be seen that increasing the D<sub>2</sub>O injections decreases continuously the total amount of methanol retained on the catalyst, whereas the proportion of both CO and CO<sub>2</sub> in the TPD spectra increases simultaneously. It indicates that the injected D<sub>2</sub>O is able to partly remove from the surface the preadsorbed methanol in accordance with the bonding strengths of the adspecies. Since the molecularly adsorbed species are weakly bonded and are

Table 3. Influence of D<sub>2</sub>O coadsorption on the desorption and decomposition of CH<sub>3</sub>OH on Pd-catalysts

Catalyst	Injection sequence	Adsorption amount of CH <sub>3</sub> OH	Product distribution mol %			
			CH <sub>3</sub> OH (31)	CH <sub>3</sub> DO (33)	CO (28)	CO <sub>2</sub> (44)
Pd5S(H <sub>2</sub> )	CH <sub>3</sub> OH + D <sub>2</sub> O	366	10	9	49	33
Pd5La8S(H <sub>2</sub> )	"	1599	16	5	62	16

Table 4. Influence of D<sub>2</sub>O injection amounts on the desorption and decomposition of CH<sub>3</sub>OH on Pd5La8S(H<sub>2</sub>)

Injection of CH <sub>3</sub> OH $\mu$ l	D <sub>2</sub> O $\mu$ l	Adsorption amount of CH <sub>3</sub> OH	Product distribution mol%			
			CH <sub>3</sub> OH (31)	CH <sub>3</sub> DO (33)	CO (28)	CO <sub>2</sub> (44)
4	1	1556	28	3	52	16
4	2	1370	20	4	59	17
4	3	908	11	5	60	24
4	4	611	6	4	51	37

easily displaced by the D<sub>2</sub>O molecules, the desorption band of molecular methanol retained on the surface must be deducted to a greater extent in comparison with the decomposition bands of CO and CO<sub>2</sub>, both of which had resulted from the adspecies of greater bonding strengths. Moreover, the thermal spectra in Fig. 2 show that, with increasing amount of coadsorbed D<sub>2</sub>O, the CO band becomes gradually flattened toward high temperature side, which again implies that for the methanol adspecies in the same band, the minute difference in bonding strength also makes the weaker adspecies displaced out of the catalyst surface by coadsorbed D<sub>2</sub>O to a greater extent. Speaking alternatively, in regards to the effect of coadsorbed D<sub>2</sub>O, the main feature of TPD spectra of methanol could be explained on the basis of intrinsic heterogeneity of the catalyst surface, and the surface migration of the admolecules is not able to have any significant influences on the surface state of

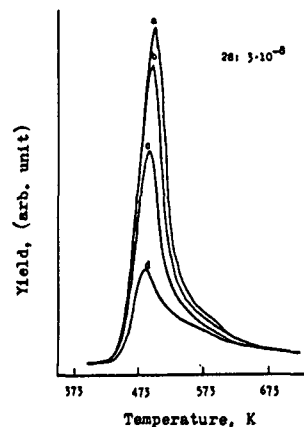


Fig. 2. The decomposition band of CH<sub>3</sub>OH on Pd5La8S(H<sub>2</sub>) in presence of D<sub>2</sub>O. The injected amount of D<sub>2</sub>O is: a), 1 l; b), 2 l; c), 4 l; and d), 8 l.

methanol adspecies other than the OH-OD exchange process on the surface.

### 3. The interaction between coadsorbed CH<sub>3</sub>OH-13C and CO

The apparent independence of the band feature for methanol in the presence of D<sub>2</sub>O and its seemingly conformity with the localized adsorption model of heterogeneous surface do not necessarily mean that the interaction between coadsorbed species is of trivial influence on the desorption and decomposition of methanol. Since the methanol molecules retained on the surface after D<sub>2</sub>O adsorption are attached on the Pd-sites with strong bonding strengths, they can very slightly be replaced by D<sub>2</sub>O adspecies of lower bonding strengths. For this thermodynamic reason, the feature of thermal spectra or the kinetics of desorption and decomposition of the methanol molecules retained on the surface can hardly be affected by coadsorbed D<sub>2</sub>O even if the interaction between coadsorbed species is not negligible at all. It is therefore worthwhile to study the TPD of CH<sub>3</sub>OH in the presence of coadsorbed CO with the understanding that if the interaction between CO adspecies can exert some decisive role in CO desorption, the desorption band of CO and the decomposition band of CH<sub>3</sub>OH-13C would interfere with each other.

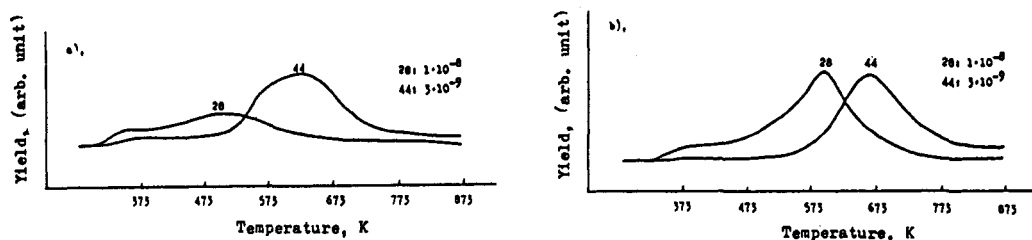


Fig. 3. The TPD diagram of CO on Pd5La8S(H<sub>2</sub>) catalyst

a). CO adsorbed at room temperature

b). CO adsorbed at 573K and cooled down to room temperature in CO stream

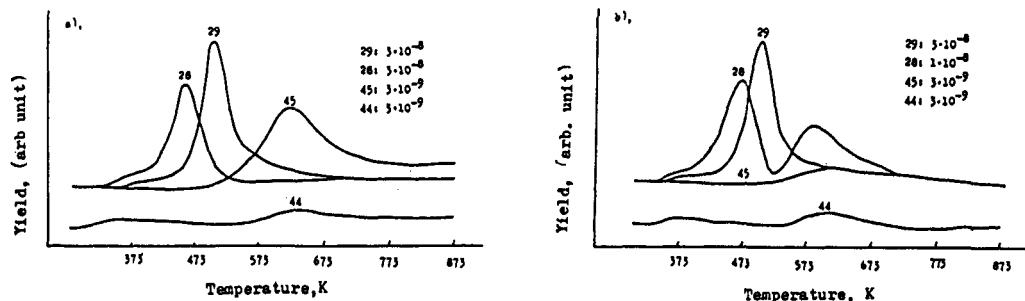


Fig. 4. The thermal desorption spectra of coadsorbed CO and CH<sub>3</sub>OH-13C on Pd5La8S(H<sub>2</sub>).

a). both CO and CH<sub>3</sub>OH adsorbed at room temperature, b). CO adsorbed at 573K cooled down to room temperature in CO stream and thereafter CH<sub>3</sub>OH adsorbed

Fig. 3 and Fig.4 are respectively the TPD diagrams observed for CO and CO + CH<sub>3</sub>OH on Pd5La8S(H<sub>2</sub>) catalyst. It is found that in the presence of CH<sub>3</sub>OH-13C, the desorption peak temperature of CO decreases markedly. Besides, the low temperature side branch of CO decomposition band of methanol is somewhat steepened, but the peak temperature is almost unchanged. The lowering of CO desorption temperature demonstrates evidently that CO desorption is greatly facilitated on the coadsorbed surface. Moreover, when the amount of coadsorbed CO is increased by raising the temperature for CO preadsorption (see Fig. 3b) and 4b)), the major part of preadsorbed CO desorbs again at lower temperature but a certain portion of strongly bonded CO still desorbs at the same temperature as in the case with CO adsorbed only. These results imply that, the lowering of desorption temperature for CO is due to its interaction with the CO-13C species formed during methanol decomposition rather than with methanol itself. The reason is in that on the supported catalyst, methanol is weakly bonded in comparison with preadsorbed CO, as inferred from the increased percentage of molecular desorption in the product distribution of methanol on the coadsorbed surface (compare Tables 5, 6 and Table 2). As illustrated in the case of coadsorbed D<sub>2</sub>O mentioned above, the weak-bonding species would

Table 5. CO and CH<sub>3</sub>OH-13C coadsorption on Pd5S(H<sub>2</sub>)

Adsorption	Product distribution mol%				
	CH <sub>3</sub> OH-13C (33)	CO-13C (29)	CO <sub>2</sub> -13C (45)	CO (28)	CO <sub>2</sub> (44)
1). CO (room temp.)	--	--	--	34	66
2). CO (573K)	--	--	--	80	20
3). 1) + CH <sub>3</sub> OH	69	18	13	59	41
4). 2) + CH <sub>3</sub> OH	69	24	7	84	16

be less able to displace or compete with the adspecies for the Pd-sites of great bonding strengths. On the other hand, since CO and CO-13C are indistinguishable for the Pd-sites and their intermingling over all Pd-sites would be quite facile provided that the surface bond of CO moiety can be appreciably weakened by the mutual repulsion between CO adspecies interacted within the coordination sphere of individual Pd-sites. Following this line of reasoning, the more the amount of CO being coadsorbed on the surface, the less the proportion of its desorption would be facilitated by CO-13C species produced from the coadsorbed methanol on the same surface. The experiment results are in good consistency with the prediction.

Table 6. CO and CH<sub>3</sub>OH-13C coadsorption on Pd5La8S(H<sub>2</sub>)

Adsorption	Product distribution mol%				
	CH <sub>3</sub> OH-13C (33)	CO-13C (29)	CO <sub>2</sub> -13C (45)	CO (28)	CO <sub>2</sub> (44)
1).CO(room temp.)	--	--	--	52	48
2).CO (573K)	--	--	--	73	27
3). 1) + CH <sub>3</sub> OH	68	28	5	86	14
4). 2) + CH <sub>3</sub> OH	71	28	1	94	6

The remaining question is concerning the mechanism of "assisted" CO desorption. The desorption of CO on metals has been elaborated by many authors (ref. 5). The desorption rate is usually expressed as the rate of unimolecular reaction by Polanyi-Wagner equation:

$$v = k \times N \times \exp(-E/RT)$$

and the effect of interaction between adspecies are often studied by investigating the functional relation between desorption energy  $E$  and surface  $N$ . In the present case, although the coadsorbed surface is covered with a total amount of CO several times greater than the methanol-free surface, it is very improbable, however, that the increased static interaction between CO adspecies would cause a lowering of desorption peak temperature as much as 100K because the Pd-sites in the surface, either in the presence or absence of coadsorption, are highly covered with CO molecules. In other words, for the present situation for supported catalysts, the carrier surface must perform certain role in facilitating the desorption of CO on Pd-sites, as the profound enhancement of desorption rate of CO is obviously related with the decomposition of the methanol molecules transferred from the carrier sites to Pd-sites. We therefore postulate the existence of ensemble state in the course of surface migration (ref. 6), which behaves as the precursory state for the desorption of mutually interacted CO adspecies with enhanced desorption rate.

#### 4. The enhancement of desorption rate of CO on Pd-sites

For a qualitative description of the ensemble concept, the thermal decomposition of Ru<sub>3</sub>(CO)<sub>12</sub> on alumina shown in Fig. 5 (ref.7) is purposely selected to simulate the CO desorption on metal sites. It clearly demonstrates how the multiplicity ( $x$ ) of the CO ensembles markedly affects the peak temperature of desorption, if the stepwise decomposition of supported Ru<sub>3</sub>(CO)<sub>12</sub> might be considered as being kinetically equivalent to the desorption behaviours of CO in various ensemble states. The profound lowering of the peak temperature of desorption on coadsorbed surface could thus be explained as the results of increasing participation of dynamic ensemble mechanism in the desorption of CO at high surface coverage. If this is true, the desorption of CO on metal should be not strictly unimolecular and the kinetics should be expressed instead by the general equation:

$$V = K \times N^x \times \exp(-E/RT) \text{ with } E \text{ and } x \text{ varied with } T \text{ and } N.$$

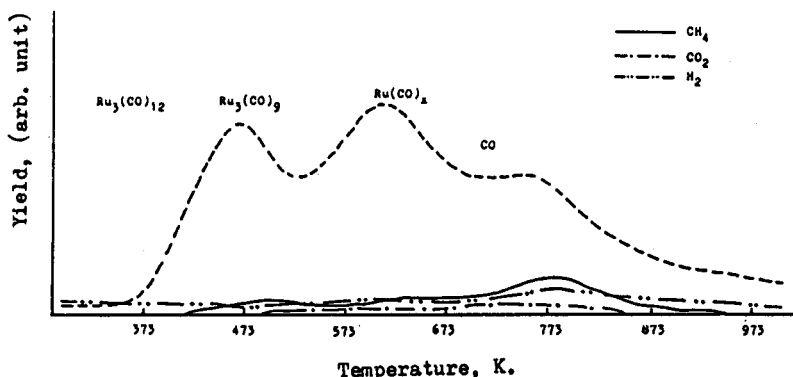


Fig. 5. Thermal decomposition profile of Ru<sub>3</sub>(CO)<sub>12</sub> on Al<sub>2</sub>O<sub>3</sub>; Al<sub>2</sub>O<sub>3</sub> support was precalcined at 1173K for 1h.

As referred elsewhere (ref. 8), it has been shown that the rate of desorption observed for CO/Pd(100) over a wide range of  $T$  and  $N$  under UHV (ultrahigh vacuum) condition (ref. 9 and see also Fig. 6) could be successfully fitted with the following equation:

$$v = b \times \exp(-(E - r \times \ln(V-))/RT) \times N^\alpha$$

$$\text{or } (1 - r/RT) \times \ln(V-) = \ln b - E/RT + \alpha \ln N$$

For a given value of  $V-$ , the rate plotted as  $\ln N$  against  $1/T$  conforms with two straight lines instead of a single line. The adequate values of  $\alpha$ ,  $b$ ,  $E$  and  $r$  parameters are given in Table 7. The high value of kinetic order  $\alpha$  for the low temperature section and/or the low value of  $\alpha$  for the high temperature section implies that the participation of ensemble mechanism in desorption inclines to increase with decreasing temperature. Moreover, if the desorption is supposed to take place at constant temperature  $T_2$ , then the dotted line in Fig.7 demonstrates that, as the surface coverage is increased, the kinetic order  $\alpha$  tends to increase with the increasing desorption rate, again implying the increasing population of CO ensembles with surface coverage.

Table 7. Parametric values of  $\alpha$ ,  $b$  and  $r$

V	high temp.		low temp.	
	$E1/\alpha_1$	$\frac{1}{\alpha_1} \ln(v/b1)$	$E2/\alpha_2$	$\frac{1}{\alpha_2} \ln(V/b2)$
5.0E+10	12.58	15.35	7.24	21.68
1.0E+11	12.40	15.79	7.21	21.96
7.0E+11	11.90	17.03	7.11	22.71
1.3E+12	11.73	17.44	7.08	22.94
1.0E+13	11.21	18.74	6.98	23.73
5.0E+13	10.79	19.78	6.91	24.34

$$1 = 1.56, b1 = 2.04, E1 = 29.6 - 0.406 \ln V;$$

$$2 = 2.60, b2 = 1.67E-14, E2 = 22.0 - 0.128 \ln V$$

As a typical example illustrating the enhancement of desorption by interaction between adspecies, it is worth mentioning briefly the "Adsorption-Assisted-Desorption" (AAD) concept reported by Tamaru's group (ref. 10) who first discovered that the absolute rate of desorption of labelled CO/Pd(100) under a pressure of ambient CO molecules is greater than that observed under UHV condition. Since the kinetic order  $\alpha$  of desorption of CO/Pd is of nonintegral value greater than 1, the absolute rate of desorption of the labelled CO, unlike the rate of unimolecular reaction, should be dependent on the multiplicity of ensemble state. The increasing trend of intrinsic rate obtained for desorption of labelled CO under a partial pressure of ambient CO molecules is thus quite understandable. The dynamic ensemble concept mentioned above, therefore provides a possible mechanistic basis in support of the AAD effect, i.e. the "isotope-switch" method used by Tamaru's group makes it possible to obtain the desorption rate of labelled CO molecules in the surface, but the increasing trend of surface coverage  $N$  in parallel with the adsorption of ambient CO molecules will, at the same time, enhance instantly the desorption rate of interacted CO molecules and, in accordance with the power rate law, the desorption of labelled CO molecules is eventually assisted.

Finally, it should be mentioned that the thermal desorption spectra on reduced catalysts exhibit a small but significant band of CO<sub>2</sub>. A slight formation of CH<sub>4</sub> is also observed at the same temperature of about 623K. The formation of CO<sub>2</sub> can be attributed as due to Boudouard reaction (ref. 11). However, it is rather surprising that on the coadsorbed surface, both bands of CO<sub>2</sub>-13C and CO<sub>2</sub> are decreased when the temperature of CO-pre-adsorption is increased. Recalling that in the presence of D<sub>2</sub>O, the decomposition spectra exhibit a similar CO<sub>2</sub> band, it seems that the CO<sub>2</sub> formation is of different origins of surface reactions. It may probably relate to several interconnected reactions, as inferred from the decomposition of Ru<sub>3</sub>(CO)<sub>12</sub>/Al<sub>2</sub>O<sub>3</sub> which also gives small amounts of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>, with the

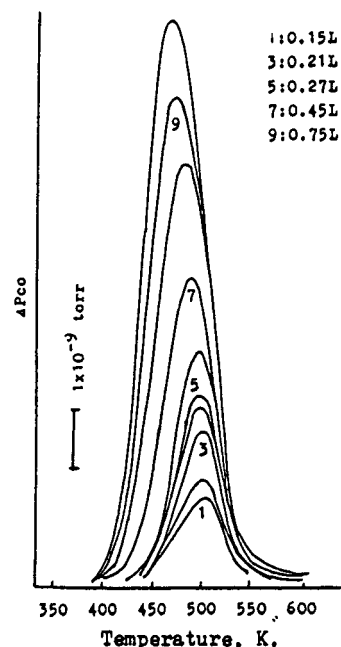


Fig. 6. Variation of TPD profiles with surface coverage for CO/Pd(100) under UHV condition

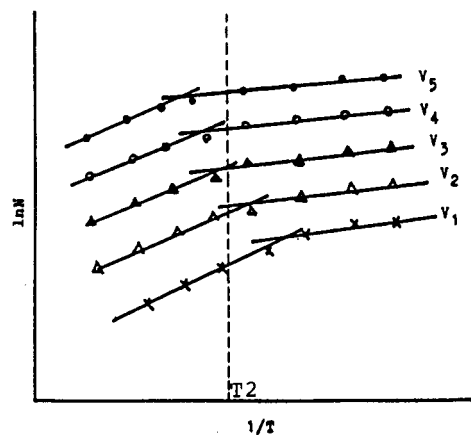


Fig. 7.  $\ln N$  vs  $1/T$  plot for desorption of CO/Pd(100) at constant desorption rates ( in moles/cm<sup>2</sup> )  
 $V_1 = 1.0E+11$ ,  $V_2 = 7.0E+11$ ,  
 $V_3 = 1.3E+12$ ,  $V_4 = 1.0E+13$ ,  
 $V_5 = 5.0E+13$ .

band areas varied sensibly with the residual content of water in alumina. Since the CO<sub>2</sub> band is much smaller than (less than one tenth of) the CO band, it can hardly affect the essential nature of interaction discussed above. We therefore just mention the results of CO<sub>2</sub> formation and will leave it without any discussion on the mechanism details.

### 5. The thermal desorption spectra of isotope methanols on Pd-catalysts

Thermal desorption spectra of coadsorbed CH<sub>3</sub>OH-13C and CH<sub>3</sub>OH-12C are studied for further investigation of the interaction effects between methanol ( and CO ) adspecies. The results are shown in Table 8. Because of their chemical identity, the isotope methanols are of equal bond-

Table 8. CH<sub>3</sub>OH-13C and CH<sub>3</sub>OH coadsorption on Pd-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts

Catalyst	Injection sequence	CH <sub>3</sub> OH(1)	CO(1)	Product distribution mol%				
				R(1)	CH <sub>3</sub> OH(2)	CO(2)	R(2)	R(3)
Pd5S(H <sub>2</sub> )	A: CH <sub>3</sub> OH-13C(1)+CH <sub>3</sub> OH(2)	29	71	0.41	50	50	1.0	0.68
	B: CH <sub>3</sub> OH(1)+CH <sub>3</sub> OH-13C(2)	17	83	0.20	62	38	1.63	0.65
Pd5La4S(H <sub>2</sub> )	A	56	44	1.27	54	46	1.17	1.21
	B	31	69	0.45	36	64	0.56	4.96
Pd5La8S(H <sub>2</sub> )	A	54	46	1.18	55	45	1.23	1.21
	B	47	53	0.89	64	36	1.78	1.28
Pd5La40S(H <sub>2</sub> )	A	76	24	3.17	70	30	2.35	2.74
	B	63	37	1.70	79	21	3.76	2.66
Pd5S(He)	A	62	38	1.64	79	21	3.76	2.60
	B	41	59	0.70	66	14	6.14	2.60
Pd5La4S(He)	A	68	32	2.13	89	31	2.23	2.18
	B	58	42	1.38	76	24	3.17	2.25
Pd5La8S(He)	A	72	28	2.59	68	32	2.13	2.38
	B	63	37	1.70	80	20	4.00	2.64
Pd5La40S(He)	A	69	31	2.23	54	46	1.17	1.65
	B	63	37	1.70	67	33	2.04	1.77

(1) and (2) represent the injection sequence of isotope methanols in the experiments  
 R(1), the ratio of CH<sub>3</sub>OH(1)/CO(1); R(2), the ratio of CH<sub>3</sub>OH(2)/CO(2);  
 R(3), the mol ratio of total methanol and total carbon monoxide in the product

ding strength with the same adsorption site. For a heterogeneous catalyst surface, the first injections of methanol are more adsorbed on the strong bonding sites and the successive injections would thereafter populate the methanol molecules over the weak-bonding sites. The sequential order of isotope injections should be reversed in the thermal desorption spectra of coadsorbed methanols. This sequence effect would be unchanged and reproducible if the ad-/de-sorption and decomposition on the surface were completely localized. It is interesting that for the highly covered catalyst surface in this work, the observed sequence effect for isotope methanols not only changes with catalysts but also differs from experiment series A to experiment series B. On the other hand, it is noted, however, that the total bands for molecular desorptions and decompositions are invariant and are quite reproducible for both experiment series. It seems obvious that methanol molecules are mutually removed from and mutually displaced on the catalyst surface rather easily and randomly during ad-/de-sorption. In other words, at high surface coverage of adspecies, the heterogeneity of supported catalysts becomes apparently homogenized in regards of the kinetic characteristics of desorption and decomposition for methanol on the surface. This apparent homogeneity obviously resulted from the fast exchange for surface sites occurred in the adlayer when the adsorbed molecules are migrating and interacting instantly within the coordination sphere of individual sites. The easy intermingling of the thermal spectra of isotope methanols thus lends us further support for the rationality of the ensemble concept on its close resemblance with the picture of exchange reactions frequently encountered in homogeneous catalysis.

### CONCLUSION

The TPD/TPDE spectra which recorded the low-temperature molecular desorption and high-temperature chemical reactions of methanol on Pd-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts have been studied. The effects of interaction with coadsorbed D<sub>2</sub>O, CO, and CH<sub>3</sub>OH-13C on the product distribution of methanol, CO and CO<sub>2</sub> in the TPD-diagrams have been examined. It was found that with the co-adsorption of D<sub>2</sub>O, the methanol molecules were displaced off from the weak-bonding surface-sites. Consequently, the relative proportion of decomposition products of CO and CO<sub>2</sub> in the TPD diagram of methanol were increased. On the other hand, in the presence of coadsorbed CO which was strongly bonded on the Pd-sites, greater proportion of molecular desorption of me-

methanol was observed. It was interesting that the desorption of CO was found to be greatly facilitated on the methanol-coadsorbed supported Pd-catalysts and a lowering of peak temperature for CO-desorption as great as 100K had been observed. This observation was very similar to the "Adsorption-Assisted-Desorption" phenomena for CO adsorbed on metals originally reported by Tamaru's group. The TPD spectra for coadsorbed isotope methanols revealed that the methanol molecules are mutually easily and randomly displaced on the catalyst surface during the course of thermal desorption process.

An ensemble concept has been postulated to account for the dynamic effect of interaction between coadsorbed species on the thermal spectra of methanol on supported Pd-catalysts. The rationality of the ensemble concept is described with its success in explaining the "Adsorption-Assisted-Desorption" and/or the "Reaction-Assisted-Desorption" effects reported by Tamaru's group and substantiated in present work as well. As a concluding remark, we tend to suggest that as pointed out in the text, the kinetic effect of ensemble states is in close resemblance with the ligand effects of active centers in homogeneous catalysis and the ensemble concept would be of some advantage for correlating our knowledge in heterogeneous and homogeneous catalysis.

### Acknowledgement

The authors are indebted to Prof. K. Tamaru for his helpful comments and discussions. The financial support of National Science Foundation is gratefully acknowledged.

### REFERENCES

1. E. L. Muttart, T. N. Rhodin et al., *Chemical Review* **79**, 91 (1979).
2. Y. Zhang et al., *J. Catal. (China)*, **1**, 299 (1980).1
3. K. Zhu, Y. Xu, J. Huang, Z. Lin and X. Guo, *The Natn'l Sym. on Stable Isotope Cpd's Chem. and Their Application (proceedings in Chinese)*, Shanghai, China (1986).
4. E. I. Ko, T. B. Benziger and R. J. Madix, *J. Catal.*, **62**, 264 (1980).
5. D. A. King, *surf. Sci.*, **93**, 431 (1980).
6. X. Guo and R. Zhai, *2nd China-Japan-U.S. Symposium on Catalysis, C-12*, Berkeley, California, U.S.A. (1985).
7. J. Wei, Y. Yang, X. Guo et al., *2nd Natn'l Sym. on Catalysis, F-12 (in Chinese)*, Shanghai, China (1986).
8. R. Zhai and X. Guo, *1st Natn'l Sym. on Chemical Kinetics, Paper No. 214*, (in Chinese), Heifei, China (1986).
9. K. Tamaru and T. Yamada, *CATALYSIS (Japan)*, **27**, 350 (1985).
10. T. Yamada, T. Onishi and K. Tamaru, *Surf. Sci.*, **133**, 533 (1983); T. Yamada and K. Tamaru, *Surf. Sci.*, **138**, 1155 (1984).
11. P. R. Wentreck, B. J. Wood and H. Wise, *J. Catal.*, **43**, 363 (1976).