

# A Set of Bases to Measure Drago-Wayland Parameters of Acid Sites on Solid Surfaces with Temperature Programmed Desorption

Shin Jung Kim and Chong Soo Han\*

Department of Chemistry, Chonnam National University, Kwangju 500-757. Received May 26, 1989

One kind of catalytic active center on solid surface is Lewis acid-base site or acceptor-donor site.<sup>1</sup> When a donor or acceptor atom in a molecule interacts with the acid or base site respectively, the molecule takes a rearrangement of electron density and the rearrangement induces a variation of interatomic distances in the molecule.<sup>2</sup> Thus the strength of the interaction may be related to the degree of catalytic activation of the adsorbate.<sup>3</sup> A quantitative approach on the strength of the Lewis acid-base bond is Drago-Wayland relation<sup>4</sup> and an application of the relation to surface sites may present a systematic understanding of the acid-base catalysis. A study is undertaken to measure Drago-Wayland  $E-C$  parameters of acid-base sites from TPD profile since it can be easily obtained with a conventional catalyst testing system and the most experimental results on the strength of acid or base sites have been described with TPD profiles of adsorbed bases or acids. We propose a suitable base set to measure the  $E-C$  parameters of acid sites with TPD.

Aluminas<sup>5</sup> were used as the media to elucidate the base set. We started the parameter measuring process with six bases, pyridine ( $C_5H_5N$ , N-donor, cyclic), triethylamine ( $N,N$ -diethylethanamine:  $(C_2H_5)_3N$ , N-donor, non-cyclic), 1,4-dioxane ( $C_4H_8O_2$ , O-donor, cyclic), 2-propanone ( $CH_3COCH_3$ , O-donor, noncyclic), tetrahydrothiophene ( $C_4H_8S$ , S-donor, cyclic), and thiobismethane ( $(CH_3)_2S$ , S-donor, noncyclic). TPD spectra were obtained with a gas chromatographic detector after adsorption of  $5 \times 10^{-6}$  mole bases on 0.5 g sample pretreated at 823 K for 1 hr.<sup>6</sup> The temperature programming rate was 4-8 K/min and the samples were heated up to 823 K under He flow, 30 ml/min. Thermodynamically, the heat of desorption,  $\Delta Hd$ , corresponding to the dissociation enthalpy of Drago-Wayland relation,  $-\Delta H$ , can be expressed as  $\Delta Hd = Ed - Ea + RT$  where  $Ed$  or  $Ea$  is activation energy of desorption of adsorption, respectively. Since  $Ed$  is available from TPD profiles,  $E-C$  parameters of acid site  $s$ ,  $(C_A)_s$  and  $(E_A)_s$  can be estimated with the model equation

$$(Ed)_{i,s} = (E_B)_i \times (E_A)_s + (C_B)_i \times (C_A)_s + \epsilon_{i,s}$$

where  $(C_B)_i$ ,  $(Ed)_{i,s}$  or  $\epsilon_{i,s}$  is  $C$  parameter of the base, the activation energy of desorption or a pooled error in the  $j$ -th experiment with base  $i$  adsorbed on acid site  $s$ , respectively. The activation energy of desorption  $Ed$  was calculated from the equation of the first order desorption process<sup>7</sup> with frequency factor of  $10^{13}/\text{sec}$  ( $kT/h$  at 480 K). It was assumed that the readsorption and the diffusion of the bases were not important during the desorption.

Figure 1-a shows TPD spectra of bases on the alumina. The number of distinct peaks with the activation energy of desorption of 20-50 kcal/mole is different depending on the bases<sup>8</sup> and it may support that the strength of acid sites can be represented with a dual or multi-scale parameter rather

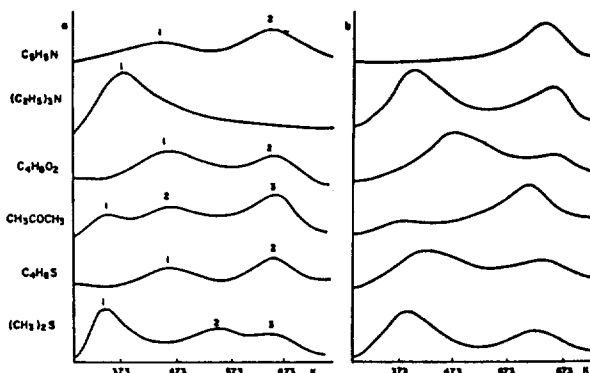
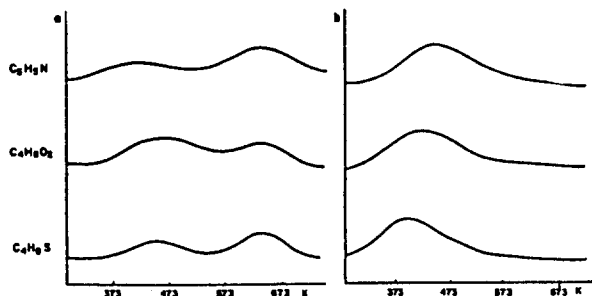


Figure 1. TPD profiles of the bases on  $\gamma$ -alumina(a) and  $\gamma$ -alumina modified with 5 wt% Cl(b). Temperature programming rate was 8 K/min and adsorbed amount of the bases were about  $5 \times 10^{-6}$  mole/0.5 g sample.

Table 1. The variation of  $E-C$  Parameters Based on TPD and the Coefficient of Determination for Typical Acid Sites on  $\gamma$ -alumina Depending on Sets of Adsorbing Bases

Site	All	Cyclic	Noncyclic	N-donor	O-donor	S-donor
111112	$E$ 18.03	18.97	13.83	27.17	100.62	330.53
	$C$ 2.07	2.53	2.11	-0.06	-32.21	-10.40
	$R^2$ 0.90	0.97	0.86	1.00	1.00	1.00
111222	$E$ 18.25	11.19	24.19	27.17	-21.19	-447.42
	$C$ 2.56	4.57	1.34	-0.06	23.58	25.06
	$R^2$ 0.85	0.94	0.84	1.00	1.00	1.00
212111	$E$ 28.75	31.57	18.03	51.14	238.25	-193.76
	$C$ 1.18	2.13	1.34	-2.20	-90.68	12.16
	$R^2$ 0.92	0.99	0.93	1.00	1.00	1.00
212223	$E$ 25.34	23.79	20.68	51.14	116.44	-8.91
	$C$ 2.48	4.18	1.98	-2.20	-34.90	6.19
	$R^2$ 0.86	0.97	0.78	1.00	1.00	1.00
212321	$E$ 33.64	23.79	41.64	51.14	-39.25	-970.94
	$C$ 1.30	4.18	-0.41	-2.20	36.41	47.59
	$R^2$ 0.88	0.97	0.90	1.00	1.00	1.00

than a monoscale one. To resolve the acid sites, it is necessary to correlate the TPD peaks of bases. The number of possible acid sites of the alumina is the product of the numbers of peaks in the TPD spectra, i.e., 72. It is well understood that a modification of surface with ions or additives results in a deactivation or a change of chemical characteristics of active site(s). Figure 1-b. shows TPD spectra of the bases on the alumina modified with 5 wt % chlorine. Tracing the TPD peaks during the modification, one can resolve 18 sites, 111112, 111122, 111212, 111222, 111312, 111322, 212111, 212113, 212121, 212123, 212211,



**Figure 2.** TPD profiles of the bases on  $\gamma$ -alumina(a) and  $\gamma$ -alumina modified with 5 wt% F(b). Temperature programming rate was 8 K/min and adsorbed amount of the bases were about  $5 \times 10^{-6}$  mole/0.5 g sample.

212213, 212221, 212223, 212311, 212313, 212321, and 212323, where site 111112 represents the site corresponding to peak 1 of pyridine, peak 1 of triethylamine, peak 1 of 1,4-dioxane, peak 1 of 2-propanone, peak 1 of tetrahydrothiophene, and peak 2 of thiobismethane. The values of the parameters, and the coefficient of determination  $R^2$  ( $R^2 = SSR/SST$ ) with respect to the groups of bases for typical sites are listed in Table 1.

In some cases, the estimated parameters are negative or  $R^2$ 's are much less than 1. The results can be explained as the peaks are mismatched or the encountering bases are not suitable for the model equation. We found that the set of cyclic bases showed reasonable values for the parameters and a good statistical reliability. It is also expected that the cyclic bases show an excellent measuring power for the parameters since they have the similar structure, different donor atoms and a wide range of the values of the parameters, *i.e.*, pyridine ( $C/E = 6.40/1.17$ ), 1,4-dioxane ( $C/E = 2.38/1.09$ ) and tetrahydrothiophene ( $C/E = 7.90/0.341$ ). Comparing TPD peaks of the bases adsorbed on the alumina and alumina modified with ammonium fluoride (Figure 2), it can be concluded that the alumina has two acid sites corresponding to the  $E-C$  parameters, 19.0, 2.5 (Site  $1 \times 1 \times 1 \times$ ); 23.8, 4.2 (Site  $2 \times 2 \times 2 \times$ ) with standard errors, 3.5, 0.6; 4.5, 0.7, respectively.

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Foundation.

## References

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3. A good catalyst is thought to be able to form chemical bonds of appropriate strength with reactant(s). W. M. H. Sachtler and J. Fahrenfort, J. Actes du Deuxieme Congres International de Catalyse, p. 831, 1960.
4. By the relation, enthalpies of adduct formation,  $\Delta H$ , have been described in the form,  $-\Delta H = E_A E_B + C_A C_B$  where  $E_A$  and  $E_B$  crudely relate to tendencies of acids and bases, respectively, to undergo electrostatic bonding and  $C_A$  and  $C_B$  are similar tendencies to undergo covalent bonding. R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).
5.  $\gamma$ -Alumina was obtained from  $Al(NO_3)_3 \cdot 9 H_2O$  (Aldrich, 99.9999%) and calcined at 873 K. Its surface area was 50  $m^2/g$ .  $\gamma$ -Alumina modified with chlorine or fluorine was prepared by treatment the alumina with  $NH_4Cl$  or  $NH_4F$  solution and calcination at 873 K.
6. In fact, the peak position of TPD profiles may depend on the adsorbed amount of bases and the experiment was performed with small amounts of adsorbed bases where the peak temperatures do not change with a further reduction of the amount of adsorbed bases.
7. P. A. Redhead, *Vacuum* **12**, 203 (1962). R. J. Cvetanovic and Y. Amenomiya, *Advan. Catal.* **17**, 103 (1967).
8. The activation energy of desorption for a chemisorbed state is generally greater than 20 kcal/mole. J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", p. 15, Academic Press, New York/London, 1967. 50 kcal/mole is the maximum activation energy of desorption which can be measured in the system since  $\gamma$ -alumina transforms to  $\alpha$ -alumina from 873 K. The desorbed gas was checked with a coupled FTIR during the desorption and the decomposition was negligible below 720 K for the aluminas.

## C-H Bond Activation and the Hydride-Mediated Ring-Cleavage of Methylene-cyclopropane by Rh(I)

Chul-Ho Jun\* and Yeong-Gweon Lim

Agency for Defense Development, P.O.Box 35, Daejeon 300-600. Received June 1, 1989

The activation of C-H bond<sup>1</sup> and C-C bond<sup>2</sup> by transition metal complexes has been one of the recent interests in organometallic chemistry. The C-H bond of aromatic aldehyde can be activated by transition metals to give cyclometallated complexes without producing any decarbonylated product<sup>3</sup>.

This C-H bond activation was applied to the synthesis of  $\beta, \gamma$ -unsaturated ketones through the  $\eta^1$ - or  $\eta^3$ -allylrhodium (III) complexes<sup>4</sup>. Recently we have studied the metal-hydride mediated C-C bond cleavage of the medium-strained ring compound having cyclobutyl group<sup>5</sup>. Although it is