© 1997 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, ***70***, *1545—1549 (1997)*

The Surface Heterogeneity of Supported Platinum Catalysts as Studied by the Interrupted Temperature-Programmed Desorption of Carbon Monoxide

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(Received January 13, 1997)

The interrupted temperature-programmed desorption of carbon monoxide was used to characterize the surface heterogeneity of supported platinum catalysts. The surface of platinum particles is divided into two different groups of desorption sites. For one group, the surface diffusion of carbon monoxide takes place easily, and it desorbs at low temperatures. For the other, the desorption of carbon monoxide requires higher temperatures, and surface diffusion does not occur. For the latter group, the distribution of the activation energy of desorption is determined by a method that the authors have recently developed (*Appl. Surf. Sci.*, **89**, 11 (1995)).

Temperature-programmed desorption (TPD) techniques have often been used to characterize the surface of catalysts and adsorbents.[1—5] The surfaces of industrial catalysts are mostly heterogeneous in that they have a number of different sites, indicating different activities in adsorption, desorption, and catalysis. The TPD spectrum represents the distribution of those different active sites. In other words, it is an expression of the surface heterogeneity. However, since the TPD spectrum depends on the operating variables, e.g., the heating schedule of the TPD measurement, it is not easy to correlate it with the catalytic activity. The surface heterogeneity is important for understanding structure-sensitive reactions over industrial catalysts.[6]

We recently developed a method by which the distribution of the activation energy of desorption can be determined from the TPD spectrum.[7] Since the activation-energy distribution does not depend on the TPD operating conditions, it is a better representation of the surface heterogeneity compared with the TPD spectrum, itself. This method was applied to supported nickel and platinum catalysts using hydrogen as a probe adsorbate. We studied the influence of the preparation variables on the state of heterogeneous surfaces of these catalysts and the phenomena of spillover and reverse spillover for platinum catalysts.[7,8]

In the present work, carbon monoxide was used as a probe adsorbate; the method has been further applied to supported platinum catalysts. It was expected that different probe species would give different results concerning the activation-energy distribution for a catalyst sample, and that this would provide more helpful information about its heterogeneous surface. It is an interesting result that the sites of desorption of carbon monoxide are divided into two groups: For one, it desorbs at low temperatures, and its surface diffusion is easy; for the other, it desorbs at higher temperatures, and surface diffusion does not take place. The activation-energy distribution can be determined for the latter group of desorption sites. The influence of platinum loading was examined, and the activation-energy distribution obtained was compared to that determined previously with hydrogen.[8]

Experimental

Sample Preparation. Wet impregnation was used to prepare supported platinum catalysts in a similar manner as used previously.[9] A porous silica gel, Silbead-N from Mizusawa Industrial Chemicals, Ltd., was ground to 32—60 mesh size and calcined in air at 700 °C for 3 h. The BET surface area was 400 $\mathrm{m^2\,g^{-1}}$. The silica powder was immersed in an aqueous solution of chloroplatinic acid and the solvent was evaporated at 50 °C under reduced pressure. The obtained sample was vacuum dried at 110 °C for 2 h and reduced by flowing hydrogen at 400 °C for 10 h. The platinum loading was 2.5 and 5.0% by weight.

TPD Measurements. Carbon monoxide was adsorbed by passing through a catalyst sample of about 50 mg in a quartz-tube reactor at 30 °C for 10 min. The amount of carbon monoxide adsorbed under these conditions was nearly equal to the saturated value at 30 °C, as confirmed by preliminary experiments with the changing adsorption time. After adsorption, helium was passed at 30 $\mathrm{ml\,min^{-1}}$ through the sample until the response of a thermal conductivity detector (TCD) became stable. For this, it took about 30 min. The sample was then heated at 30 $\mathrm{K\,min^{-1}}$ to collect the TPD spectrum. For interrupted TPD, the sample was first heated in the same fashion up to a certain temperature (T_0); this temperature was maintained until the TCD response decreased to a level of less than 5% of the maximum observed in the first TPD. T_0 is called the interrupted temperature in the following. The sample was then cooled to 30 °C at about 50 $\mathrm{K\,min^{-1}}$ (not controlled), and was again heated in order to measure the interrupted TPD spectrum. The apparatus and procedures used have been described in more detail in previous papers.[7,10]

To confirm that desorption is the rate-determining step and free from the influence of readsorption, pore diffusion, and equilibrium desorption, it is required to arrange the experimental conditions. These were arranged from preliminary TPD measurements by changing the quantity and size of the sample, the rate of the carrier-gas flow, and the rate of heating. The obtained results were described in a previous paper,[7] and the present TPD measurements were conducted in the range of such arranged conditions.

A Proposed Method. The authors previously proposed a method for analyzing the interrupted TPD spectra and determining the distribution of the activation energy of desorption.[7] It is assumed that the surface of the supported metal particles comprises different groups of desorption sites with an identical activation energy for the sites of each group, and that the overall TPD spectrum is given by a linear combination of the contribution from each group. Such a group can be sampled by interrupted TPD.

For a given set of two interrupted TPD spectra with a small difference in T_0, the differential spectrum between them is assumed to come from a certain group of desorption sites with an approximately identical activation energy. The desorption kinetic parameters are determined for such a differential spectrum using the following rate expression,

$$-\,\mathrm{d}\theta/\mathrm{d}T = (\nu_0/\beta)\exp(-E_\mathrm{d}/RT)\theta^n, \qquad (1)$$

provided that the desorption is the rate-determining step. Here, θ denotes the coverage of the surface occupied by the adsorbate, T the desorption temperature, E_d the activation energy, ν_0 the pre-exponential factor, β the heating rate, R the gas constant, and n the order of desorption. E_d and ν_0 are assumed to be coverage-independent. Strictly speaking, these two parameters may be a function of θ; however, knowledge concerning the dependence of E_d and ν_0 on θ is not sufficient at present.[11,12]

Equation 1 is rewritten as follows:

$$\ln((-\mathrm{d}\theta/\mathrm{d}T)/\theta^n) = (-E_\mathrm{d}/R)(1/T) + \ln(\nu_0/\beta). \qquad (2)$$

Using a given value of n, $\ln((-\mathrm{d}\theta/\mathrm{d}T)/\theta^n)$ is plotted against $1/T$; when this plot is a straight line, it gives the values of E_d and ν_0 from the slope and the intercept, respectively.

The above analysis is performed for several differential spectra. When kinetic parameters are known for any E_d's, the overall TPD spectrum, $-\mathrm{d}\Theta/\mathrm{d}T$, is given by the summation

$$-\,\mathrm{d}\Theta/\mathrm{d}T = \Sigma(-\mathrm{d}\theta(E_\mathrm{d})/\mathrm{d}T)p(E_\mathrm{d}) \qquad (3)$$

over the range of E_d, taking into account a density-distribution function of activation energy of desorption ($p(E_\mathrm{d})$). The distribution function for a given catalyst is determined by fitting the calculated spectrum with the experimental one. It is convenient that the activation-energy distribution be readily determined from a single TPD spectrum collected at a low starting temperature, which was 30 °C in the present work.

Results and Discussion

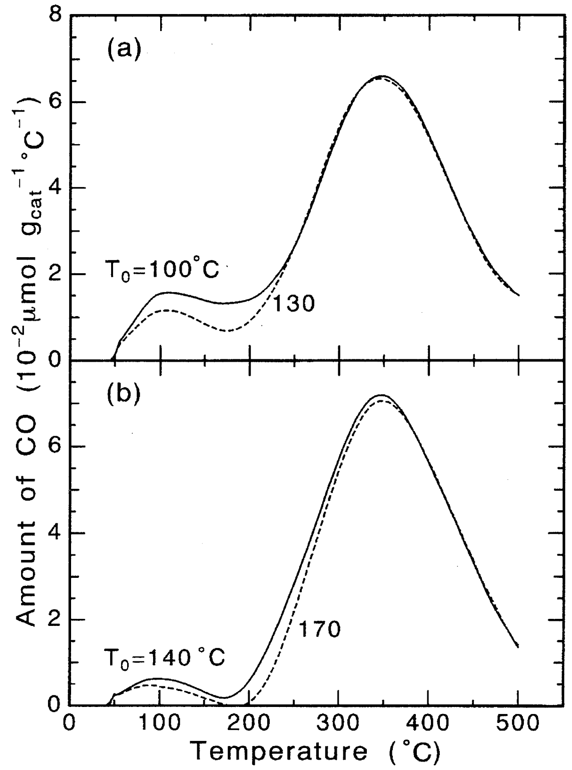

Fig. 1. Interrupted TPD spectra with different interrupted temperatures of T_0 given for a 2.5 wt% platinum catalyst sample.

Interrupted TPD. In the usual interrupted TPD measurements, desorption takes place at temperatures higher than T_0. This is the case for supported nickel catalysts with hydrogen, as previously indicated.[7] For supported platinum catalysts with carbon monoxide, however, the desorption was observed to occur at temperatures lower than T_0 when it was not very high. Figure 1 shows typical interrupted TPD spectra with different T_0's. One can see that the desorption starts at the same temperature of around 40 °C, and significant amounts of carbon monoxide desorb at temperatures much lower than T_0. The amount of carbon monoxide desorbing up to T_0 is larger for a lower T_0. The desorption profiles at higher temperatures (>300 °C) are very similar, irrespective of T_0. Those observations of lower temperature desorption may be explained by the surface diffusion of adsorbed carbon monoxide species, which can easily move over the surface of platinum particles. Probably, during the cooling stage after the first heating up to T_0, the adsorbed species move to unoccupied sites and some are located on these sites. That is, carbon monoxide can be adsorbed again by the surface sites where the desorption energies are smaller than kT_0 (k: Boltzmann constant). Thus, the desorption takes place at lower temperatures on the following interrupted TPD, as shown in Fig. 1. Similar results were previously seen for supported platinum catalysts with hydrogen. However, they were explained by a hydrogen spillover.[8] For carbon monoxide, however, a spillover is unlikely to occur.

When higher temperatures of T_0 were used, normal spectra were obtained. Figure 2a shows the results for T_0=200 °C and 230 °C. It is possible to analyze the differential spectrum between these two interrupted spectra and to determine the kinetic parameters of n, E_d, and ν_0. This is described in the following section.

It is interesting to note, from the results of Figs. 1 and 2, that the surface of platinum particles is divided into two groups of desorption sites. For one group, carbon monoxide desorbs at low temperatures, and surface diffusion takes place easily between the sites of this group. For the other, the desorption of carbon monoxide requires higher temperatures,

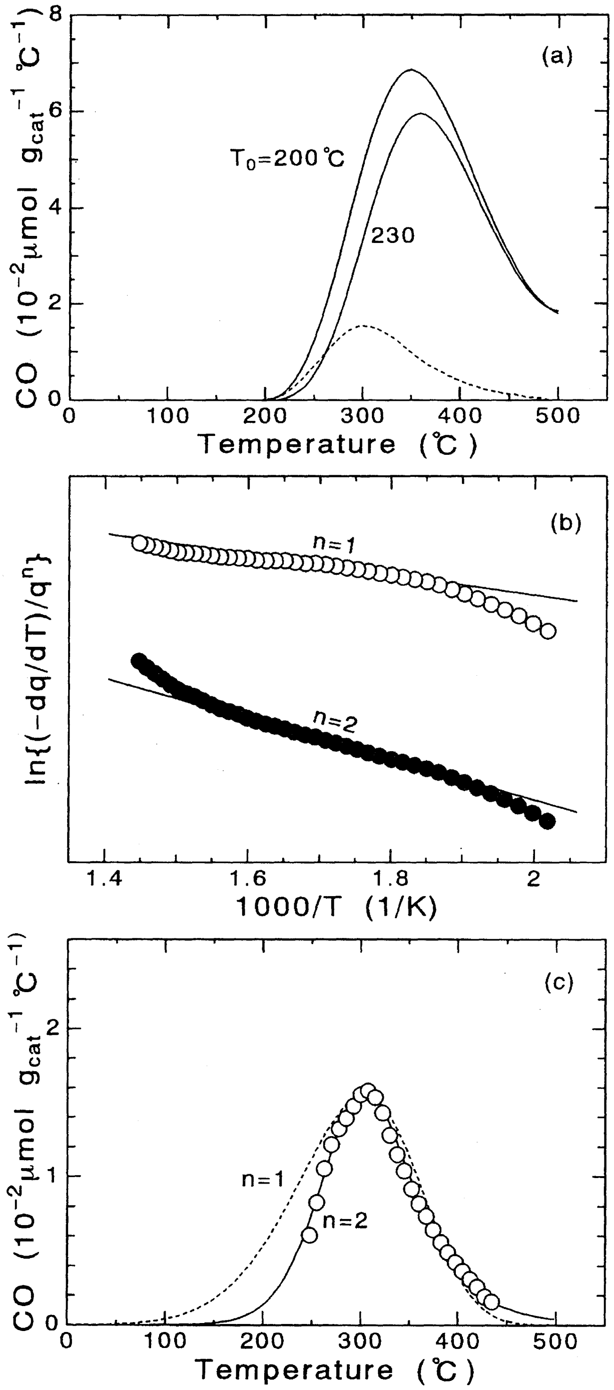

Fig. 2. TPD spectra and desorption kinetics analysis results for a 2.5 wt% platinum loaded catalyst sample. (a) Interrupted TPD spectra (solid lines) with T_0=200 °C and T_0=230 °C and differential spectrum (broken line) from them; (b) Arrhenius-type plot based on Eq. 2 with n=1 and n=2. Circles and lines indicate experimental and fitted results, respectively; (c) Comparison of the experimental differential spectrum (circle) with the fitted ones with n=1 (broken line) and n=2 (solid line).

and surface diffusion does not occur. The former group may correspond to the sites on low Miller-index planes, on which the surface diffusion of carbon monoxide easily occurs. It was reported, for example, that the surface diffusion was rapid for a Pt(111) surface.[13)]

Desorption Kinetics Analysis. The kinetic parameters were determined for several differential spectra, each of which was obtained from a pair of interrupted spectra with high T_0's. In the cases of lower T_0's, the interrupted spectra included the influence of surface diffusion, as mentioned above. It was impossible to determine the desorption kinetic parameters from those spectral data.

Figure 2 shows a typical pair of interrupted spectra and the differential spectrum, an Arrhenius-type plot based on Eq. 2, and a comparison between the experimental and fitted results. The experimental spectrum was fitted well by a calculation with n=2, which was also suggested by the symmetrical shape of the differential spectrum. It was found that n=2 gave good fitting results for several other measured differential spectra. Figure 3 presents a plot of the pre-exponential factor against the activation energy, indicating a so-called compensation effect,[14,15)] which was also observed for supported nickel and platinum catalysts with hydrogen.[7,8)]Figure 3 includes the ν_0–E_d relationship for hydrogen and platinum catalysts previously reported. At the same E_d, ν_0 is larger for hydrogen than for carbon monoxide, implying some difference in the desorption behavior between carbon monoxide and hydrogen. It was reported that the activation energy of desorption for Pt(111) was larger for carbon monoxide than for hydrogen, being 42 and 29 kJ mol^{-1} at a coverage of 0.66 and 1.0, respectively.[11)]

Activation Energy Distribution. Figure 4 shows the overall TPD spectrum for a 2.5 wt% platinum catalyst, indicating two desorption peaks. Since the peak at higher temperatures does not include the influence of surface diffusion, it was analyzed in order to determine the activation-energy distribution. The density-distribution function ($p(E_d)$) is a continuous function of E_d. It is difficult, however, to obtain this continuous function through Eq. 3. A few discrete E_d values were selected, and the corresponding $p(E_d)$ values were determined in the present calculation as in previous

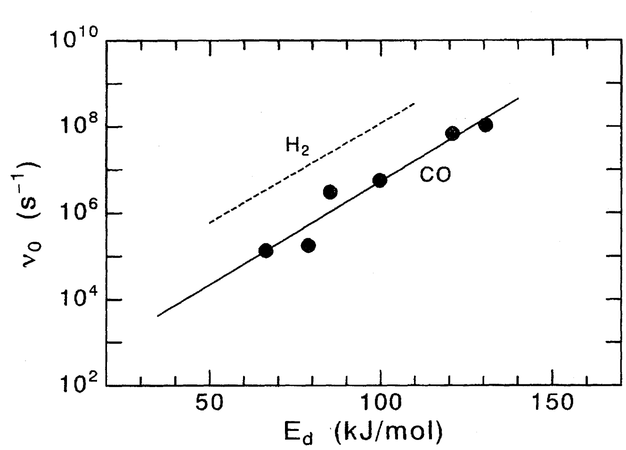

Fig. 3. Plot of the pre-exponential factor against the activation energy determined for a 2.5 wt% platinum loaded catalyst sample. Solid line is the linear regression result and broken line shows the ν_0–E_d relation obtained previously with hydrogen.

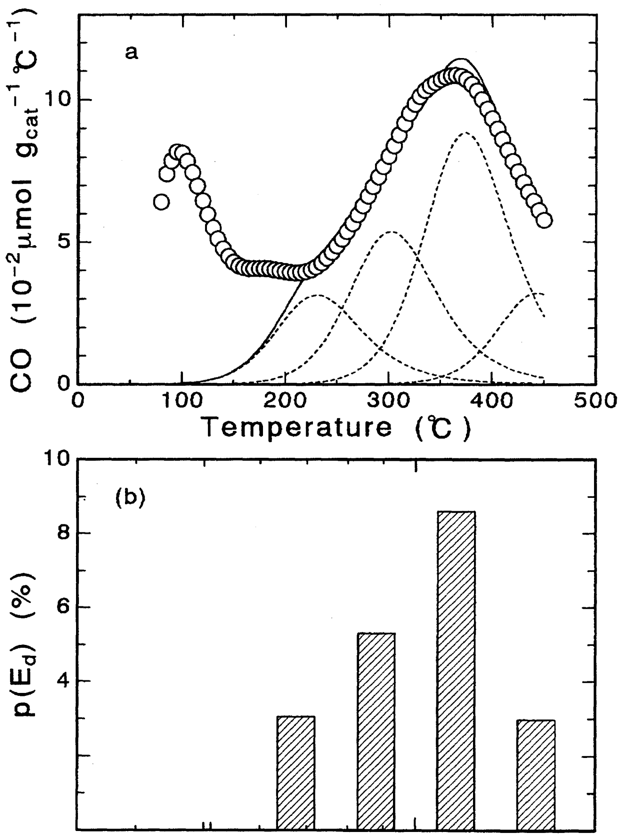

Fig. 4. The experimental overall TPD spectrum (circle) and the fitted result (solid line) for a 2.5 wt% platinum loaded catalyst sample. Broken lines are the deconvoluted spectra corresponding to selected E_d values.

studies.[7,8] Figure 4a includes fitting results in which each broken line is the deconvoluted spectrum corresponding to a selected E_d and solid line is the overall spectrum from those deconvoluted spectra. Figure 4b shows the determined density-distribution function ($p(E_d)$), which is expressed in such a way that the sum of $p(E_d)$'s is equal to the total amount of carbon monoxide desorbing up to 450 °C relative to the total amount of platinum atoms loaded.

Figure 5a compares $p(E_d)$ for 2.5 and 5.0 wt% platinum catalysts. The former catalyst has a clear maximum at around E_d=110 kJ, while the latter shows a flatter distribution. This trend is similar to that observed with hydrogen, as can be seen in Fig. 5b.[8] A difference is present, however, in that $p(E_d)$ is larger at smaller E_d for carbon monoxide, while it is larger at higher E_d for hydrogen. The desorption of carbon monoxide from platinum was investigated in several studies using different single-crystal surfaces, such as Pt(110), Pt(100), Pt(111), and Pt(210). It was reported that the activation energy of desorption for Pt(111) and Pt(210) was 42 kJ mol^{-1} at a coverage of 0.66 and 83 kJ mol^{-1} at a coverage of 0.95, respectively.[11] In addition, it was indicated that desorption at higher temperatures during TPD was due to step or defect sites on the surfaces of platinum.[13,16,17] From those results, one can assume that the desorption sites with low E_d correspond to those on low Miller-index planes, while the sites with larger E_d are present on some defects and high Miller-index planes. If the E_d value could be related to particular sites, for example a particular crystal plane, for the two probe adsorbates used, the E_d distribution would provide more information about the heterogeneous surface of catalyst samples. However, the relevant data are presently limited to only a few surfaces of low Miller-index planes.[11]

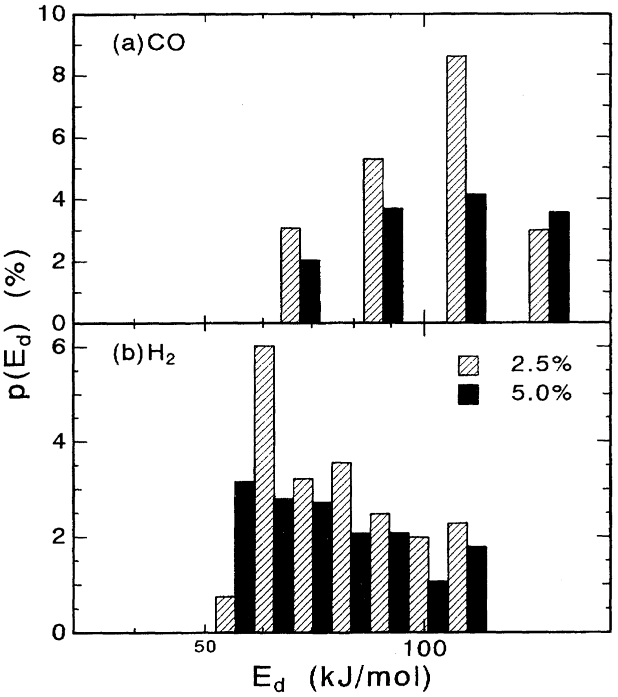

Fig. 5. The distribution of activation energy of desorption for 2.5 and 5.0 wt% platinum loaded catalyst samples determined with carbon monoxide (a) and hydrogen (b) used as a probe adsorbate.

A description of the surface heterogeneity with $p(E_d)$ may be useful for examining the catalysis of supported metal particles for structure-sensitive reactions. An examination of the relation of the activity with $p(E_d)$ would help us to study the nature of active sites and the corresponding (true) turnover frequency (TOF). In most cases, since the surface heterogeneity is not taken into account, the TOF is an average value. The authors have been examining the relation between $p(E_d)$ and the catalytic activities; the results for supported nickel catalysts for ethane hydrogenolysis will be given elsewhere.[19] From a practical point of view, $p(E_d)$ may be used to fingerprint the surfaces of supported metal catalysts, better than the TPD spectrum and the degree of metal dispersion (fraction exposed).

Conclusion

It has been demonstrated that interrupted TPD is useful for investigating the heterogeneous surface of supported metal catalysts. The use of carbon monoxide indicates the presence of two groups of desorption sites on the surface of supported platinum particles, which are different in the desorption temperature and in the possibility of surface diffusion. The distribution of the activation energy of desorption over silica-supported platinum catalysts is different between carbon monoxide and hydrogen used as probe adsorbates. The present TPD analysis is an approximate treatment of desorption. For example, it does not take into account the influence of coverage. However, the proposed method may be a helpful way to measure the surface heterogeneity of catalysts having a number of different active sites.

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