The distribution of activation energy for hydrogen desorption over silica-supported nickel catalysts determined from temperature-programmed desorption spectra

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Abstract

A method has been developed that can calculate the distribution of activation energy for desorption of hydrogen from temperature-programmed desorption (TPD) spectra for characterizing the heterogeneity of the surfaces of supported metal catalysts. This method is based on the idea of Hashimoto et al. [Stud. Surf. Sci. Catal. 28 (1986) 503] who determined the distribution of acid strength of solid acid catalysts from the TPD spectra of ammonia. The surface of a catalyst is regarded as a collection of groups of desorption sites with identical activation energy in each group. These groups are experimentally sampled from a series of TPD spectra and a set of desorption kinetic parameters are determined for each group. An overall TPD spectrum is given by the summation of the contribution from each group characterized by a particular activation energy. The fitting of a calculated spectrum to an experimental one determines the activation energy distribution. This method has been applied to study the surfaces of silica-supported nickel catalysts in the present work. The surface state of the catalysts is influenced by various preparation variables, and their influence is expressed in terms of the distribution of activation energy for hydrogen desorption.

1. Introduction

Temperature-programmed desorption (TPD) has frequently been employed as a useful technique for characterizing the surfaces of catalysts and adsorbents [1–3]. The surfaces of these materials are mostly heterogeneous; namely, they have a number of sites being different in catalytic and adsorptive activities. The TPD spectrum does not directly express the distribution of those different active sites present on the surfaces and it depends on operating conditions, e.g., heating schedule in the TPD measurement.

Previously, Hashimoto et al. [4] developed a method for determining the distribution of activation energy of desorption from the TPD spectrum. The overall rate of desorption from a heterogeneous surface is the sum of those from a number of sites having different activation energies of desorption. When the rate of desorption is known for a given activation energy, the overall TPD spectrum can be calculated by taking into account the activation energy distribution. By comparing the experimental

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and theoretical TPD spectra, one can determine this distribution, which clearly describes the heterogeneity of the surface. The procedures needed in this method are described in the following section.

Hashimoto et al. applied their method to determine the distribution of activation energy for the desorption of ammonia, i.e., the distribution of acid strength of several solid acid catalysts [4]. This method is applicable to the characterization of supported metal catalysts using selected probe molecules. In the present work, we have applied it to silica-supported nickel catalysts, using hydrogen as a probe. It was previously found from the TPD of hydrogen that the state of nickel dispersion strongly depends on such preparation variables as metal content, heat treatment, and/or pretreatment of supports [5–7]. We tried to describe the effects of these variables more clearly in terms of the distribution of activation energy for hydrogen desorption.

2. A proposed method for determining the distribution of activation energy for hydrogen desorption

It can be envisaged that the surface of a supported nickel catalyst is composed of several groups of sites for hydrogen desorption [8]. Each group is characterized by a value of activation energy of desorption, \( E_d \). In addition to \( E_d \), other kinetic parameters like pre-exponential factor are also needed to calculate the contribution of each group to the overall TPD spectrum. The sampling of such groups and the determination of kinetic parameters for each group can be performed by collecting and analyzing a series of TPD spectra as follows.

On TPD, a catalyst sample is first heated up to a certain temperature, \( T_0 \). The temperature is maintained at \( T_0 \) until no desorption is detected. After that, the sample is heated again to collect the spectrum ranging up to a maximum temperature, \( T_m \). This is called the starting temperature. A series of TPD spectra with different starting temperatures are collected by that procedure. From this series of TPD spectra, we pick up a pair of spectra with a small difference in the starting temperature. The differential spectrum between these two is assumed as a spectrum that comes from a certain group. A set of kinetic parameters for this group is obtained by analyzing the differential spectrum by the following procedure.

The TPD spectrum for a homogeneous surface characterized by an activation energy \( E_d \) is given by

\[
\frac{-d\theta}{dT} = \left( \frac{v_0}{\beta} \right) \exp(-E_d/RT) \theta^n,
\]

(1)

provided the desorption is the rate-determining step. \( \theta \) denotes the coverage of the surface occupied by hydrogen, \( T \) the desorption temperature, \( v_0 \) the pre-exponential factor, \( \beta \) the heating rate, \( R \) the gas constant, and \( n \) the order of the desorption. \( E_d \) and \( v_0 \) are assumed to be coverage-independent. Strictly speaking, these two parameters may be a function of \( \theta \); however, the knowledge about the dependence of \( E_d \) and \( v_0 \) on \( \theta \) is not sufficient at present [9,10].

Eq. (1) is rewritten as follows:

\[
\ln\left[ \frac{(-d\theta/dT)}{\theta^n} \right] = (-E_d/R)(1/T) + \ln\left( \frac{v_0}{\beta} \right).
\]

(2)

Using a given value of \( n \), \( \ln((-d\theta/dT)/\theta^n) \] is plotted against \( 1/T \); when this plot is a straight line, it will give the values of \( E_d \) and \( v_0 \) from the slope and the intercept, respectively.

The above analysis is performed for several differential spectra. When kinetic parameters are known for any \( E_d \), the overall TPD spectrum \( -d\Theta/dT \) will be given by the summation:

\[
-d\Theta/dT = \sum \left[ -d\theta(E_d)/dT \right] p(E_d)
\]

(3)

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

3. Experimental procedure

3.1. Sample preparation

Silica-supported nickel catalysts were prepared by a method of wet impregnation [5,6]. A porous silica gel, Silbead-N supplied by Mizusawa Industrial
Chemicals, Ltd., was used as a starting support material. It was ground to powder of 0.5–0.25 mm in size and calcined in air at 700°C for 3 h. After the calcination, the silica gel had a surface area of 370 m²/g. It was impregnated with nickel nitrate from its aqueous solution for the metal content to be 7.0, 5.0, or 0.5 wt%. The reduction to metallic nickel was carried out by flowing hydrogen at 400°C for 10 h.

3.2. TPD measurements

The TPD spectra for various \( T_0 \) were collected with the same apparatus and procedures as described previously [6]. The weight of catalyst sample used was 0.15 g and the height of the sample bed was 3 mm. The amount of desorbing hydrogen was measured with a thermal conductivity detector (TCD), using argon as a carrier gas. Adsorption of hydrogen was performed in the following manner. The catalyst was heated in flowing argon up to an adsorption temperature of 350°C. When it reached this temperature, argon was switched to hydrogen flowing at 30 ml/min. The catalyst was maintained at 350°C for 4 min and cooled to 30°C, about 5 min being needed for this cooling. Thus, the catalyst was exposed to flowing hydrogen totally for 10 min. Under the present conditions used, the amount of hydrogen adsorbed was comparable to the number of exposed nickel atoms estimated by X-ray diffraction line broadening, indicating that the initial coverage is approximately unity [6]. After hydrogen adsorption, argon was passed and the catalyst was heated up to a certain desired starting temperature \( T_0 \). This temperature was maintained until the TCD response of the effluent gas stream became stable. The TPD spectrum was then collected at a heating rate of 30 K/min and an argon flow rate of 30 ml/min. The heating was limited to a maximum temperature of 450°C to avoid thermal effects on the state of nickel for repeated TPD measurements.

3.3. Examination of TPD conditions

For analyzing TPD spectra, the influence of re-adsorption and pore diffusion should be considered. A few preliminary experiments were carried out to ascertain that TPD spectra collected under the conditions described above were free from the influence of re-adsorption and pore diffusion. The re-adsorption of desorbing species on the downstream catalyst was examined by changing the weight of the catalyst sample used (the height of the catalyst sample bed). The possibility of re-adsorption was ruled out from the result that the TPD spectrum was hardly altered by decreasing the sample weight from 0.15 to 0.05 g. The influence of pore diffusion was examined with a catalyst sample of fine particles. The original catalyst of 0.5–0.25 mm in size was ground to a powder of 20–1 μm in an agate mortar. To retain the flow conditions as before, the powder was mixed with a certain amount of the metal-free support granules of 0.5–0.25 mm in size and subjected to the TPD measurement. The height of the sample bed was set up at 3 mm. The spectrum obtained was found to be in good agreement with that for the catalyst sample of 0.5–0.25 mm in size. In addition, TPD was conducted using a slower heating rate of 9 K/min under normal conditions for the other experimental variables. It was shown that the TPD spectrum was dependent on the heating rate and the distribution of activation energy of hydrogen desorption determined from the spectrum at 9 K/min by procedures as described below was in good agreement with that from the spectrum at the normal heating rate of 30 K/min. From those results, it is concluded that the TPD spectra obtained under normal conditions are substantially free from the influence of re-adsorption and pore diffusion and far from equilibrium desorption, and so the spectra can be analyzed by Eq. (1). The TPD spectrum on nickel/silica catalyst is changed by preparation variables and the change of spectrum reflects the change in the surface state of nickel particles of the catalyst.

4. Results and discussion

4.1. Overall and differential TPD spectra

Figs. 1a and 2a give typical TPD spectra with different starting temperatures for 7 wt% nickel/silica catalyst before and after heat treatment in hydrogen at 750°C for 1 h, respectively. The heat treatment markedly decreases the amount of hydrogen desorbing at temperatures above 150°C, indicating that the surface state of supported nickel particles
is significantly changed by this treatment. Figs. 1b and 2b show differential spectra obtained from the four pairs of the original spectra given in Figs. 1a and 2a. Note that those differential spectra are symmetrical. Totally 13 differential spectra were collected and they were analyzed by the following procedures.

4.2. Desorption kinetics analysis

For each differential spectrum obtained, kinetic parameters were determined in terms of Eq. (2). In Fig. 3, typical plots of log\((-d\theta/dT)/\theta^n\) against \(1/T\) are shown for \(n = 1\) and \(n = 2\). It was found that the plots with \(n = 2\) indicate better linear relationships for all the differential spectra analyzed (13 spectra) except for the higher-temperature ends where there were relatively large experimental errors due to the difference between very small amounts of desorbing hydrogen. From this fact and from the symmetrical shape of the spectra as seen in Figs. 1b and 2b, \(n\) seems to be 2, agreeing with previous results of Konvalinka et al. [13] and Lee and Schwarz [14]. The value of \(n\) may be estimated by other methods [2,11], for example, with a skewness parameter \(\chi\) [12],

\[
\chi = 100\left[\left(T'' - T_p\right) - \left(T_p - T'\right)\right]/\left(T'' - T'\right),
\]

where \(T_p\) is the temperature at peak maximum and \(T'\) and \(T''\) are lower and upper temperatures at half maximum. For 13 differential spectra obtained, the \(\chi\) values are > 0 and the average of them is 10 (±4.5). This would also give an estimate of \(n = 2\). The \(\chi\) values are larger than the range of \(\chi\) predicted by Chan et al. [12]. This is mainly due to that the pre-exponential factor they used in their model calculation \((10^8-10^{15} \text{ s}^{-1})\) is larger compared with
what we have experimentally determined ($10^4$ to $10^8$ s$^{-1}$) as will be described below. It is implied from $n = 2$ that hydrogen is dissociatively adsorbed on the surface of nickel particles and the recombination of those adsorbed hydrogen atoms is the rate-determining step for the desorption. The kinetic parameters, $E_d$ and $\nu_0$, were determined by linear regression analysis of the plots with $n = 2$, using data of which the desorption temperatures were from $T_p - \Delta T/2$ to $T_p + \Delta T/2$, $\Delta T (= T'' - T')$ being the peak width at half maximum. Figs. 1b and 2b also include the TPD spectra calculated using the kinetic parameters so determined. One can see good agreement between the experimental and calculated spectra.

Fig. 4 shows the relationship between the pre-exponential factor and activation energy obtained. It gives a good linear relationship, indicating the validity of the so-called compensation effect [15] in the present case. From this relationship, the value of $\nu_0$ can be determined for any $E_d$. As a result, one can calculate the TPD spectrum for a given $E_d$ by Eq. (1) with $n = 2$ and the overall spectrum for a given activation energy distribution by Eq. (3).
4.3. Activation energy distribution

Considering the result of Fig. 4, we used a certain set of discrete values of $E_d$ ranging from 35 to 135 kJ mol$^{-1}$ in the present work. The corresponding distribution of $p(E_d)$ was calculated through Eq. (3) for a given TPD spectrum, using the TPD data of which the desorption temperatures ranged from 50 to 400°C. This calculation was carried out by a least-squares method with linear Taylor’s differential interpolation; starting with certain initial estimates, the values of $p(E_d)$ were repeatedly improved.

Figs. 5 and 6 show the results of the above calculation for 7 and 0.5 wt% nickel/silica catalysts, respectively. Here, $p(E_d)$ is expressed by the ratio of the number of exposed nickel atoms in a group characterized by $E_d$ to the total number of nickel atoms present in the catalyst. The sum of the $p(E_d)$ is equal to the degree of metal dispersion. The TPD spectrum for 7 wt% nickel catalyst is significantly changed by the heat treatment, which markedly decreases the amount of hydrogen desorbing at temperatures above 150°C as described in Fig. 2a. This decrease is described by a decrease of $p(E_d)$ at high $E_d$ values. The 0.5 wt% nickel catalyst indicates a larger amount of hydrogen desorbing at higher temperatures compared with the 7 wt% nickel catalyst. This is shown by the larger $p(E_d)$ values at higher $E_d$. The TPD spectrum for 0.5 wt% nickel catalyst was little influenced by the heat treatment.

In addition, the surface state of silica-supported nickel particles is significantly influenced by pretreatments of the support [7]. As shown by the TPD spectra in Fig. 7a, it was found that the doping with a calcium compound prior to the impregnation of
nickel increased the amount of hydrogen desorbing at higher temperatures, while the hydroxylation by immersing in hot water decreased it. Fig. 7b shows the distribution of activation energy for hydrogen desorption determined from the three spectra. The calcium doping gives larger $p(E_d)$ values at high $E_d$; in contrast, the hydroxylation gives smaller $p(E_d)$ values.

As demonstrated above, those effects of heat treatment, metal content, and support pretreatment on the surface state of nickel particles are more clearly described by the changes in the distribution of activation energy for hydrogen desorption. The effects would be mainly related to the variation in the surface morphology of nickel particles [6,7].

4.4. Comparison with previous results

Previously, Lee and Schwarz [14] measured TPD spectra of hydrogen for a nickel/silica catalyst in which the metal content was about 50 wt% and made a line-shape analysis of the spectra measured. They showed the order of desorption to be 2 in accord with our result, and determined the activation energy for desorption as a function of the initial coverage. It was found to decrease from 90 to 55 kJ/mol as the coverage increased up to unity. This range of the activation energy is smaller than what we have determined (135–35 kJ/mol). The adsorption of hydrogen on their catalyst is non-activated; in contrast, our catalysts have both activated and non-activated adsorption sites of which the populations depend on the metal content and thermal history. These differences indicate that the surface state of nickel particles in our catalysts is different from that of the catalyst Lee and Schwarz used. This is probably due to the difference in the metal content and the catalyst preparation conditions, e.g., heat-treatment temperature. The presence of activated hydrogen-adsorption sites on supported nickel catalyst was reported by Weatherbee and Bartholomew [16].

Konvalinka et al. [13] measured TPD of hydrogen for several supported nickel catalysts and they observed a few peaks for the TPD spectra. For a spectrum obtained, they analyzed the peak at the lowest temperature by comparing the line shape with calculated ones [17,18]. They subtracted this peak from the original spectrum and performed the same line-shape analysis for the resulted spectrum. Their analysis showed the presence of 6 or 7 peaks in the range of −100 to 550°C. The order of desorption that they determined for the peaks at temperatures above 50°C is 2, being in accordance with our results.

Although the pre-exponential factor, as well as the activation energy, is an important kinetic parameter, only a few data were reported in the literature as reviewed by Christmann [3], Seebauer et al. [9] and Zhdanov et al. [10]. Christmann et al. [19] studied the desorption of hydrogen adsorbed at very low and high coverages on low-Miller-index planes of nickel crystal. At a high coverage of $\sim 0.9$, $E_d$ and $\nu_0$ were respectively reported to be 50 kJ/mol and
$10^{3.5} \text{ s}^{-1}$ for Ni(110) and $59 \text{ kJ/mol}$ and $10^7 \text{ s}^{-1}$ for Ni(111). In our work, the coverage is comparable to the saturated value and the value of $v_0$ determined is $10^4-10^8 \text{ s}^{-1}$ for a range of $E_d$ of 40–120 kJ/mol. The values of $v_0$ determined by Christmann et al. fall in this range of $v_0$. It would be interesting to assign a value of $E_d$ to a particular crystal plane for characterizing the heterogeneous surface of supported nickel particles in more detail. To do so, however, it is further necessary to obtain information about the desorption kinetics on various nickel crystal planes of different Miller indices including the dependence of $E_d$ and $v_0$ on the coverage.

![Graph](image-url)

Fig. 7. Results of the TPD analysis for as-reduced 5 wt% nickel/silica catalysts using untreated (1), hydroxylated (2), and 1 wt% calcium-doped (3) supports. (a) Overall spectra. (b) The distribution of activation energy for hydrogen desorption.
The pre-exponential factor for desorption of hydrogen and other adsorbates has often been reported in experimental works to be significantly lower than expected from kinetic models [9]. For example, the smallest value of $v_0$ is predicted to be larger than $10^{10}$ s$^{-1}$ on the basis of transition-state theory [3]. Smaller values of $v_0$ have been reported at high coverages as in our experiments. The surface of adsorbents would be changed by interactions with adsorbed species at high coverages, influencing $v_0$ in manners that cannot be predicted from theoretical models. In the case of hydrogen and metallic adsorbents, the absorption of hydrogen by the surface layer of the adsorbents might have some effects. To make a clear explanation of the desorption behavior at high coverages, however, both experimental and theoretical studies are further needed [3,9].

5. Concluding remarks

The present method can determine the distribution of activation energy of desorption of hydrogen from the TPD measurements over silica-supported nickel catalysts. The activation energy distribution over a given catalyst can readily be determined by collecting and analyzing a single TPD spectrum. It more directly characterizes the heterogeneous surface of the catalyst than does a TPD spectrum itself. For the correlation and evaluation of the catalytic activity, it would be more informative to use the activation energy distribution. It would depend on the species of probe molecules used, so the combination of two or more probe molecules could give a clearer description of the heterogeneity of the surface of supported metal catalysts.

The present TPD analysis is an approximate treatment that does not take into account the influence of coverage. The treatment includes the heterogeneity that there are different desorption sites on the surface having different desorption kinetic characters and that there are lateral interactions among adsorbed hydrogen species due to high coverage. However, the proposed method is useful for characterizing the surfaces of supported metal catalysts, for which we still do not have sufficient information about the kinetic parameters. If the dependence of desorption kinetic parameters on coverage would clearly be known, our treatment could similarly be applied and the analysis would be improved.

References

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