The kinetics of H$_2$ adsorption on supported ruthenium catalysts

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Abstract

Ruthenium catalysts supported on SiO$_2$, Al$_2$O$_3$ and TiO$_2$ were prepared by the impregnation method. Temperature-programmed desorption (TPD) method was applied to investigate the kinetics of hydrogen adsorption/desorption on these catalysts. All the TPD results show two-peak profile, except Ru/SiO$_2$. The low-temperature peak was assigned to the hydrogen adsorbed on the Ru metal. The high-temperature peak was attributed to the spillover of hydrogen atoms from metal to the support. Both are activated process. The amount of adsorbed hydrogen increased with increasing adsorption temperature, and the maximum adsorption occurs at above 200 °C. The activation energy of adsorption is a function of catalyst support and the reduction temperature. It decreases in the order of Ru/TiO$_2$ (500 °C reduction) > Ru/Al$_2$O$_3$ > Ru/TiO$_2$ (300 °C reduction) > Ru/SiO$_2$. The results demonstrated that the strong metal–support interaction exerted on Ru/TiO$_2$ would suppress hydrogen chemisorption at room temperature due to its high activation energy. However, hydrogen chemisorption on Ru/TiO$_2$ was not suppressed at high temperature. One is able to measure the Ru dispersion by adsorption of hydrogen at high temperature.
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1. Introduction

The study of Fischer–Tropsch synthesis (FTS) has become an important technical and fundamental subject since Fischer and Tropsch first developed the process of producing synthetic hydrocarbons in 1923 [1]. Although metal catalysts with high FTS activity such as iron, nickel and cobalt have used in commercial application, the group VIII metals transition metals have been reported as the good FTS catalyst with high activity and selectivity [2]. Ruthenium has been reported to be the most active and the most selective catalyst among the group VIII metals [2–4]. Recently, many works have been done on ruthenium-based catalysts which exhibited high hydrogenation selectivity in partial hydrogenation of benzene to cyclohexene [5,6]. To develop a more active and selective catalyst, it is important to understand the factors affecting the reaction, such as the type of support; dispersion of metal; the adsorption–desorption kinetics of the reactant gas, such as hydrogen, on the catalyst.

The adsorption of hydrogen on group VIII metals has been extensively studied. Numerous studies have been devoted to investigate the hydrogen adsorption phenomena over the surface of ruthenium single crystal by temperature-programmed desorption (TPD) [7], angle-resolved photoemission spectroscopy [8] and low-energy electron diffraction (LEED) [7,9]. The dynamics of hydrogen adsorption/desorption on ruthenium single crystal indicated that there are two different binding states which were observed in work-function changes and well correlated with the two desorption peaks in TPD spectra between ruthenium and hydrogen [10,11]. However, the characteristics of hydrogen adsorption on metal–support systems would be different from that on the single crystals because of the metal–support interactions, which are affected by the factors including particle size, catalyst preparation, reduced temperature, etc. Bhatia et al. [12] have investigated the dynamics of hydrogen adsorption on silica-supported ruthenium catalysts by means of in situ NMR techniques. Two hydrogen-on-ruthenium peaks were observed at 300–473 K, the upfield NMR peak at ~−60 ppm (α-peak) observed at low pressures ($P <$ 133 mbar) could be attributed to hydrogen dissociatively adsorbed on ruthenium particles; the second peak (β-peak) occurring at ~−30 ppm at pressures greater than 133 mbar represented weakly bound hydrogen. It has been reported [13] that hydrogen chemisorption is strongly suppressed on

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the TiO_2-supported catalysts in SMSI state. Therefore, one cannot use the amount of hydrogen adsorption to determine the metal dispersion. However, the chemisorption of hydrogen on these catalysts was carried out at room temperature. No results have been reported for the chemisorption at high temperature.

Comparing to other analytical techniques, TPD measurement provides information closely rated to the catalytic properties and has been widely applied to supported catalyst in the study of adsorption–desorption kinetics [14–16]. Lee and Schwarz [15] developed a method to calculate the activation energy for adsorption from the TPD spectra. The analysis was successfully used in research works of detailed kinetic information for activated hydrogen adsorption and desorption from cobalt in unsupported and supported on Al_2O_3, SiO_2, TiO_2 and carbon [16].

In the present work, the hydrogen adsorption on the Ru catalysts with various supports was carried out at various temperatures. TPD method was then applied to investigate the adsorption state of hydrogen on these catalysts. The phenomenon of activated hydrogen adsorption on ruthenium supported on Al_2O_3, SiO_2 and TiO_2 was elucidated. We also tried to develop a technique to measure the metal dispersion for the catalysts which exerted SMSI state.

2. Experimental

2.1. Catalysts preparation

Ru catalysts containing 5% on various supports were prepared by the incipient-wetness impregnation method. $RuCl_3 \cdot 2H_2O$ (Strem Chemicals) was dissolved in distilled water. A small amount of support (about 1 g support to $0.7 \sim 1$ ml distilled water) was added into the solution. After vigorous stirring, the slurry was dried overnight at 40 °C. The supports used in this study were Al_2O_3 (Strem Chemicals, surface area 225 m^2/g), SiO_2 (Davison, surface area 300 m^2/g), and TiO_2 (Degussa P-25, surface area 50 m^2/g).

2.2. Temperature-programmed desorption

About 0.3 g catalyst was placed in a quartz reactor (6 mm outside diameter). The sample was reduced in flowing H_2 (30 ml/s) at a rate of 5 °C/min from room temperature to 420 °C. The sample was kept 30 min at 100 and 200 °C during the heating procedure and kept at 300 °C (low-temperature reduction, LT reduction) or 500 °C (high-temperature reduction, HT reduction) for 2 h, then cooled under hydrogen-flow to room temperature. After that, the sample was held at 400 °C for 30 min under flowing Ar (30 cm^3/min) in order to remove physisorbed H_2 during the hydrogen reduction.

The hydrogen adsorption was proceeded by two methods: (i) adsorption under cooling after reduction at the maximum temperature. The adsorption of hydrogen was proceeded by exposing the catalyst to a 10% H_2/Ar mixture under cooling from 400 °C to room temperature and stayed at room temperature for 2 h; (ii) adsorption at a fixed temperature. The catalyst was cooled to room temperature in an Ar flow (30 cm^3/min) after reduction. The adsorption was proceeded at 50, 100, 150, 200 and 250 °C, respectively, for 2 h by exposure to a 10% H_2/Ar mixture for 60 min. After adsorption, the system was purged with an Ar flow (30 cm^3/min) to remove H_2 left in the reactor and the physisorbed hydrogen.

After adsorption, the catalyst was heated at 10 °C/min from room temperature to 400 °C, and the amount of desorbed hydrogen was determined by a thermal conductivity detector (Shimadzu GC-8A).

3. Results and discussion

3.1. TPD after adsorption of H_2 under cooling from maximum reduction temperature

Fig. 1 shows the TPD profiles of H_2 desorbed from 5 wt.% ruthenium catalysts supported on Al_2O_3, SiO_2, TiO_2, and carbon, respectively, where the H_2 adsorption were pro-
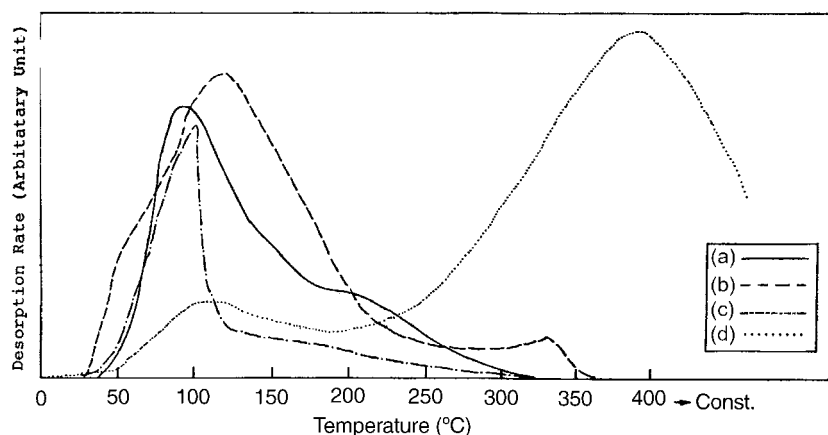

Fig. 1. The TPD spectra of 5% Ru on different supports: (a) Ru/TiO$_2$ reduced at 500 °C; (b) Ru/Al$_2$O$_3$; (c) Ru/SiO$_2$; (d) Ru/carbon.

Table 1
Ru dispersions and activation energies of H_2 adsorption on Ru catalysts

Catalyst	Dispersion (%)	E_{Aa} (kJ/mol)
5% Ru/TiO_2 reduced (300 °C)	36	22.42
5% Ru/TiO_2 reduced (500 °C)	85	31.31
5% Ru/Al_2O_3	56	27.45
5% Ru/SiO_2	44	20.23

ceeded under cooling from the maximum reduction temperature. All the TPD results show two-peak profile, except Ru/SiO_2. As shown in Fig. 1, a low-temperature peak with maximum appeared in the TPD profiles on all of the catalysts at 85–125 °C, depending on the nature of the support. The position of the low-temperature peak in the TPD profiles decrease in the order of $Ru/TiO_2 > Ru/SiO_2 > Ru/Al_2O_3$. It should be noted that although TiO_2-supported Ru catalyst exhibited good performance in hydrogenation of CO, the amount of hydrogen desorption from Ru/TiO_2 was less than that from Ru/Al_2O_3. This demonstrates that Ru/TiO_2 had a higher metal dispersion than Ru/Al_2O_3 (see Table 1). The results also show that metal–support interaction plays an important role on the adsorption state of hydrogen on metal. The dispersion of Ru metal was calculated from the area of the low-temperature peak, because the low-temperature peak was attributed to the hydrogen desorption from the Ru metal. The results show that the dispersion of Ru/TiO2 upon high-temperature reduction is higher than that upon low-temperature reduction, as shown in Table 1. In addition, the dispersion of Ru on alumina is greater than that on silica, all are not low. It indicates that very few amount of chlorine was present in the catalysts after hydrogen reduction at 400 °C.

The high-temperature peaks in the TPD profiles appeared in a wider range of temperature on various catalysts. The high-temperature peaks in the TPD profile of Ru/Al_2O_3 was at around 325 °C, and a broad high-temperature peak on the TPD profile of Ru/TiO_2 was at around 200 °C.

No high-temperature peak was observed on the profile of Ru/SiO_2. Moreover, the TPD profile of Ru/carbon showed a large amount of hydrogen desorbed at about 400 °C. If one assumed that all the hydrogen was adsorbed on the Ru metal and the stoichiometric ratio of hydrogen atom to surface Ru atom is 1, the metal dispersions of these catalysts were greater than 100%. This implies that not all of the hydrogen was adsorbed on the metal. It should be noted that adsorption energy of hydrogen on metal is not so strong that hydrogen could desorb at such high temperature (>300 °C). Based on these arguments, one can attributed that the high-temperature peak is due to the hydrogen spillover from Ru metal to the support. During desorption process, these hydrogen atoms on the support would migrate back to metal, then recombine to hydrogen molecules and desorb.

The results also show that the high-temperature peak in the TPD profiles was influenced by the metal–support interaction. To investigate how metal–support interaction affects the forms of the high-temperature peak in the TPD profiles, the TPD studies of the catalyst on the same support with various metal loading were performed. The TPD spectra of 5% Ru/Al_2O_3 and 3% Ru/Al_2O_3 are shown in Fig. 2, the low-temperature peak of TPD profile on 5% Ru/Al_2O_3 was at about 120 °C, which was only about 5 °C lower than that on 3% Ru/Al_2O_3. The area under the low-temperature peak of 5% Ru/Al_2O_3 was greater. In contrast, the high-temperature peak of TPD profile on 5% Ru/Al_2O_3 is about 60 °C higher than that of 3% Ru/Al_2O_3. It can be seen that the area of the high-temperature peak of 5% Ru/Al_2O_3 is smaller than that of 3% Ru/Al_2O_3. The same phenomena were observed on 3% Ru/TiO_2 and 5% Ru/TiO_2 samples reduced at 300 and 500 °C, respectively, as shown in Figs. 3 and 4. Different from those on 3% Ru/TiO_2, the area of high-temperature peak in TPD profile of 5% Ru/TiO_2 is much smaller than that of the low-temperature peak. It is believed that the high-temperature TPD peak is due to the spillover of H_2 from Ru metal to the support. Hydrogen was dissociatively adsorbed on the metal
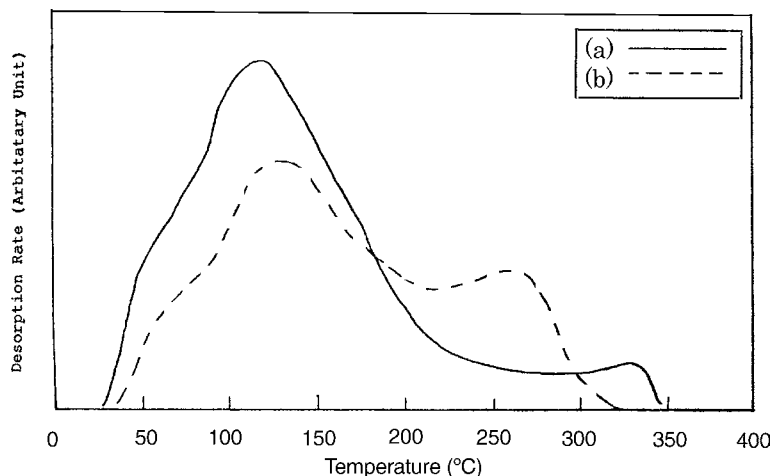

Fig. 2. The TPD spectra of different metal loading on Al_2O_3 support: (a) 5% Ru/Al_2O_3; (b) 3% Ru/Al_2O_3.
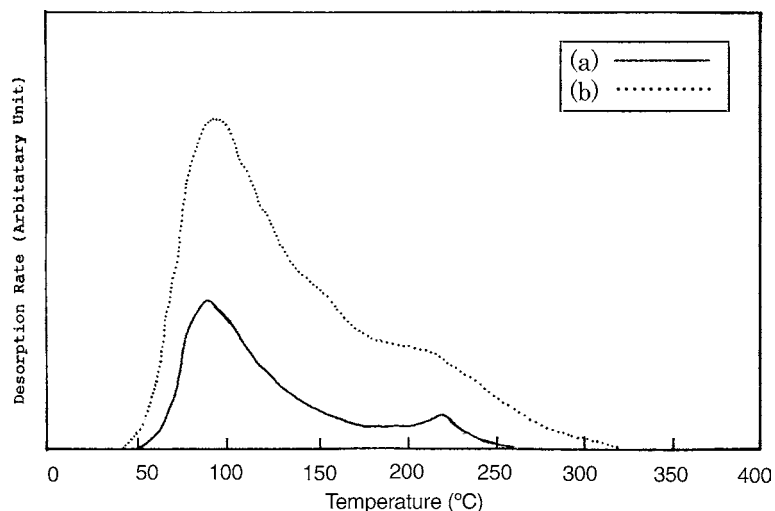
Fig. 3. The TPD spectra: (a) 5% Ru/TiO$_2$ reduced at 300 °C; (b) 5% Ru/TiO$_2$ reduced at 500 °C.

then spillover to the support. During desorption, these hydrogen atoms would migrate to the metal then desorb in the molecule form. Hydrogen spillover is related to the metal–support interaction and the perimeter of the interface between metal and support. Moreover, the TPD profile of Ru/carbon showed a large amount of hydrogen desorbed at about 400 °C, which could be referred to the large amount of spillover of hydrogen. It is known that carbon support has significant hydrogen spillover phenomena [17].

Furthermore, TPD profiles of Ru/TiO$_2$ samples reduced at 500 and 300 °C, clearly show that increasing the temperature of reduction leads to an increase in hydrogen adsorption. It had been reported that the capability of hydrogen chemisorption on group VIII metals supported on reducible metal oxides, such as titania, decreased with an increase of reduction temperature due to the strong metal–support interactions (SMSI) [18,19]. However, the adsorption of hydrogen reported in [18,19] was carried out at room temperature. If the hydrogen adsorption is an activated process, they should have higher amount of hydrogen adsorbed at high temperature. In this study, the adsorption of hydrogen was proceeded during the whole cooling process from 400 °C. It will pass through the maximum adsorption temperature during cooling, no matter what is the maximum temperature. In other words, the hydrogen adsorption proceeded in the cooling process would overcome the activation barrier of adsorption and give the maximum amount of adsorption. Using this technique, one is able to measure the exact metal dispersion no matter how high the activation barrier is.

For the Ru/SiO$_2$ catalyst, Bhatia et al. [12] have reported the NMR studies of hydrogen adsorbed on high metal loading of 29% Ru/SiO$_2$ and 19% Ru/SiO$_2$ catalysts. They indicated that there were two types of binding states of hydrogen interacting with ruthenium, the peak observed at low pressures ($P < 133$ mbar) labeled as α- and β-peak was observed at high pressures ($P > 133$ mbar). The α-peak was attributed to the strongly bound hydrogen and the heat of adsorption was about 40 kJ/mol in low pressure region ($P < 133$ mbar). The large β-peak showed the interaction of hydrogen and ruthenium conduction electrons indicated the
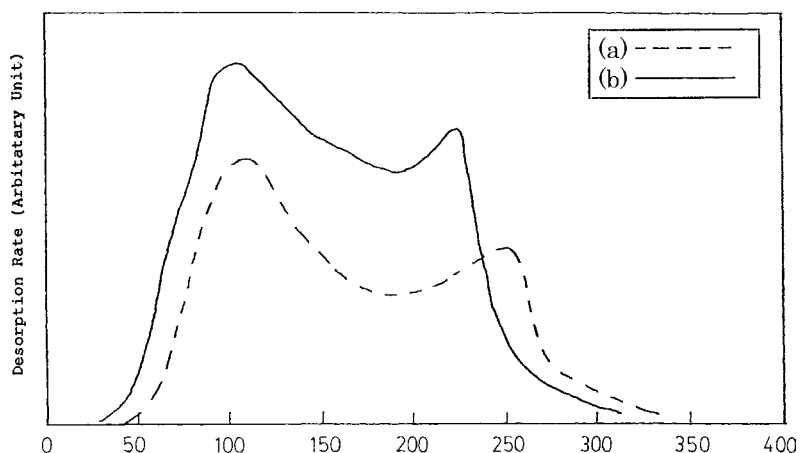

Fig. 4. The TPD spectra: (a) 3% Ru/TiO$_2$ reduced at 300 °C; (b) 3% Ru/TiO$_2$ reduced at 500 °C.

binding states was not mainly physical adsorption and the heat adsorption of β hydrogen was approximately 10 kJ/mol. In the present work, only one main peak was observed on the TPD profile of 5% Ru/SiO$_2$, since the TPD was taken in atmospheric pressure, where the desorption measurement of α bond hydrogen was difficult. The results of this study show that the activation energy of hydrogen adsorption on Ru/SiO$_2$ is 20.23 kJ/mol (Table 1), which is in a certain degree of agreement with the NMR result reported in [12].

3.2. TPD after hydrogen adsorption at constant temperature

Figs. 5–8 show the H$_2$ desorption profiles of 5 wt.% Ru supported on Al$_2$O$_3$, SiO$_2$ and TiO$_2$, respectively. The Ru/TiO2 catalyst was reduced at 300 and 500 °C, respec-
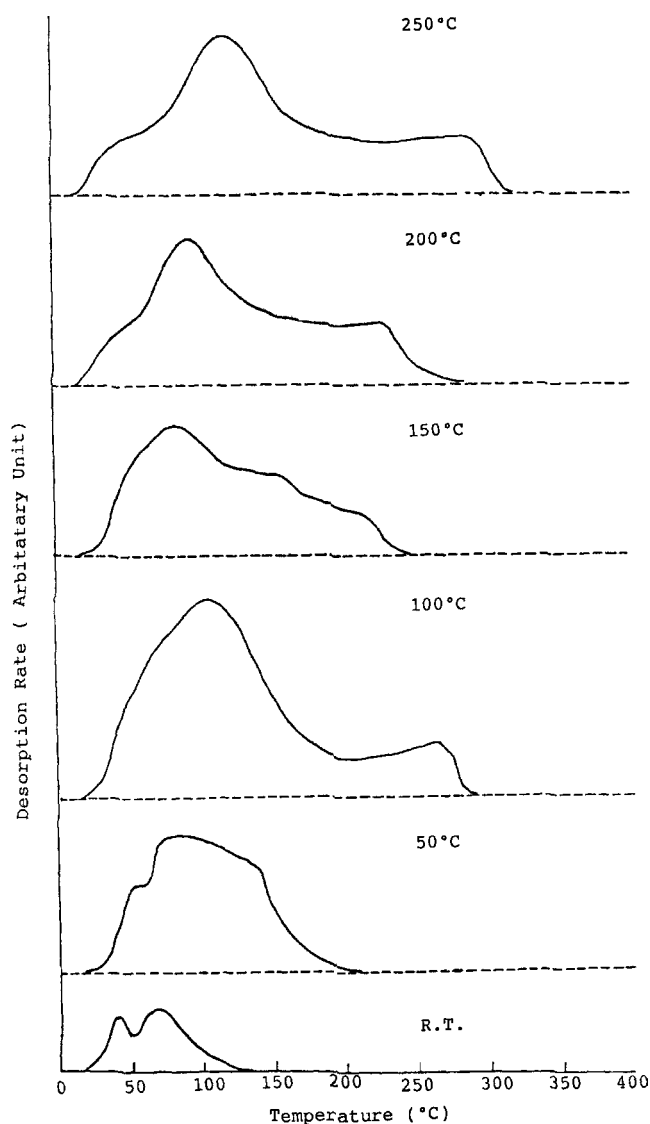

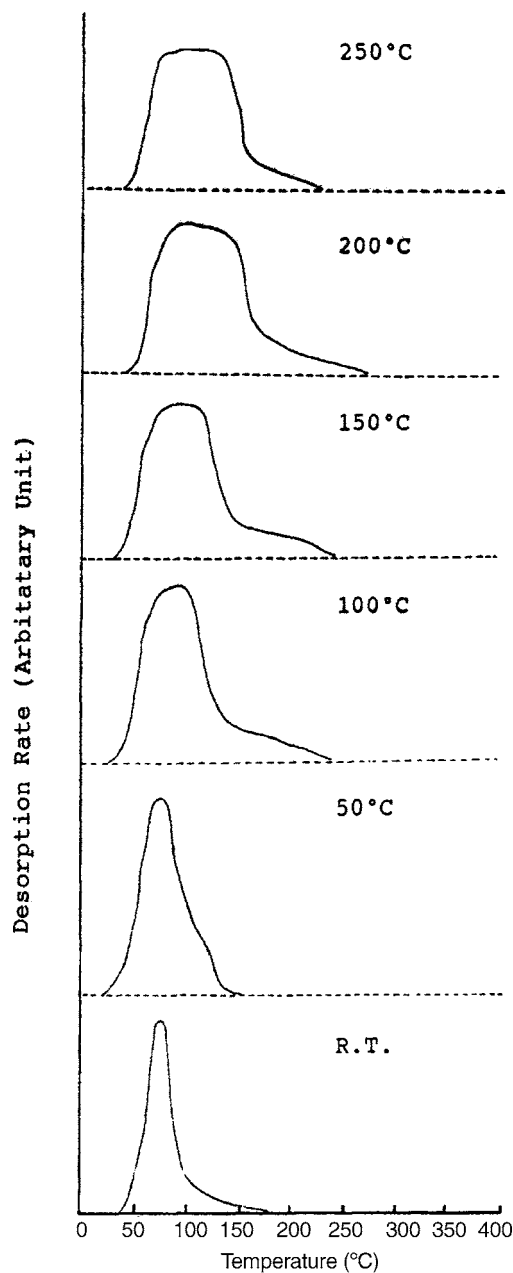Fig. 5. The TPD spectra of 5% Ru/Al$_2$O$_3$ adsorbed at different temperatures.

Fig. 6. The TPD spectra of 5% Ru/SiO$_2$ adsorbed at different temperatures.

tively. It is well-known that Ru/TiO2 reduced at 500 °C would have strong metal–support interaction. The H$_2$ adsorption was at fixed temperature, i.e. at room temperature, 50, 100, 150, 200 and 250 °C, respectively. The increase in the area of low-temperature peak with an increase of adsorption temperature demonstrates that hydrogen adsorption is an activated process on these catalysts. The area of high-temperature peak is also increased with increasing temperature. It is expected because hydrogen spillover is an activated process. The results of the amount of hydrogen adsorption versus adsorption temperature are shown in Fig. 9. The amount of hydrogen adsorption was calculated from
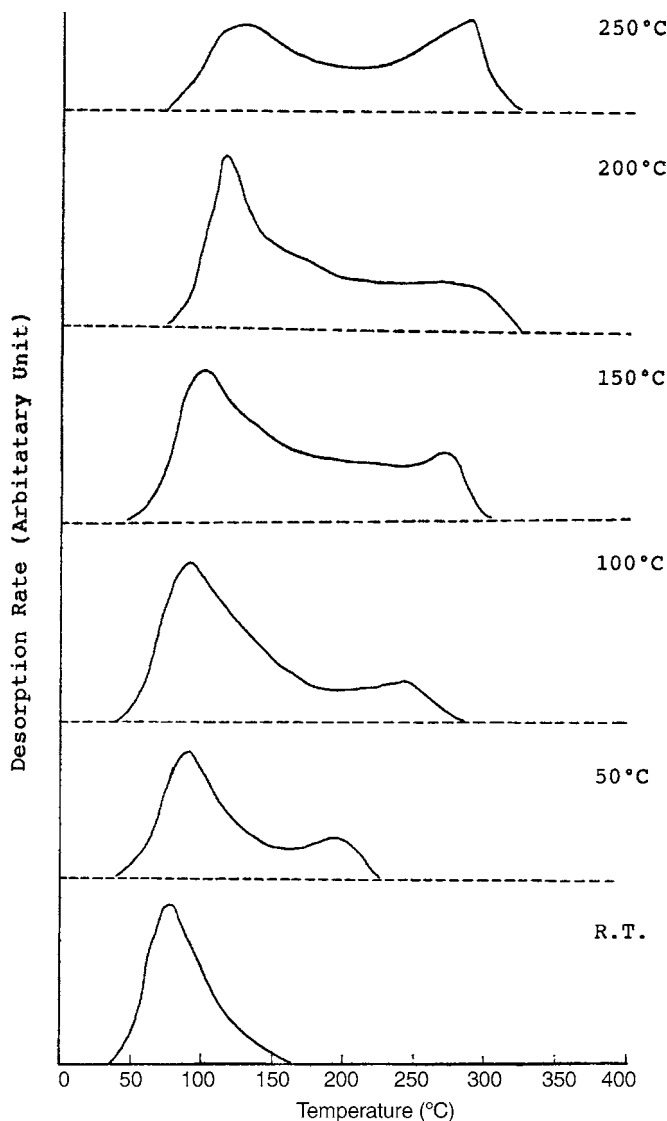
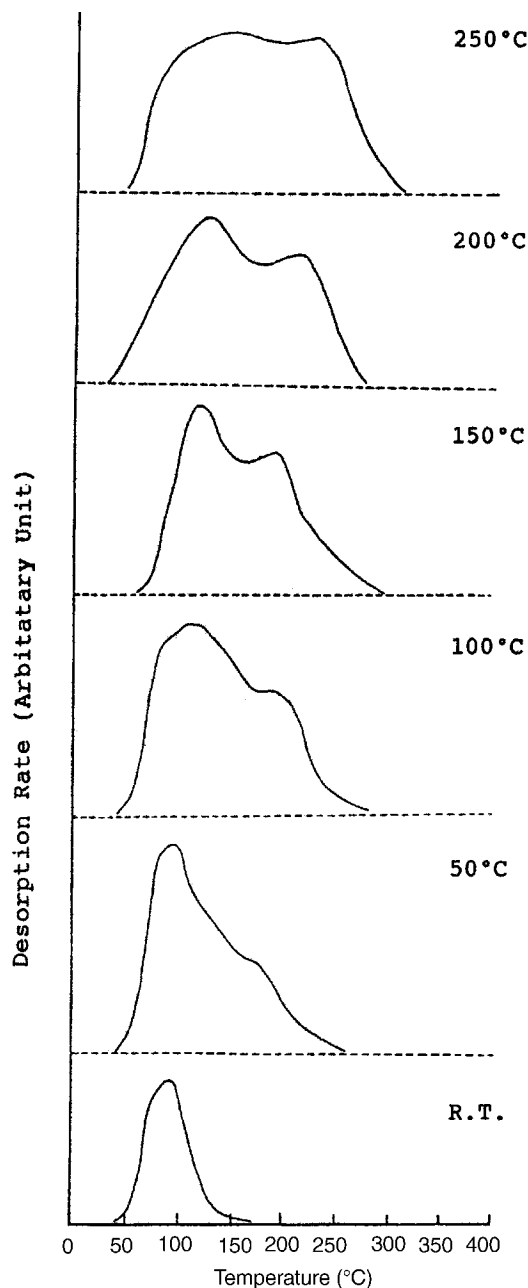Fig. 7. The TPD spectra of 5% Ru/TiO$_2$ which was reduced at 300 °C adsorbed at different temperatures.

the TPD profile by Simpson quadrature method. As shown in Fig. 9, the maximum adsorption on Ru/TiO$_2$ reduced at 300 °C and Ru/SiO$_2$ catalysts occurred at about 200 °C, and on Ru/TiO$_2$ reduced at 500 °C and Ru/Al$_2$O$_3$, the temperature of maximum adsorption was higher than 250 °C. If the adsorption is not an activated process, at higher temperature, the hydrogen adsorption would decrease with the increasing kinetic energy of hydrogen molecular. Therefore, the amount of adsorption should decrease with an increase of adsorption temperature. For an activated adsorption system, the increased thermo energy could offer the energy of hydrogen molecules to overcome the potential barriers of adsorption. Although it is normally believed that hydrogen adsorption on transition metals is not an activated process, the activated adsorption of hydrogen on metals has been reported in [16]. According to the method developed by

Fig. 8. The TPD spectra of 5% Ru/TiO$_2$ which was reduced at 500 °C adsorbed at different temperatures.

Lee and Schwarz [15], the activation energy of adsorption could be calculated by:

$$\frac{\theta_f}{1 - \theta_f} = \nu_a e^{-E_a/RT} u^{-1}$$

where ν_a is the frequency factor of adsorption and u the flow velocity, which is a constant in this study. Thus, the activation energy of adsorption, E_a, can be calculated with the fractional coverage θ_f from the TPD profile. Table 1 lists the activation energy of adsorption which decreases in the order of Ru/TiO$_2$ (500 °C reduction) > Ru/Al$_2$O$_3$ > Ru/TiO$_2$
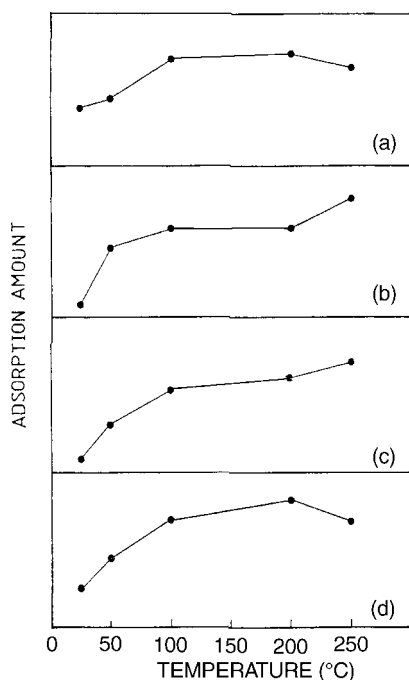
Fig. 9. The relation between the adsorption amount of hydrogen and adsorption temperature: (a) 5% Ru/TiO_2 reduced at 300 °C; (b) 5% Ru/TiO_2 reduced at 500 °C; (c) 5% Ru/Al_2O_3; (d) 5% Ru/SiO_2.

(300 °C reduction) > Ru/SiO_2. Previous investigation [16] has shown that the activation energy of H_2 adsorption was affected by the electronic modification of metal due to the metal–support interactions. For cobalt catalysts, the activation energy of H_2 decreases in the order of Co/Al_2O_3 > Co/SiO_2 > unsupported Co. The results of this study are in accord.

It can be seen in Figs. 5–8, for Ru/TiO_2 (500 °C reduction), Ru/Al_2O_3 and Ru/TiO_2 (500 °C reduction) samples, a high-temperature peak, overlapping with the low-temperature peak, appeared at 250–300 °C while adsorption temperature was greater than 50 °C. This high-temperature desorption peak was attributed to the different adsorbed states of hydrogen, i.e. by hydrogen spillover which involved hydrogen dissociation on the metal, then spillover to the support. A TPD study of hydrogen has been reported by Kramer and Andre [20]. They reported that the desorption peak appeared at high temperature was cased by hydrogen spillover from metal to the support, and the rate of hydrogen spillover increased with an increase of the partial pressure of hydrogen, adsorption temperature and metal dispersion. This study showed that the areas of the high-temperature TPD peaks have a good correlation with the adsorption temperature. In addition, a significantly increase of the area of the high-temperature peak was observed at the highest adsorption temperature. The results indicated that the second peak was not due to the physical adsorption where the adsorption would decrease at high adsorption temperature.

4. Conclusion

Hydrogen adsorption on ruthenium catalysts supported on Al_2O_3, SiO_2 and TiO_2 were characterized using temperature-programmed desorption method to investigate the adsorption–desorption behaviors. All the TPD results show two-peak profile, except Ru/SiO_2. The low-temperature peak was assigned to the hydrogen adsorbed on the Ru metal. The high-temperature peak was attributed to the spillover of hydrogen atoms from metal to the support. Both are activated process. The amount of adsorbed hydrogen increased with increasing adsorption temperature, and the maximum adsorption occurs at above 200 °C. The activation energy of adsorption is a function of catalyst support and the reduction temperature. It decreases in the order of Ru/TiO_2 (500 °C reduction) > Ru/Al_2O_3 > Ru/TiO_2 (300 °C reduction) > Ru/SiO_2. The results demonstrated that the strong metal–support interaction exerted on $Ru/TiO2$ would suppress hydrogen chemisorption at room temperature due to its high activation energy. However, hydrogen chemisorption on $Ru/TiO2$ did not suppress at high temperature. One is able to measure the Ru dispersion by adsorption of hydrogen at high temperature. If the adsorption of hydrogen proceeds during cooling from the reduction temperature, it will pass through the maximum adsorption temperature. In other words, it will overcome the energy barrier of adsorption. Using this technique, one is able to measure the metal dispersion no matter how high is the energy barrier for hydrogen adsorption on transition metals.

Acknowledgements

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