Kinetics study of hydrogen adsorption over Pt/MoO₃

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ABSTRACT

The rate controlling step and the energy barrier involved in the hydrogen adsorption over Pt/MoO₃ were studied. Rates of hydrogen adsorption on Pt/MoO₃ were measured at the adsorption temperature range of 323–573 K and at the initial hydrogen pressure of 6.7 kPa. The rate of hydrogen uptake was very high for the initial few minutes for adsorption at and above 473 K, and reached equilibrium within 2 h. At and below 423 K, the hydrogen uptake still continued and did not reach equilibrium after 10 h. The hydrogen uptake exceeded the H/Pt ratio of unity for adsorption at and above 423 K, indicating that hydrogen adsorption involves hydrogen atom spillover and surface diffusion of the spiltover hydrogen atom over the bulk surface of MoO₃ followed by formation of HₓMoO₃. The hydrogen uptake was scarcely appreciable for Pt-free MoO₃. The rate controlling step of the hydrogen adsorption on Pt/MoO₃ was the surface diffusion of the spiltover hydrogen with the activation energy of 83.1 kJ/mol. The isosteric heats of hydrogen adsorption on Pt/MoO₃ were 18.1–16.9 kJ/mol for the hydrogen uptake range 2.4–2.8×10^{19} H-atom/g-cat. Similarities and differences in hydrogen adsorption on Pt/SO₄²⁻–ZrO₂, Pt/WO₃–ZrO₂ and Pt/MoO₃ catalysts are discussed.

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1. Introduction

Solid acid catalysts such as SO_4^{2-}–ZrO₂, WO₃–ZrO₂ and MoO₃ types exhibit stable and regenerable properties and are highly active at a wide range of reaction temperature, so they have been investigated extensively in recent years [1–3]. The effects of Pt loaded and the presence of hydrogen are essentially identical for those catalysts. They enhance the activity and stability of catalysts in the isomerization of alkanes.

The features of Pt/SO₄²⁻–ZrO₂ and Pt/WO₃–ZrO₂ are essentially the same; both possess strong acid sites and exhibit high activity for the isomerization of alkanes. We have reported the interaction of hydrogen with the surfaces of Pt/SO₄²⁻–ZrO₂ and Pt/WO₃–ZrO₂ catalysts in relation to the generation of active sites from hydrogen and kinetics studies of the hydrogen uptakes [4–7]. The concept of "Molecular hydrogen-originated protonic acid sites" is applicable for both catalysts based on the pyridine preadsorbed IR studies. Hydrogen molecules are dissociatively adsorbed on Pt sites to form hydrogen atoms that spillover onto the supports and undergo surface diffusion. Each spiltover hydrogen atom reaches a Lewis acid site and donates an electron to form an H⁺. The H⁺ is stabilized on an O atom near the Lewis acid site. The Lewis acid site trapping an electron reacts with a second spiltover hydrogen to form an H⁻ bound to a Lewis acid site. The difference between Pt/SO₄²⁻–ZrO₂ and Pt/WO₃–ZrO₂ was the formation temperature of protonic acid sites. The formation was appreciable at 473 and 373 K for Pt/SO₄²⁻–ZrO₂ and Pt/WO₃–ZrO₂, respectively. Kinetics studies of hydrogen adsorption suggested that the rate controlling steps of hydrogen adsorption were surface difussion for Pt/SO₄²⁻–ZrO₂ with the apparent activation energy of 84 kJ/mol [6] and spillover of hydrogen atom for Pt/WO₃–ZrO₂ with the apparent activation energy of 35.5 kJ/mol [7]. The hydrogen adsorption on Pt/SO₄²⁻–ZrO₂ continued for a long time; equilibrium could not be reached even in 24 h at and above 493 K. For the adsorption at and below 473 K, the rate of hydrogen uptake increased to a small extent. However, the hydrogen adsorption on Pt/WO₃–ZrO₂ reached the equilibrium in 2 h at and above 473 K. The hydrogen uptake exceeded the H/Pt ratio of unity for both catalysts.

The roles of Pt and hydrogen on MoO₃ in the formation of HₓMoO₃ have been discussed by several research groups in recent years. Matsuda et al. reported that the improvement of the catalytic activities of MoO₃ could be obtained by addition of Pt to the catalyst and by carrying out the reaction under hydrogen atmosphere [8]. They suggested that the reduction of Pt/MoO₃ proceeded through the formation of high surface areas of HₓMoO₃ which act as active sites for isomerization of alkane. The highest

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activity of catalyst H_xMoO_3 was obtained when MoO_3 was reduced to MoO_2 by 60–70%. Jentoft and co-workers also reported that H_xMoO_3 was found prior to the complete reduction of MoO_3 [9]. They proposed that H_xMoO_3 was the intermediate product in the reduction of MoO_3 to obtain MoO_2. Flanagan and co-workers studied the formation of H_xMoO_3 through the reaction of hydrogen molecules with Pd/MoO_3 [10]. They suggested that H_xMoO_3 can be formed only through H atoms. This result indicated that Pd could act as well as Pt for dissociative adsorption of hydrogen molecule and that the formation of H_xMoO_3 proceeded via spillover and surface diffusion on hydrogen atoms.

Hoang-Van and Zegaoui [11] and Cheng et al. [12] have reported the formation of H_xMoO_3 on Pt/MoO_3 through the hydrogen spillover process over the specific active sites. Hoang-Van reported that the formation of H_xMoO_3 occurs via spillover of hydrogen over Pt at 298–673 K with the value of x in H_xMoO_3 laid between 1.44 and 2.10. Cheng et al. illustrated that the formation of H_xMoO_3 was initiated by dissociation of hydrogen on Pt_6 cluster followed by spillover of the dissociated hydrogen atom onto the support surface and protonation of support to form H_xMoO_3.

Indeed, although extensive researches have been done on the formation, characterization and catalytic activity of H_xMoO_3, there is no report regarding the study of hydrogen adsorption on Pt/MoO_3. In the present work, the interaction of hydrogen with the surface of Pt/MoO_3 was evaluated in relation to the hydrogen uptake, apparent activation energy, heat of adsorption and rate controlling step involved in the hydrogen adsorption based on the assumption that the hydrogen adsorption on Pt/MoO_3 involves dissociative adsorption of hydrogen, spillover of dissociated hydrogen, or surface diffusion as in the cases of $Pt/SO_4^{2-}–ZrO_2$ and $Pt/WO_3–ZrO_2$. The similarities and differences among $Pt/SO_4^{2-}–ZrO_2$, $Pt/WO_3–ZrO_2$ and Pt/MoO_3 are discussed.

2. Experimental

2.1. Catalyst preparation

The MoO_3 sample was prepared by calcination of H_2MoO_4 at 673 K for 3 h. The Pt/MoO_3 was prepared by impregnation of MoO_3 with an aqueous solution of H_2PtCl_6 followed by calcination at 673 K in air. The surface areas of MoO_3 and Pt/MoO_3 were 58 and 65 m^2/g and the content of Pt was 0.5 wt%.

2.2. Hydrogen adsorption

The hydrogen uptake was measured with the automatic gas adsorption apparatus Belsorp 28SA. A catalyst sample was placed in an adsorption vessel and pretreated in a hydrogen flow at 623 K for 6 h, followed by outgassing at 623 K for 6 h, and then cooled to an adsorption temperature and held at that temperature. The adsorption temperature was varied from 373 to 573 K. 6.7 kPa of hydrogen was then introduced into the adsorption system, and the pressure change was monitored with time in order to calculate the hydrogen uptake.

3. Results

Fig. 1 shows the variations in hydrogen uptake on MoO_3 and Pt/MoO_3 as a function of time at 423 K. For Pt/MoO_3, hydrogen uptake occurred very fast and still continued after 10 h. The hydrogen uptake reached 3.8×10^{19} H-atom/g-cat in 10 h. The amount of hydrogen uptake corresponds to the H/Pt ratio of 2.5 which exceeds unity. For Pt-free MoO_3, 2×10^{17} H-atom/g-cat of hydrogen uptake was obtained in 10 h. The amount of hydrogen uptake for Pt/MoO_3 was about 190 times larger than that of Pt-free MoO_3. It is obvious that the presence of Pt is essential for hydrogen uptake on MoO_3.
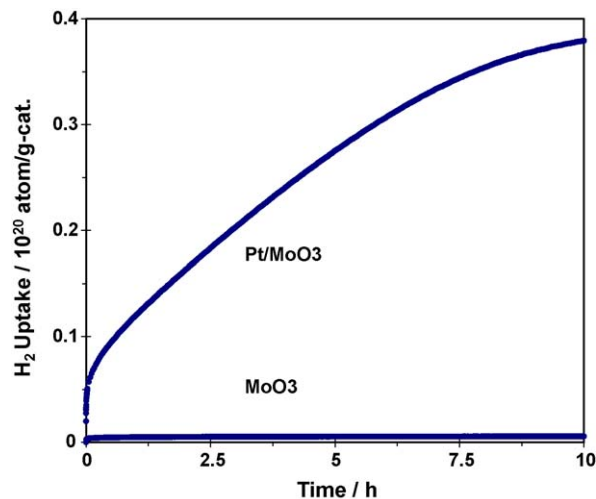

Fig. 1. Variations of hydrogen uptake as a function of time at 423 K for MoO_3 and Pt/MoO_3.
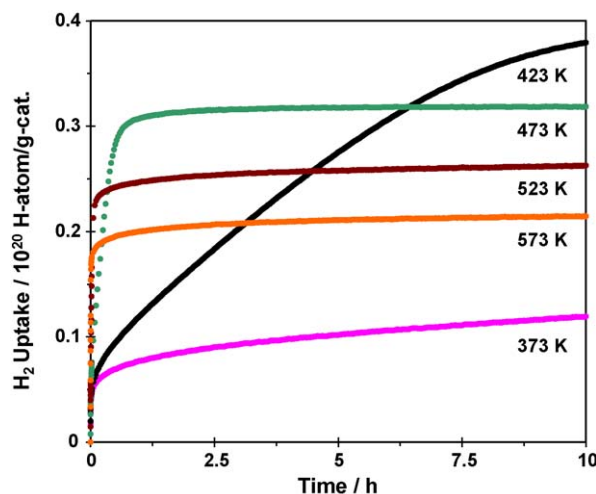

Fig. 2. Variations of hydrogen uptake on Pt/MoO_3 as a function of time at different temperatures.

The variations in hydrogen uptake on Pt/MoO_3 as a function of time at different temperatures are shown in Fig. 2. For the initial few minutes, very fast adsorption occurred at all adsorption temperatures. Almost identical features were obtained when hydrogen adsorption were measured as a function of time at and above 473 K. The hydrogen uptake reached equilibrium within 2 h and the hydrogen uptake was larger for the adsorption at lower temperature. At and below 423 K, the hydrogen uptake was still increasing after 10 h.

Fig. 3 shows the variations in hydrogen uptake on Pt/MoO_3 as a function of time at different initial pressures of hydrogen at a constant temperature of 473 K. The hydrogen uptake reached equilibrium within 2 h for initial hydrogen pressures of 2, 4 and 6.7 kPa. Although these are not shown here, similar figures were obtained when hydrogen uptakes were measured as a function of time at 523 and 573 K for initial hydrogen pressure in the range of 2.0–8.7 kPa. Fig. 4 shows the adsorption isotherma at 473, 523 and 573 K.

4. Discussion

The hydrogen uptake was larger for Pt/MoO_3 than for Pt-free MoO_3. The presence of Pt might facilitate the dissociative adsorption of hydrogen molecules into hydrogen atoms. At 373
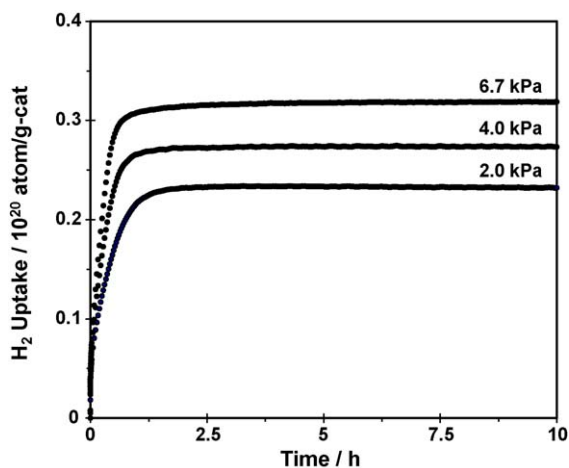
Fig. 3. Variations of hydrogen uptake on Pt/MoO$_3$ at 473 K as a function of time at different hydrogen pressures.
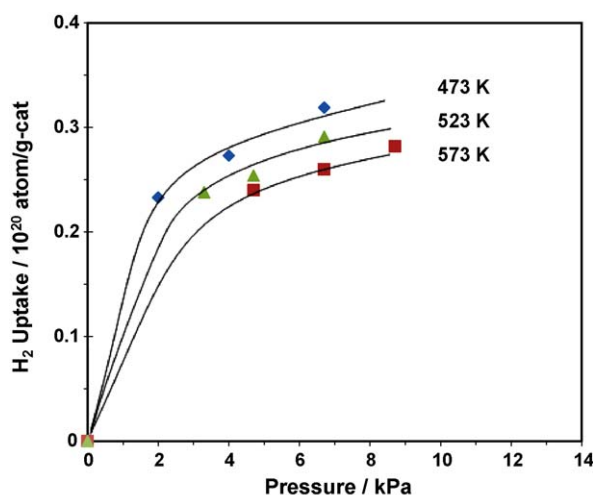

Fig. 4. Plot of equilibrium hydrogen uptake as a function of hydrogen pressure for hydrogen adsorption on Pt/MoO$_3$ at different temperatures.

and 423 K, the rate of hydrogen adsorption on Pt/MoO$_3$ increased slowly and did not reach equilibrium even in 10 h. At and above 473 K, the hydrogen adsorption was very fast and the hydrogen uptake reached equilibrium within 2 h. The hydrogen uptake increased with the increase in the adsorption temperature up to 423 K and decreased at the adsorption temperatures above 423 K. The decrease in the hydrogen uptake with an increase in the temperature indicated that the hydrogen adsorption on Pt/MoO$_3$ is an exothermic process. The hydrogen uptake exceeded the H/Pt ratio of unity for adsorption at and above 423 K.

The features of hydrogen adsorption on Pt/MoO$_3$ strongly suggested that the hydrogen adsorption involves the same successive four steps as in the cases of Pt/SO$_4^{2-}$–ZrO$_2$ [6] and Pt/WO$_3$–ZrO$_2$ [7] type catalysts: dissociative adsorption of hydrogen on specific sites, spillover of the dissociated hydrogen onto the surface of MoO$_3$, surface diffusion of the spillover hydrogen atom over the bulk surface of MoO$_3$ followed by formation of H$_x$MoO$_3$. In the cases of Pt/SO$_4^{2-}$–ZrO$_2$ and Pt/WO$_3$–ZrO$_2$ type catalysts, spillover hydrogen released electrons near the Lewis acid sites and generated protonic acid sites. The H/Pt ratio exceeds unity for all Pt/SO$_4^{2-}$–ZrO$_2$, Pt/WO$_3$–ZrO$_2$ and Pt/MoO$_3$ type catalysts.

Differences among Pt/SO$_4^{2-}$–ZrO$_2$, Pt/WO$_3$–ZrO$_2$ and Pt/MoO$_3$ were observed in the rate of hydrogen adsorption. For Pt/SO$_4^{2-}$–ZrO$_2$, the hydrogen uptake had not reached equilibrium after 24 h [6], while the equilibrium was reached within 6 h and 2 h for Pt/WO$_3$–ZrO$_2$ [7] and Pt/MoO$_3$, respectively. At and above 423 K, increases in the adsorption temperature increased the hydrogen uptake for Pt/SO$_4^{2-}$–ZrO$_2$ but decreased the hydrogen uptake for Pt/WO$_3$–ZrO$_2$ and Pt/MoO$_3$. The other difference is the necessity of active sites to facilitate the dissociative adsorption of hydrogen. The specific active sites such as Pt are required for SO$_4^{2-}$–ZrO$_2$ and MoO$_3$ types, but the hydrogen uptake was considerable for Pt-free WO$_3$–ZrO$_2$. It seems that reduced WO$_3$ acts as active sites to dissociate hydrogen molecule to hydrogen atoms, but no such sites exist on SO$_4^{2-}$–ZrO$_2$ and MoO$_3$.

In general, hydrogen adsorption on Pt sites is fast and it occurs easily at room temperature. Thus, hydrogen adsorption on Pt sites should not be the rate controlling step for continuous hydrogen adsorption which was observed for all adsorption temperature ranges.

In the case where the spillover of the dissociated hydrogen onto the surface of MoO$_3$ is the rate controlling step, the rate of hydrogen adsorption would be expressed by

$$\frac{dC}{dt} = k(C_e - C) \tag{1}$$

where C represents the concentration of the spiltover hydrogen on the support and has the same value regardless of the distance from Pt-support interface, and C_e represents the concentration of the spiltover hydrogen on the support equilibrated with the hydrogen in gas phase on Pt site.

Integration of Eq. (1) yields

$$-\ln\left(1 - \frac{C}{C_e}\right) = kt \tag{2}$$

The value of C/C_e is equal to the value of M/M_e where M_e represents a saturated hydrogen uptake. Eq. (2) can be expressed by

$$-\ln\left(1 - \frac{M}{M_e}\right) = kt \tag{3}$$

where M and M_e represent the hydrogen uptake at time t and at equilibrium, respectively.

The plots of $-\ln(1 - (M/M_e))$ as a function of t are shown in Fig. 5. Since the real values of M_e are unknown for adsorption temperatures at 373 and 423 K, we applied the value of M at 10 h for the values of M_e. Plots of $-\ln(1 - (M/M_e))$ as a function of t for
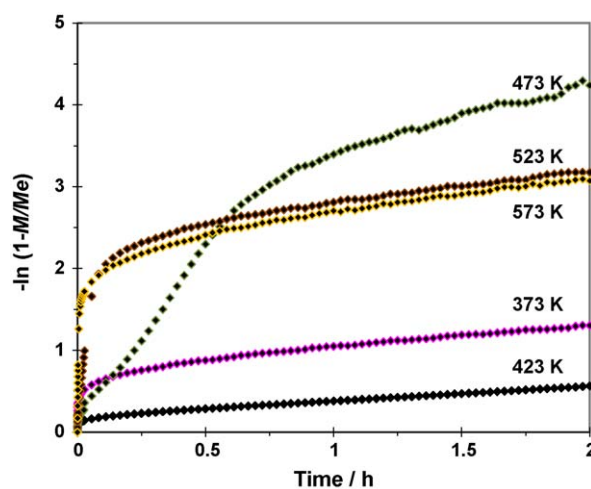

Fig. 5. Plot of $-\ln(1 - (M/M_e))$ as a function of t for hydrogen adsorption at different adsorption temperatures for Pt/MoO$_3$.

different adsorptions deviated far from straight lines for all adsorption temperature range. These results suggested that the spillover of the dissociated hydrogen onto the surface of MoO_3 is not the rate controlling step for the hydrogen adsorption on Pt/ MoO_3.

In the case where the surface diffusion of spiltover hydrogen atoms is the rate controlling step, the rate of adsorption would be expressed by the equation for Fick's second law for surface diffusion.

$$\frac{\partial C}{\partial t} = \frac{D}{x}\left(\frac{\partial}{\partial x}\right)\left(x\frac{\partial C}{\partial x}\right) \quad (4)$$

where C, x, and D represent a surface concentration of hydrogen atoms diffusing over the surface, a distance from the center of hydrogen dissociation site, and a diffusion coefficient of the hydrogen atom, respectively.

The initial and boundary conditions are $C = 0$ when $t = 0$ and $x > a$ and $C = C_0$ at $x = a$ when $t > 0$, where a and C_0 represent a radius of the hydrogen dissociation site, and the concentration of the hydrogen atom on the diffusing surface equilibrated with hydrogen on the hydrogen dissociation site, respectively. These conditions are based on the diffusion into a semi-infinite surface.

Introducing boundary conditions to Eq. (4) yields the following equations when Dt/a^2 is small [7].

$$M = 4\pi^{1/2}aC_0D^{1/2}t^{1/2} \quad (5)$$

where M represents the hydrogen uptake, that is, the amount of the diffusing hydrogen atom.

Plots of M as a function of $t^{1/2}$ for different adsorption temperatures are shown in Fig. 6; and the straight lines were obtained for all adsorption temperature ranges. These results indicated that the surface diffusion of spiltover hydrogen atom is a rate controlling step for the hydrogen adsorption on Pt/MoO_3. The slope of this plot is proportional to the square root of the diffusion constant D. Thus the square of the slope is $16\pi a^2 C_0^2 D$. The diffusion constant is expressed as a function of the temperature T:

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \quad (6)$$

The activation energy is obtained by the Arrhenius plot of the square of the slope, though the values of a and C_0 are unknown. Fig. 7 shows the Arrhenius plot where the slopes of the initial
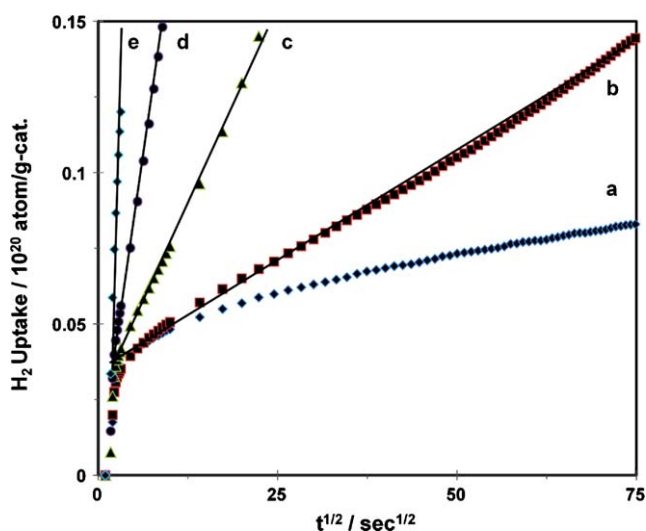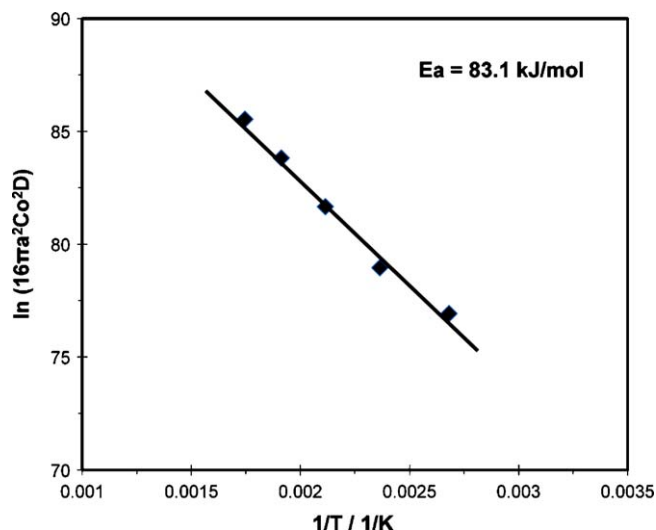

Fig. 7. Plot of $\ln(16\pi a^2 C_0^2 D)$ as a function of $1/T$ for hydrogen adsorption on Pt/ MoO_3.

period of adsorption are taken for all adsorption temperatures. The activation energy is obtained as 83.1 kJ/mol.

Since the rate of hydrogen adsorption on Pt/MoO_3 was expressed by Eq. (5) and was not successfully represented by Eq. (3), it is obvious that the surface diffusion of spiltover hydrogen atoms over the bulk surface of MoO_3 is the rate controlling step for hydrogen adsorption on Pt/MoO_3.

The rate controlling step of the spiltover hydrogen for Pt/MoO_3 is the same for Pt/SO_4^{2-}–ZrO_2. The activation energy of the surface diffusion of hydrogen atoms over Pt/MoO_3 was close to the value reported for Pt/SO_4^{2-}–ZrO_2 [6]. Such results indicated that the interactions between atomic hydrogen and surface site of SO_4^{2-}–ZrO_2 and MoO_3 were almost identical in strength. The activation energy of the surface diffusion of hydrogen atoms over Pt/WO_3–ZrO_2 was reported to be 25.9 kJ/mol [7], indicating that the interaction between atomic hydrogen and surface site is weak for WO_3–ZrO_2 as compared to those for Pt/MoO_3 and Pt/SO_4^{2-}–ZrO_2.

For both Pt/MoO_3 and Pt/SO_4^{2-}–ZrO_2 catalysts, the presence of specific sites such as Pt is required to facilitate the dissociation of hydrogen molecule to hydrogen atoms, whereas for WO_3–ZrO_2, the presence of Pt was not indispensable.

One other difference among Pt/SO_4^{2-}–ZrO_2, Pt/WO_3–ZrO_2 and Pt/MoO_3 was observed in the rate of hydrogen adsorption. The hydrogen uptake began to exceed the H/Pt ratio of unity at and above 423 K for Pt/SO_4^{2-}–ZrO_2 and Pt/MoO_3, while hydrogen uptake exceeded the H/Pt ratio of unity at and above 323 K for Pt/ WO_3–ZrO_2. The differences in the rate of hydrogen adsorption and apparent activation energy are suggested to be caused by the easiness of the surface diffusion of hydrogen atoms; the interaction between atomic hydrogen and surface sites is weaker for Pt/WO_3–ZrO_2 than that for Pt/SO_4^{2-}–ZrO_2 and Pt/MoO_3.

Several research groups have also studied the kinetics and quantitative analysis of hydrogen adsorption based on the assumption that hydrogen adsorption takes place through the steps of spillover of hydrogen atoms and surface diffusion of spiltover hydrogen atoms on the surface of support. Yang et al. analyzed the hydrogen adsorption data on Pt-activated carbon promoted-IRMOF-8 in the adsorption temperature range of 273– 348 K and in the hydrogen pressure range of 1.01×10^2– 1.01×10^4 kPa [13]. They concluded that the rate controlling step of hydrogen adsorption on Pt-activated carbon promoted-IRMOF-8 was surface diffusion with the apparent activation energy of 9.3 kJ/ mol. Kramer and Andre reported that the rate controlling step was

Fig. 6. Plot of hydrogen uptake on Pt/MoO_3 as a function of square root of time at different temperatures: (a) 373 K; (b) 423 K; (c) 473 K; (d) 523 K; (e) 573 K.
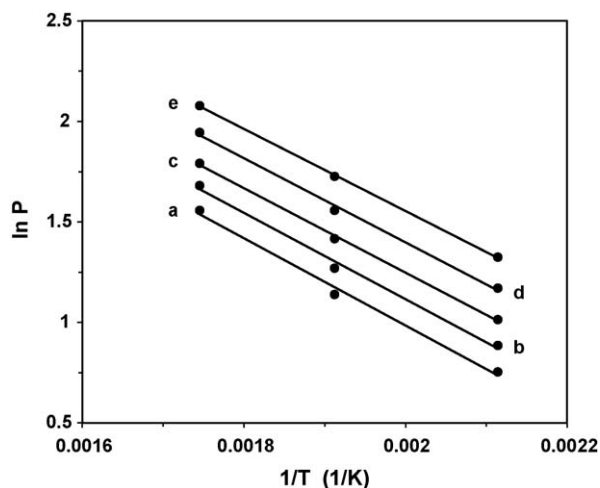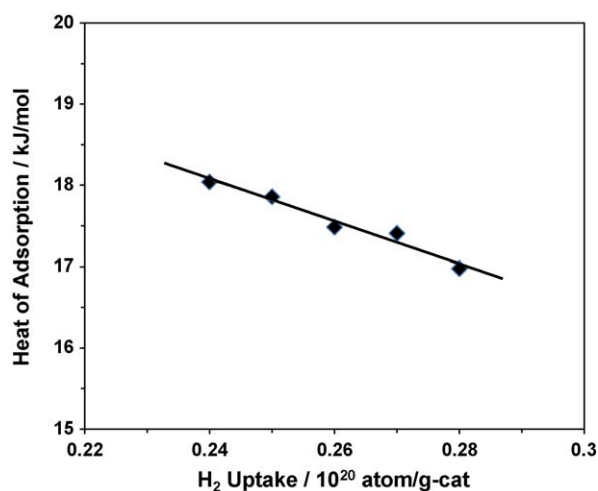
Fig. 8. Plot of $\ln(p)$ as a function of $1/T$ at different hydrogen uptake amounts on Pt/MoO$_3$: (a) 2.4×10^{19} H-atom/g-cat; (b) 2.5×10^{19} H-atom/g-cat; (c) 2.6×10^{19} H-atom/g-cat; (d) 2.7×10^{19} H-atom/g-cat; (e) 2.8×10^{19} H-atom/g-cat.

Fig. 9. Plot of heat adsorption of hydrogen as a function of hydrogen uptake for hydrogen adsorption on Pt/MoO$_3$.

also surface diffusion with the apparent activation energy of 119 kJ/mol for hydrogen adsorption on Ni/Al$_2$O$_3$ in the temperature range of 423–673 K [14]. The hydrogen uptake on Ni/Al$_2$O$_3$ was 1.5–2.0×10^{12} H-atom/cm^2, which was 1/10 the amount for Pt/MoO$_3$ (1.8–5.8×10^{13} H-atom/cm^2) obtained in the present experiment. The difference in the apparent activation energy was caused by the differences in the adsorption conditions and in the properties of surface sites.

Finally, isosteric heats of adsorption of hydrogen were calculated by applying the Clapeyron–Clausius equation to the adsorption isotherms at different temperatures as shown in Fig. 3. Fig. 8 shows a plot of $\ln(p)$ against $1/T$ for the hydrogen uptake

range of 2.4–2.8×10^{19} H-atom/g-cat on Pt/MoO$_3$. The plots give straight lines and the adsorption constants K's can be obtained from the slope of the plots for each hydrogen uptake. Fig. 9 shows isosteric heat of adsorption as a function of hydrogen uptake. The isosteric heats of adsorption are obtained as 18.1–16.9 kJ/mol for the hydrogen uptake range of 2.4–2.8×10^{19} H-atom/g-cat. We reported that the isosteric heats of adsorption for hydrogen adsorption on Pt/WO$_3$–ZrO$_2$ were 1.6–8.0 kJ/mol for the hydrogen uptake range of 2.0–3.0×10^{19} H-atom/g-cat [7]. The heat adsorption of hydrogen on Pt-activated carbon promoted-IRMOF-8 was reported in the range of 20–25 kJ/mol for the hydrogen pressure range of 0–101 kPa [13]. Thus, the 18.1–16.9 kJ/mol for heat adsorption of hydrogen on Pt/MoO$_3$ is a reasonable result compared to the results in previous reports.

5. Summary

(1) The presence of specific sites such as Pt is required in the hydrogen adsorption on MoO$_3$ type catalyst. The hydrogen uptake was scarcely appreciable on Pt-free MoO$_3$.

(2) The hydrogen adsorption on Pt/MoO$_3$ involves dissociation of hydrogen molecule to hydrogen atoms, spillover of the dissociated hydrogen onto the surface of MoO$_3$, surface diffusion of the spiltover hydrogen over the bulk surface of MoO$_3$ and formation of H$_x$MoO$_3$.

(3) The rate controlling step is surface diffusion with the activation energy of 83.1 kJ/mol.

(4) The isosteric heats of hydrogen adsorption are 18.1–16.9 kJ/mol for the hydrogen uptake range of 2.4–2.8×10^{19} H-atom/g-cat.

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