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Application of macro-TG (Shimadzu TGA-51) to hydrogen spillover in a tungsten(VI) oxide system¹

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Abstract

The TGA-51, a new macro-TG which can detect slight weight changes (μg order) in samples of 10 g was developed. As one of applications using this TG, a weight change of Pt-loaded tungsten(VI) oxide in H_2 atmosphere was measured. It is well known that the sample forms hydrogen insertion compounds H_xWO_3 ($x = 0.3\text{--}0.4$) at ambient temperature by hydrogen spillover. Above 373 K, the sample showed a period of delayed reaction of approximately 30 min before the hydrogen insertion and the value of x was lower than that observed at room temperature.

Keywords: TGA-51; Tungsten(VI); Hydrogen insertion

1. Introduction

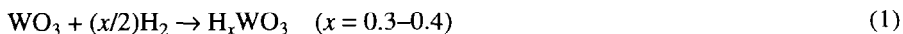
TG analysis is one of the important techniques to determine the thermal properties of materials, that is, a weight change due to oxidation, dehydration, decomposition, etc. However, with most commercially supplied TG instruments it is difficult to measure samples with weights above 1–2 g. Many researchers have requested a macro-TG which can be used for high mass or high volume samples having a slight weight change. To resolve such a request, the Shimadzu Corporation has developed the TGA-51, a new macro-TG [1]. This instrument can analyze a sample weighing up to a maximum of 10 g, and can detect a microgram change in weight.

WO_3 is well known to form hydrogen insertion compounds [2–3]. Especially, WO_3 , which is loaded on a precious metal catalyst, reacts with H_2 at ambient temperature to

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form the mixed conductor H_xWO_3 which has a deep blue color [4]. This catalytic reaction is termed hydrogen spillover. The reaction is represented by Eq. (1):



Because of this formula, WO_3 has been utilized as a sensing device material [5–7] or an electrochromism device (ECD) material [8–10]. If the hydrogen inserting property could be examined without fabricating a device, it would be easy to evaluate the property.

Thermal analysis is generally performed with increasing or decreasing temperature, but in this study, hydrogen insertion was evaluated as a weight change under isothermal conditions.

2. Experimental sample

The method of preparation of the samples is shown in Fig. 1 [11]. A $H_2PtCl_6 \cdot 6H_2O$ (Nacalai tesque, guaranteed reagent, Pt content 37.0%) aqueous solution (10 g l^{-1}) was

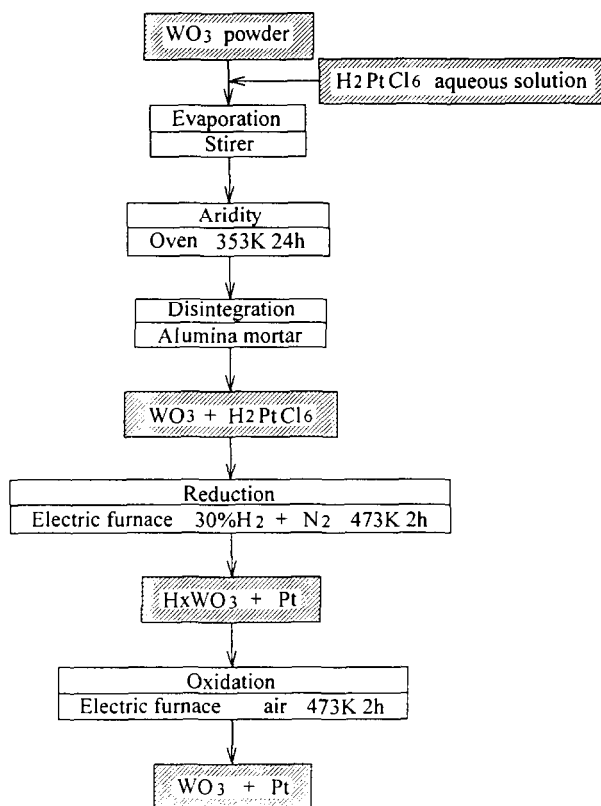


Fig. 1. Method of preparation of Pt loaded WO_3 .

prepared. WO_3 powder (Nacalai tesque, extra pure reagent) was treated with H_2PtCl_6 solution in a beaker to obtain WO_3 which was loaded with 0.01 and 0.1 wt.% of Pt. The mixture was evaporated with stirring and then dried for 24 h at 353 K in an oven. The dried mixture was disintegrated by mechanical mixing. The mixture was then heated to reduce H_2PtCl_6 at 473 K in a flowing atmosphere (100 ml min^{-1}) of Ar containing 30% H_2 . This preparation converts WO_3 to H_xWO_3 at the same time, and the sample was re-heated to oxidize H_xWO_3 to WO_3 under the same conditions in a flowing atmosphere of air.

Ar containing 10% H_2 (Takachiho Kagaku Kogyo Co. Ltd.) was used as a testing gas, and Ar (Iwatani gas Co., purity >99.9999%) was used as a carrier gas.

3. Instrumentation

A schematic of the experimental system is shown in Fig. 2. The flow of the carrier or sample gas was selected along with a Shimadzu FC-40 which consists of two stop valves and two flow meters.

The amount of hydrogen insertion was evaluated on the basis of the weight change of the sample. The weight ratio of H to H_xWO_3 expected is less than 1/600, therefore, a detector is required to detect such a slight weight change. For example, the sample weight for a TG analysis is commonly 10–20 mg and it is doubtful whether such a slight weight change as ca. $30 \mu\text{g}$ can be detected. But, the weight change increases in proportion to

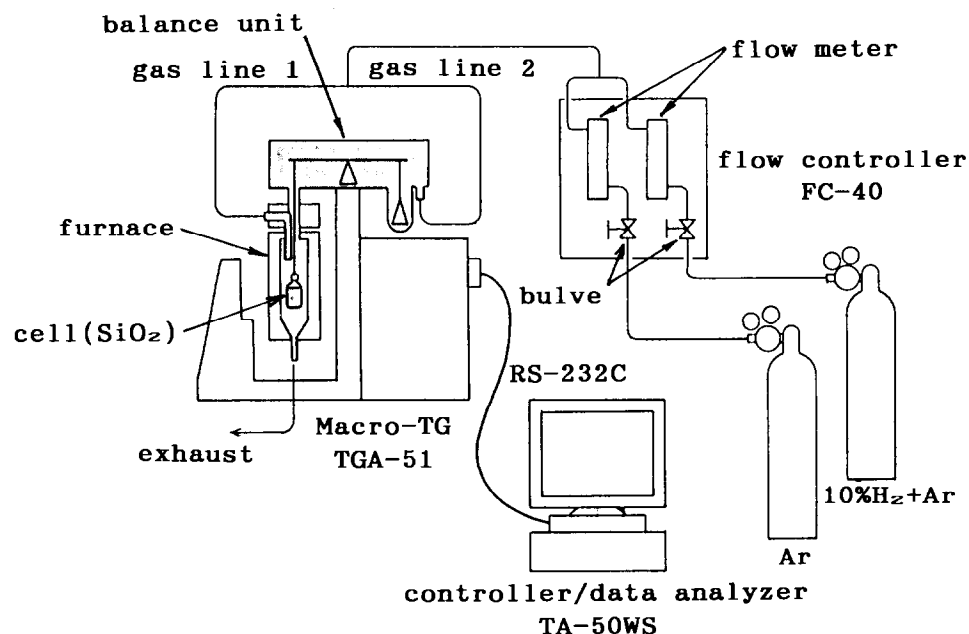


Fig. 2. Schematic of the experimental system.

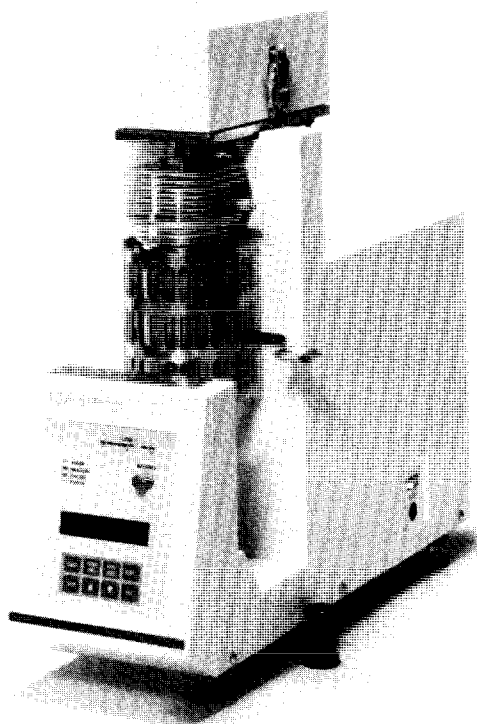


Fig. 3. Exterior of TGA-51.

the sample weight, so it is effective to use a macro-TG because this instrument can detect very slight weight changes. The Shimadzu TGA-51 (a macro-TG) was adopted as the detector in this study. Its specifications are shown in Table 1, and its exterior is shown in Fig. 3.

The gas passing through the FC-40 was divided into two lines, one was introduced into the top of the TG furnace and the other was introduced into the case of the balance mechanism. The sample, about 1.1–1.5 g, was held in a crucible cell (11 × 14, ca. 700 mg) which was made of SiO₂. It is important to use an SiO₂ cell because it does not act as a catalysis. The cell was suspended in the furnace.

The control system, data accumulation and data analysis were performed with the TA-50WS system which consists of a personal computer and software [12].

4. Measurement profile

Fig. 4 shows a typical measurement profile. The sample was heated to 473°K in air to completely remove all inserted hydrogen. After 1 h, Ar gas was introduced and main-

Table 1
Specifications of TGA-51

Item	Ability
Balance type	Taut band
Temperature range	Type (M): room temp. ~1000°C (thermocouple: Chromel-alumel) Type (H): room temp. ~1500°C (thermocouple: Pt-10%Rh-Pt)
Max. sample weight	10 g (including tare)
Atmosphere	Air, inert gas, gas stream, vacuum (<0.5 Torr)
Readability	1 μ g
Measuring range	± 20 mg, ± 200 mg, ± 2000 mg
Accuracy	$\pm 1\%$ each range
Heating rate	Type (M): 0.1–99.9°C min ⁻¹ or °C h ⁻¹ Type (H): 0.1–50.0°C min ⁻¹ or °C h ⁻¹
Holding time	0–999 min or h

tained for 30 min. In order to evaluate the insertion of hydrogen, the sample was then cooled to the testing temperature and held for 30 min. After these preprocesses, the testing gas, i.e. Ar containing 10% H₂ was isothermally introduced.

5. Results and discussion

5.1. Insertion properties

The hydrogen insertion profiles of Pt-loaded (0.01 wt.%) WO₃ at 333 K and 423 K are shown in Fig. 5. At 333 K, a weight gain was observed as soon as the hydrogen was in-

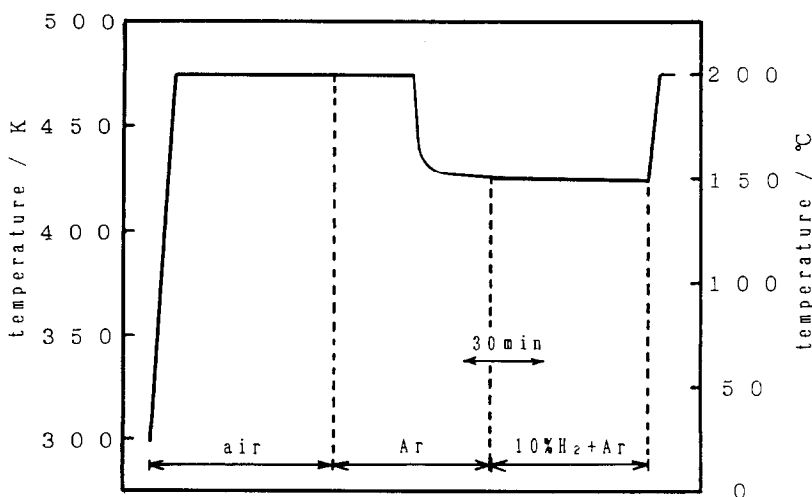


Fig. 4. Temperature and atmosphere conditions of the measurement.

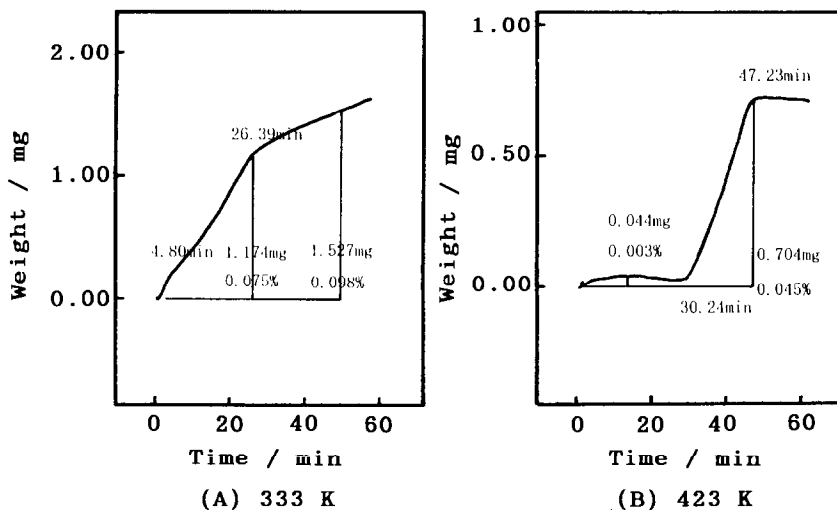


Fig. 5. Hydrogen insertion properties of Pt-loaded (0.01 wt.%) WO_3 in Ar containing 10% H_2 at (a) 333 K and (b) 423 K (sample weight = 1.556 g).

roduced, and it continued for over 50 min. The weight gain is expected to stop at an x value of 0.3 which is reported to be the maximum value for H_xWO_3 .

On the other hand, a different property was observed at 423 K. A $40 \mu\text{g}$ weight gain was observed during the initial 30 min, and a rapid weight gain was observed after this period of delayed reaction. The weight gain stopped at $700 \mu\text{g}$. This value is translated into an x value of 0.12.

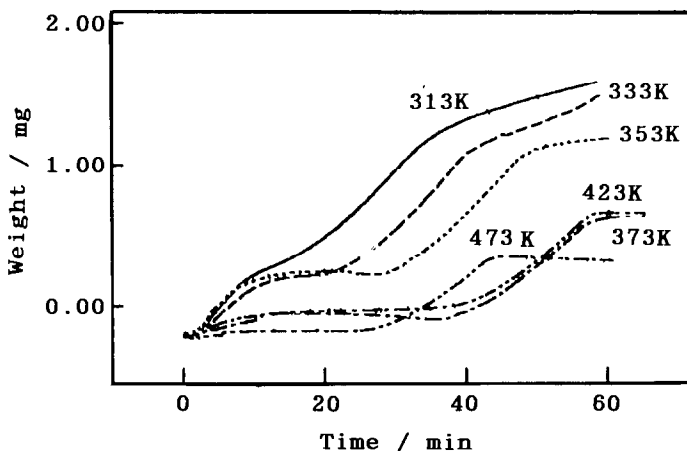


Fig. 6. Hydrogen insertion properties of Pt-loaded (0.1 wt.%) WO_3 in Ar containing 10% H_2 from 313 K to 473 K.

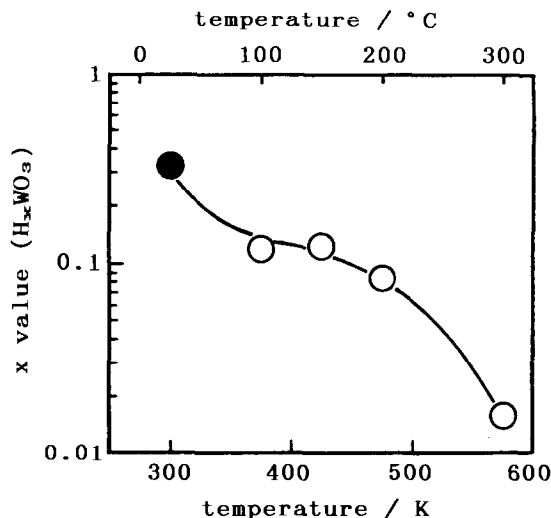


Fig. 7. Maximum hydrogen contents of Pt-loaded (0.1 wt.%) WO₃ in Ar containing 10% H₂ at several temperatures (O, this study; ●, already reported).

5.2. Temperature effects

Hydrogen insertion properties of Pt-loaded (0.1 wt.%) WO₃ from 313 K to 473 K were compared. The results are shown in Fig. 6. The hydrogen content decreases with increasing temperature. The most important point is that there are two groups which can be divided at 373 K. The period of delayed reaction appeared above 373 K, and it is noteworthy that the temperature corresponds to the boiling point of H₂O.

Fig. 7 shows the maximum hydrogen content at each temperature. The values decrease with increasing temperature. The reason for this phenomenon is not obvious but hydrogen may be not able to exist in WO₃ just like a hydrogen storage alloy at higher temperature, because of thermodynamic instability [13].

5.3. Reaction mechanism hypothesis

The insertion properties changing at 373 K shows that H₂O seems to play an important role in the main step. The reaction mechanism was assumed as follows.

Fig. 8 shows the proposed reaction mechanism. Pt-loaded WO₃ is a hydrogenation catalyst. If O₂ remains in the voids among the powders, adsorbed and disassociated hydrogen reacts with O₂ in the atmosphere on the surface of Pt-loaded WO₃ and forms H₂O (Eq. 2) before hydrogen insertion into the WO₃ bulk (Eq. 1).



Apparent insertion rates observed below 373 K were higher than those observed above 373 K. Below 373 K, the H₂O formed remains on the surface and a rapid weight

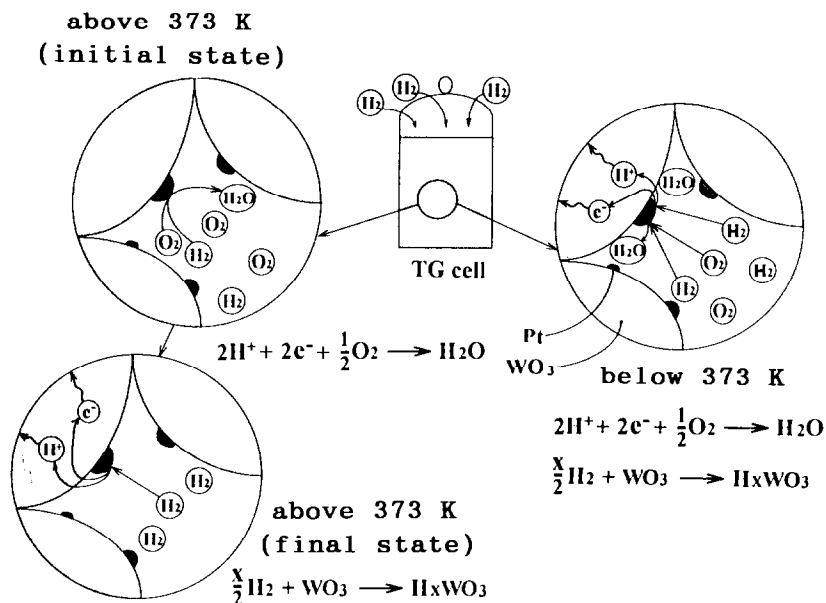


Fig. 8. Schematic reaction mechanism above 373 K and below 373 K to appearance of the period of delayed reaction.

gain is observed. In addition, many studies on WO_3 have reported that the existence of H_2O accelerates the insertion reaction [9,14].

Above 373 K, the H_2O formed evaporates from the surface of the Pt-loaded WO_3 so that the weight gain from hydrogen insertion is not observed until the residual O_2 has been consumed.

5.4. Residual oxygen

If O_2 in the voids of the sample can be removed, the period of delayed reaction is expected to disappear. To completely remove O_2 , a more careful preparation was done. A sample with regulated particle size of 60–100 mesh was used to easily exchange gas. A combination of reducing the pressure of the system to 2 Pa and introducing Ar as the atmosphere was done 10 times during the exchange process. Afterwards, the sample was exposed to 50 ml min^{-1} flowing Ar for 12 h, and heated to the testing temperature in the same atmosphere.

The results are shown in Fig. 9. The period of delayed reaction disappeared but a limitation of hydrogen content still existed. The x value was 0.1 and it was not affected by the period of delayed reaction.

However, there was a possibility that the sample was damaged by the reducing pressure, therefore, this sample was re-measured according to the previous method to check the sample. Fig. 10 shows the reproducibility of the sample in a reducing pressure.

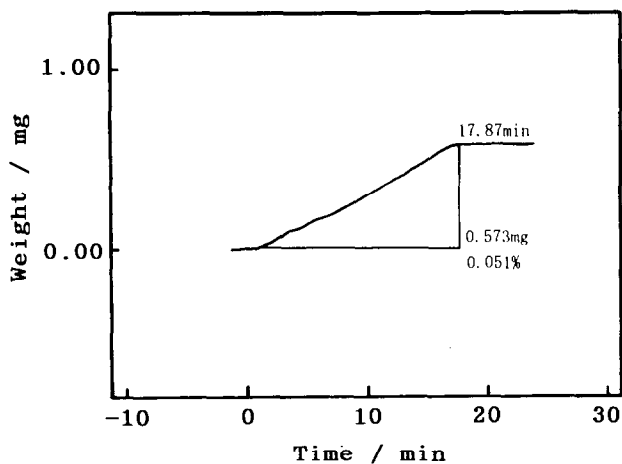


Fig. 9. Response curve of the weight change of Pt-loaded (0.1 wt.%) WO_3 in Ar containing 10% H_2 at 423 K after the preprocess; reducing the pressure to 2 Pa and introducing Ar 10 times. Ar flow for 12 h at room temperature.

The results of these experiments show that the period of delayed reaction is caused by the existence of O_2 .

5.5. Coexistence of hydrogen and oxygen

If the proposed reaction mechanism is correct, the weight gain from hydrogen insertion would not be observed above 373 K in air. The experiment was performed on Pt-loaded (0.1 wt.%) WO_3 at 333 K and 423 K in an air containing 1% H_2 atmosphere.

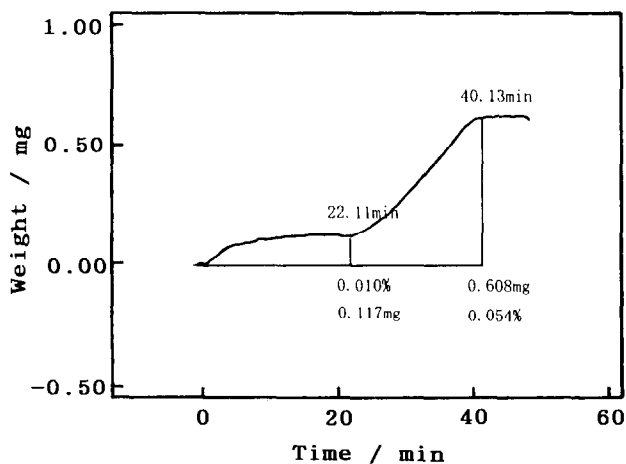


Fig. 10. Reproducibility of the period of delayed reaction.

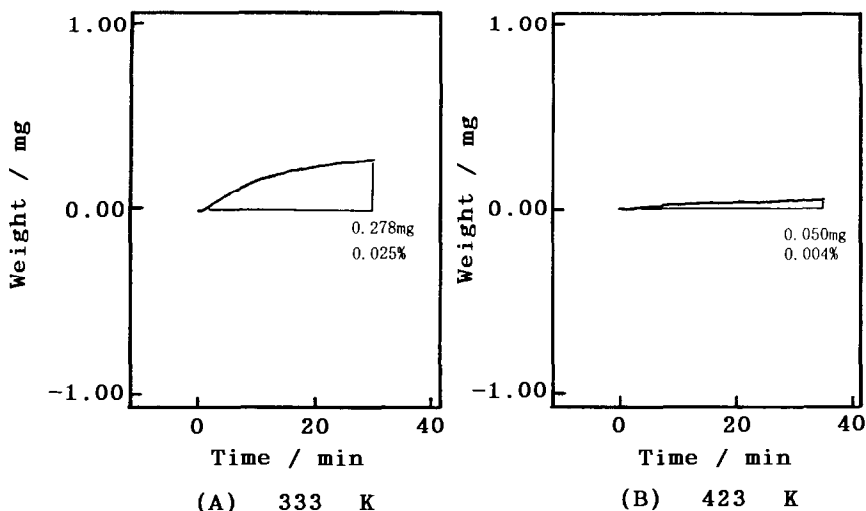


Fig. 11. Hydrogen insertion properties of Pt-loaded (0.1 wt.%) WO_3 in air containing 1% H_2 at (a) 333 K and (b) 423 K (sample weight = 1.121 g).

Fig. 11A shows the hydrogen insertion profile at 333 K, i.e. below 373 K. A $270 \mu\text{g}$ weight gain gave a total weight of 1.121 g. This fact indicated that the value of x was changed to 0.06 in spite of the presence of oxygen. On the other side, Fig. 11B shows a $40 \mu\text{g}$ weight change was observed at 423 K, i.e. above 373 K, however, the change can be regarded as a negligible value.

The difference in these phenomena, just as described in the previous section, seems to indicate that it was caused from the presence or absence of H_2O evaporation. It is assumed that reaction (2) occurred on the sample's surface in both cases because of the presence of O_2 . At 333 K, the weight gain continued with reactions (1) and (2) in equilibrium. But at 423 K, the H_2O formed was continuously evaporated, and little weight gain was observed under this condition.

The reason for the appearance of the period of delayed reaction above 373 K can be reasonably explained by the presence of residual oxygen.

6. Conclusions

The hydrogen insertion properties of Pt-loaded WO_3 were evaluated using a macro-TG. The maximum hydrogen contents of Pt-loaded WO_3 decreased with increasing temperature. Also, the hydrogenation catalysis of Pt-loaded WO_3 and temperature affected hydrogen insertion properties when O_2 was present in the atmosphere, because H_2 reacted with O_2 on the surface of the Pt-loaded WO_3 . If the temperature was below 373 K, the H_2O formed remained on the surface, but the insertion reaction can go on at the same time, then a weight gain was rapidly observed. But above 373 K, H_2O formed was con-

tinuously evaporated, and a conspicuous weight gain was not observed until all of the O₂ in the atmosphere had been consumed.

The aim was to evaluate the capability of thermal analysis for hydrogen insertion. It is concluded that the macro-TG is useful to evaluate such application.

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