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Dehydrogenation of tetralin on Pd/C and Te-Pd/C catalysts in the liquid-film state under distillation conditions

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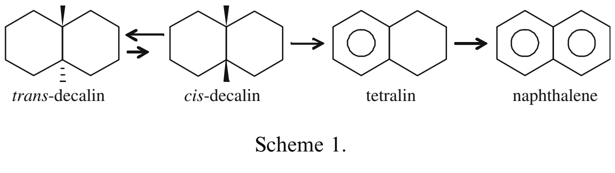
The dehydrogenation of tetralin to naphthalene in the liquid-film state on Pd/C and Te-Pd/C catalysts was investigated under reactive distillation conditions at 493 K. The conversion of tetralin was high, when observed using 0.3 g of Pd/C at a specific volume of tetralin (0.9 mL) was used, while the addition of tellurium into the Pd/C catalyst resulted in a similar high conversion using 0.3 g of Te-Pd/C with a somewhat wider volumetric range (0.8–1.1 mL) of tetralin.

KEY WORDS: dehydrogenation; tetralin; naphthalene; palladium; tellurium.

1. Introduction

The combination of decalin/naphthalene system has been proposed as an effective carrier of hydrogen [1]. The catalytic hydrogenation of naphthalene to decalin was established in the 1940s [2] while active catalysts for the dehydrogenation of decalin to naphthalene have been developed more recently. Saito and co-workers reported that, under reactive distillation conditions, the catalytic dehydrogenation of decalin could be accomplished effectively in the liquid-film state with a Pt/C catalyst [3–5]. In the liquid-film state, the volume of decalin and catalyst are limited, not to suspend the catalyst but to keep wet. For example, the combination of a specific volume of decalin (1.0 mL) and catalyst (0.3 g) was suggested for the liquid-film state while a volume of decalin less or more than 1.0 mL was not suitable for use in the liquid-film state [3–5]. Under these conditions, the temperature of the catalyst layer in the ‘‘liquid-film’’ state exceeds the boiling point of the solution. It has been proposed that such high temperature conditions accelerate the rates of both dehydrogenation and product desorption [5]. Different from conventional gas or liquid phase reactions, the dehydrogenation of decalin (boiling point, 458 and 466 K for the trans- and cis-isomers, respectively) occurs efficiently at 483 K on Pt/C in the ‘‘liquid film state’’ because of the smooth release of hydrogen from the reaction media and the suppression of the reverse reaction [6]. However, such limited conditions are not suitable from a practical point of view since it is difficult to maintain the specific ratio of the catalyst/substrate in a commercial reaction system. If various volumes of substrate instead of a specific volume of substrate could be employed, that is, if the reaction conditions can be extended, the present system might have more commercial applicability. This might be achieved via a use of a catalyst, has high activity under the extended liquid-film conditions. Furthermore, the decalin/naphthalene system has some disadvantages: (1) a rather low affinity between decalin and the catalyst [7]; (2) the formation of the less reactive trans-decalin than the more reactive cis-decalin from the hydrogenation of naphthalene [8] (Scheme 1). If tetralin was employed instead of decalin, the above two disadvantages could be avoided since tetralin has an aromatic ring that may lead to advantageous adsorption on the catalyst [7] and tetralin does not exist as isomers. It has previously been reported that Pd/C catalysts have substantial activities for the dehydrogenation of tetralin in the liquid phase [7]. Furthermore, it has been reported that the activities of Pd/C catalysts for dehydrogenation can be enhanced by the addition of tellurium to the catalysts [9,10]. In the present study, tellurium was introduced into a Pd/C catalyst, in order to enhance its activities for the dehydrogenation of tetralin to naphthalene under the extended liquid-film states.



Scheme 1.

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2. Experimental

The 5 wt.% Pd/C catalyst was purchased from Wako Pure Chemicals (Osaka, BET surface area: 824 m^2/g) and was used as supplied. The Te-Pd/C catalyst was prepared by impregnating commercially available 5 wt.% Pd/C with a given amount of H_6TeO_6 (Kanto Kagaku, Tokyo) dissolved in distilled water. The suspension was reduced with a formalin solution (37%, Wako) at 343 K for 2 h. The suspension was separated by filtration and the residue was washed and dried at 343 K overnight *in vacuo*. In the present study, 5 wt.% Pd/C, 0.6 wt.% Te-5 wt.% Pd/C, 1.5 wt.% Te-5 wt.% Pd/C and 1.8 wt.% Te-5 wt.% Pd/C were prepared and are hereafter referred to Pd/C, 0.6Te-Pd/C, 1.5Te-Pd/C and 1.8Te-Pd/C, respectively. The surface areas of 0.6Te-Pd/C, 1.5Te-Pd/C and 1.8Te-Pd/C were 911, 855 and 807 m^2/g, respectively. The batch-wise catalytic dehydrogenation of decalin was performed in a two-necked Kjeldahl flask with a short neck (50 mL) equipped with a reflux condenser, which was cooled at 278 K, connected to a gas burette and a liquid-supplying/sampling port. Unless otherwise stated, the typical procedure for obtaining mild reactive distillation conditions in the liquid-film state was as follows [11]. A prescribed amount (0.3 g) of catalyst was placed in the reactor, which was then evacuated at 433 K for 1 h *in vacuo*. After adjusting the temperature of the reactor to room temperature, N_2 was introduced, followed by the careful introduction of tetralin (Iwatani Gas, Osaka) onto the catalyst under an N_2 atmosphere, in order to avoid scattering both the catalyst and the tetralin in the reactor. The catalyst and tetralin was then homogeneously dispersed by ultrasonic treatment, to reach reproducible experimental results. The temperature was again raised to the reaction temperature (493 K) and the evolution of hydrogen was monitored volumetrically for 2.5 h. The deviation in volumetric data after 2.5 h was within 10%. After the reaction, the residue in the reactor was analyzed by TCD-GC (Shimadzu GC-8APT) with a 3 mm × 3 m Silicone OV-1/Unioport HP at 373 K. The surface areas of the catalysts were calculated from adsorption isotherms obtained using a conventional BET nitrogen adsorption apparatus (Nippon Bel, BELSORP 18). Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500 × diffractometer, using monochromatized Cu–Kα radiation. The patterns were recorded over the 2 θ range of 5–60 degrees. X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-1000AX) was carried out using monochromatized Mg Kα radiation. Since the catalysts employed in the present study were not molded using an ordinary method, a mixture of BN (Wako) and catalyst (1:2 by weight) were finely triturated and pressed at 6 t into a pellet and was used in the XPS analysis. The binding energy was corrected using 284.3 eV for C 1s from the support since signal due to an internal standard was completely overlapped with that of the support.

3. Results and discussion

It has previously been reported that more evolution of hydrogen together with a high conversion of decalin is achieved in the liquid-film state in the dehydrogenation of decalin with Pt/C than the suspended and dried states [1,3–5,8,11]. It should be noted that the liquid-film state could be obtained in the specific ratio of the catalyst and decalin. In the dehydrogenation of decalin with Pt/C, the combination of 0.3 g of the catalyst and 1 mL decalin resulted in liquid-film state. In order to further investigate the liquid-film state in the dehydrogenation of tetralin with the Pd/C catalyst, the conversion of tetralin was carried out using various volumes of tetralin (0.7, 0.8, 0.9, 1.0 and 1.1 mL) and a constant amount of Pd/C (0.3 g) at 493 K for 2.5 h. As shown in figure 1, the conversion of tetralin after 2.5 h showed a maximum value for a volume of tetralin of 0.9 mL. The present catalyst state corresponds to the "liquid-film" state previously proposed in the dehydrogenation of decalin with Pt/C [1,3–5,8, 11]. It should be noted that it is difficult to maintain the reaction conditions required for the liquid-film state since a specific volume and weight of the substrate and catalyst (0.9 mL and 0.3 g, respectively) needs to be employed. In order to overcome these disadvantageous, tellurium was introduced into the Pd/C used in the dehydrogenation of tetralin. As shown in figure 2, the higher conversion of tetralin, corresponding to the conversion at 0.9 mL of tetralin with Pd/C (0.3 g), was observed over a rather wide volume range of tetralin from 0.8 to 1.1 mL with the 0.6Te-Pd/C and 1.8Te-Pd/C catalysts. However, such an improvement by the introduction of Te into Pd/C was not observed in the case of 1.5Te-Pd/C. It is evident that

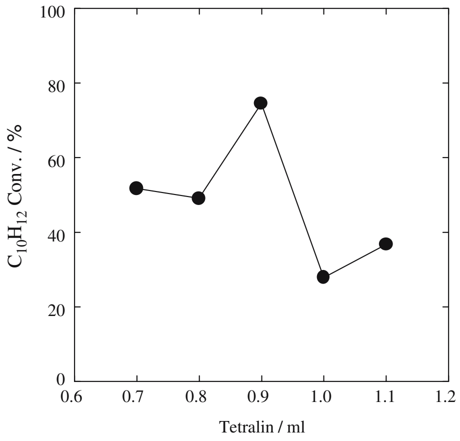


Figure 1. Dehydrogenation of various amounts of tetralin with 5 wt.% Pd/C (0.3 g) at 493 K. The conversion was obtained after 2.5 h.

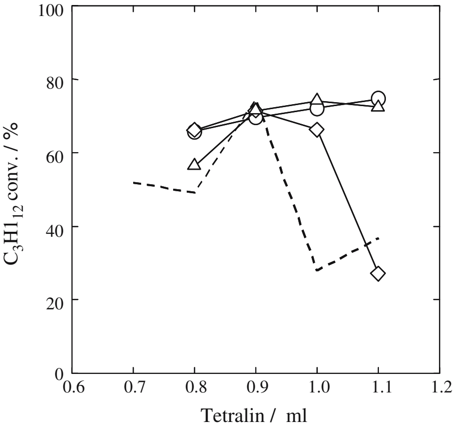


Figure 2. Dehydrogenation of various amounts of tetralin with 5 wt.% Pd/C (dashed line), 0.6 wt.% Te-5 wt.% Pd/C (○), 1.5 wt.% Te-5 wt.% Pd/C (◇) and 1.8 wt.% Te-5 wt.% Pd/C (△) at 493 K. Amount of catalyst : 0.3 g. The conversion was obtained after 2.5 h.

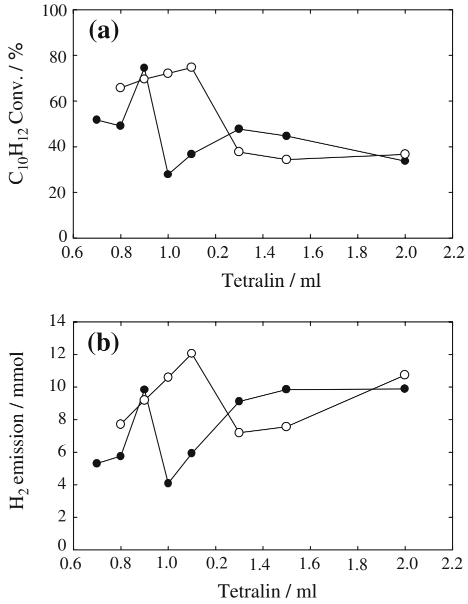


Figure 3. Dehydrogenation of various amounts of tetralin with 5 wt.% Pd/C (●) and 0.6 wt.% Te-5 wt.% Pd/C (○) at 493 K. Amount of catalyst : 0.3 g. The conversion was obtained after 2.5 h. (A) and (B) were the conversion of tetralin and hydrogen emission after 2.5 h, respectively.

the introduction of a certain amount of tellurium into the Pd/C resulted in an enhancement in the conversion of tetralin, which is of interest, from a practical point of view. In order to estimate the effect of tellurium on the evolution of hydrogen in the initial duration, the initial rate of hydrogen evolution was calculated (table 1). It is evident that the effects of tellurium on the conversion of $C_{10}H_{12}$ are different from those on the initial activity. The dehydrogenation of tetralin was observed when an amount of tetralin from 0.7 to 2.0 mL with 0.6Te-Pd/C (0.3 g) was employed, in an examination of the effect of the introduction of tellurium into Pd/C on the liquid-film and suspended states (figure 3). Figure 3 (A) and (B) shows the conversion of tetralin and hydrogen emission after 2.5 h, respectively. Unfortunately an enhancement by the addition of tellurium to Pd/C was not observed in the suspended state. Figure 4 shows XRD patterns of 0.6Te-Pd/C before (A) and after obtaining the results shown in figure 3 for amounts of tetralin of 0.8 (B), 1.1 (C), and 1.3 mL (D), respectively. Information on Te could not be obtained from XRD data due to the small amount of tellurium in the catalysts while an XRD pattern due to metallic Pd (JCPDS 46–1043) was detected from those samples regardless of the conditions employed. In order to obtain information on the catalyst surface, four catalysts before use in the dehydrogenation reactions were analyzed by XPS. The signal due to Pd $3d_{5/2}$ was observed at 335.4 $\pm$ 0.2 eV from those catalysts and no shoulder was detected in XPS spectra of Pd $3d_{5/2}$. Although a signal due to Te $3d_{5/2}$ from 1.8Te-Pd/C was detected at 576.7 eV without

Table 1
Initial rate of hydrogen evolution (mmol/h) for various Pd-C and Te-Pd-C (both 0.3 g) at 493 K

	Tetralin (mL)			
	0.8	0.9	1.0	1.1
0 wt.% Te-5 wt.% Pd/C	21.6	10.4	10.7	13.4
0.6 wt.% Te-5 wt.% Pd/C	29.3	27.1	13.6	12.8
1.5 wt.% Te-5 wt.% Pd/C	30.1	23.3	9.8	9.3
1.8 wt.% Te-5 wt.% Pd/C	26.8	29.2	12.1	11.9

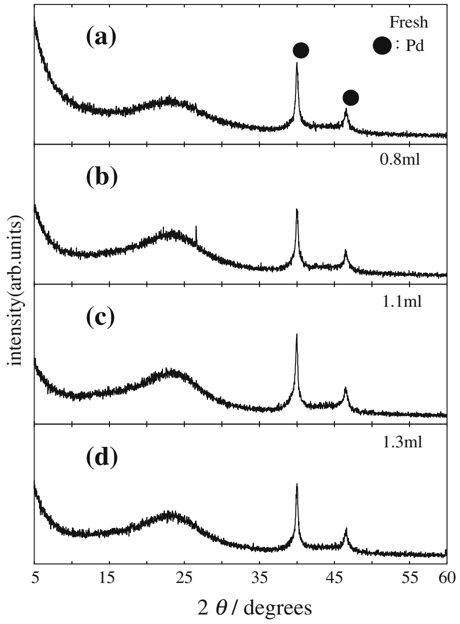
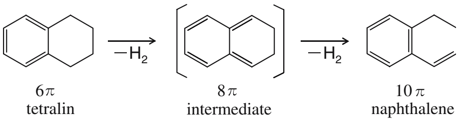


Figure 4. XRD pattern of 0.6 wt.% Te-5 wt.% Pd/C before (A) and after obtaining the results shown in figure 3, for an amount of tetralin of 0.8 (B), 1.1 (C), and 1.3 mL (D), respectively.



Scheme 2.

any shoulder, the correct binding energy for Te $3d_{5/2}$ from 1.5Te-Pd/C and 0.6Te-Pd/C could not be read due to the unacceptable S/N ratio. It should be noted that the atomic ratios on the surface of Te/Pd in 1.8Te-Pd/C, 1.5Te-Pd/C and 0.6Te-Pd/C were 0.17, 0.02 and 0.03, respectively, indicating that the effects of Te on the dehydrogenation cannot be explained by the surface composition of Pd and Te, and not by the corresponding bulk composition.

As described in the present study, the introduction of tellurium into Pd/C resulted in an enhancement in catalytic activities in the liquid-film state while the introduction of a specific amount of tellurium resulted in a decrease in the activities. Similar effects of the introduction of tellurium into Pd/C have already been reported in the liquid phase deacetoxylation of 1,3-butadiene [9] and the liquid phase oxidative dehydrogenation of sodium lactate to the corresponding pyruvate [10]. In both reactions, the introduction of a certain amount of tellurium into the Pd/C resulted in an enhancement in the activities while a decrease in activities was observed with catalysts containing an excess amount of tellurium [9,10]. It has been suggested that the formation of Pd_3Te (Te/Pd = 0.33) contributes to the decrease of the activities in the latter reaction [10]. In the Te-Pd system, various intermediate phases of Pd_4Te (Te/Pd = 0.25), Pd_3Te (Te/Pd = 0.33), $Pd_{2.5}Te$ (Te/Pd = 0.40), Pd_2Te (Te/Pd = 0.50), PeTe (Te/Pd = 1.0) and $PdTe_2$ (Te/Pd = 2.0) were identified [12]. It should be noted that the atomic ratio of Pd_4Te is similar to that for the 1.5Te-Pd/C catalyst (Te/Pd = 0.25), which showed somewhat lower activities than 0.6Te-Pd/C (Te/Pd = 0.10) and 1.8Te-Pd/C (Te/Pd = 0.30) near the liquid-film state (figure 2), indicating that the formation of those intermediate phases or the corresponding precursors may be responsible for the rather low activities. Unfortunately the reason for why Te-Pd/C showed higher activities near the liquid-film state is not yet clear. However, it is noteworthy that the catalyst appears to possess a favorable affinity for the reactant and the products. Takehira *et al.* proposed that Te-Pd-C system has a great affinity for the conjugated systems such as π-allyl intermediate [9]. It is possible that a 8π-conjugated system together with 6π-(tetralin) and 10π- (naphthalene) conjugated systems contributes to the dehydrogenation of decalin on the Te-Pd/C catalysts (Scheme 2). Furthermore, hydrogen formed from the dehydrogenation of decalin also interacts with tellurium since it is generally known that tellurium possesses various valences of 6+, 4+, 2+, 0 and −2, the latter of which forms H_2Te analogous to H_2O and H_2S. Therefore, it is possible that the introduction of tellurium into Pd/C results in the formation of a unique site, which has a favorable affinity for both reactants and products, leading to the enhancement in the activities in the liquid-film state.

4. Conclusion

The liquid-film state was confirmed in the dehydrogenation of tetralin (0.9 mL) with 5 wt.% Pd/C catalysts (0.3 g) at 493 K. When tellurium was introduced at 0.6 and 1.8 wt.% into the 5 wt.% Pd/C, an enhancement in the activities was observed near the liquid-film state. The results herein reveal that the conditions required for producing needed to the liquid-film state for decalin on Pt/C can be extended and can be more easily employed for the dehydrogenation of tetralin.

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