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Selectivity controlling in the hydrogenation of 1,3-butadiene on Tl-modified Pd catalyst

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The selectivity and reactivity in the hydrogenation of 1,3-butadiene catalyzed by Tl-modified 5 wt% Pd/Al_2O_3 catalysts vary with amounts of Tl loading and with the reduction temperatures, that is, the main product was 1-butene and trans-2-butene for values of Tl loading of 0.5 and 2 in Tl/Pd atomic ratio, respectively, when the catalysts were reduced at 673 K. 1,3-butadiene was hydrogenated selectively towards 1-butene and trans-2-butene when the Tl modified 5 wt% Pd/Al_2O_3 catalyst of Tl/Pd = 2 was reduced at 300 and 373 K or above, respectively. On the catalyst with Tl/Pd = 2 reduced at 373 K or above, the butenes formed are not hydrogenated to butane, even after a long reaction time. These results suggest the formation of Pd–Tl alloy or intermetallic compounds during the reduction procedure which is responsible for the selectivity controlling in the reaction. TPR and XRD results were in consistence with the reaction data.

Keywords: Tl; Pd; bimetallic; alloy; intermetallic; catalyst; hydrogenation; 1,3-butadiene; selectivity

1. Introduction

Small metal particles on various supports diffuse, coalesce or break up when the temperature is high enough [1]. For example, TEM studies show that Pd metal film deposited on alumina breaks up into metal crystallites at 423 K in H_2 atmosphere which eventually sinter to bigger crystallines at 737 K [2,3]. The metal particle size influences catalytic performances, especially catalytic activity in structure-sensitive reactions, such as hydrogenolysis of ethane and CO hydrogenation [4]. The preparation of small and stable metal particles may be realized by the choice of a suitable support or the selection of the preparation method. But, when it comes to bimetallic particles, the situation will be much more complex.

It has been previously reported [5,6] that Tl-modified palladium catalysts exhibit remarkably high selectivities in the hydrodechlorination of CFC-113 (1,1,2-

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trichlorotrifluoroethane) towards trifluoroethene on low-loading Tl and chlorotrifluoroethene on high-loading Tl catalysts. We report here that the Tl-modified Pd catalysts show a drastic change of selectivity and reactivity with Tl loading and with H_2 reduction temperature of the catalysts in the hydrogenation of 1,3-butadiene. The structure controlling of the Tl-modified catalysts has been discussed in conjunction with the facile formation of a Tl–Pd binary alloy or intermetallic compounds.

2. Experimental

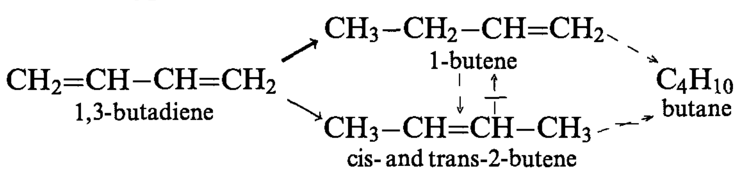
5 wt% palladium supported on alumina (averaged Pd particle size = 4 nm, dispersion determined by CO chemisorption = 18%) was purchased from N.E. Chemcat. Co. and was impregnated with an aqueous thallium nitrate solution. The modified catalysts are expressed as nTlmPd/Al_2O_3 (n = Tl/Pd in atomic ratio, m = Pd loading in wt%), e.g. 1Tl5Pd/Al_2O_3 stands for a 5 wt% Pd on Al_2O_3 catalyst impregnated with Tl to an atomic ratio Tl/Pd of 1. After drying at 373 K overnight the catalyst was charged in a reactor. Hydrogenation of 1,3-butadiene was conducted in a closed circulating system (ca. 150 ml volume) of Pyrex glass. After reduction at a set temperature for 2 h and evacuation at the same temperature for 10 min, the catalyst was exposed to a reaction mixture consisting of 1,3-butadiene : H_2 = 1 : 2 (total pressure = 33 kPa) at 273 K. In some cases, a reaction mixture of 1,3-butadiene : cis-2-butane : H_2 = 1 : 1 : 4 (total pressure = 33 kPa) was used. The reaction products were analyzed by a GC (Hitachi 023 type) with a 4 m VZ-7 column at room temperature. Depending on the activity of the catalyst, the amount of catalyst and the reaction temperature were adjusted between 10–100 mg and 235–473 K, respectively, so as to get a proper reaction rate.

Temperature programmed reduction experiments (TPR) were performed with an Altamira AMI1. A sample pretreated with flowing dry air at a set temperature for 1 h and cooled down to 230–240 K in flowing Ar gas with a liquid nitrogen bath was exposed to a flowing gas mixture of H_2 : Ar = 9.8 : 91.2 mol% (Hokusan Co., pure gas) with a flow rate of 15 ml/min. It takes several minutes for complete switching of gas flow from Ar to the mixing gas. After the complete switching, recording of the TPR spectrum started and the liquid nitrogen bath was removed. The sample was allowed to stand for another 20 min. Then, the linear temperature ramp from 303 to 870 K at 5 K/min was started. The TPR spectrum shows the plot of hydrogen consumption normalized with the weight of catalyst against time on stream, which can be converted to a temperature between 303 and 870 K. The X-ray diffraction pattern was obtained on a MXP-3 (Mac Sci. Co.) diffractometer with Cu Kα radiation. Samples for XRD measurements were reduced at 673 K in H_2 stream and passivated in low purity N_2 stream. Details of the experiments are described elsewhere [5,6].

3. Results and discussion

The time course of the 1,3-butadiene hydrogenation on 0.5Tl5Pd/Al_2O_3 reduced at 673 K is shown in fig. 1A. The concentration of 1-butene increased with time on stream when 1,3-butadiene was present in the gas phase. Close to 0% of 1,3-butadiene concentration, the concentration of 1-butene decreased to 0% but the concentrations of other products, trans- and cis-2-butene and butane, increased. This shows that 1-butene is hydrogenated to butane and is isomerized to trans- and cis-2-butene on the catalysts. As shown in fig. 1B, plots of 1,3-butadiene concentration against a product concentration at a given time fell on a straight line between 100 and 10% concentrations of 1,3-butadiene on the 0.5Tl5Pd/Al_2O_3 catalyst. This means that butenes produced did not react further under the conditions. Selectivity for the formation of each primary product was calculated from the slope and listed in table 1. The reaction catalyzed by 0.5Tl5Pd/Al_2O_3 gave 1-butene as the main reaction product at 55% selectivity (No. 2 in table 1). The presence of cis-2-butene in the reaction mixture did not affect the selectivity (No. 3), indicating that cis-2-butene is not isomerized under the experimental conditions. The reaction route for 0.5Tl5Pd/Al_2O_3 (type A) can be illustrated as follows:

route for type A reaction



- - → at close to 100% conversion of 1,3-butadiene
—— no reaction

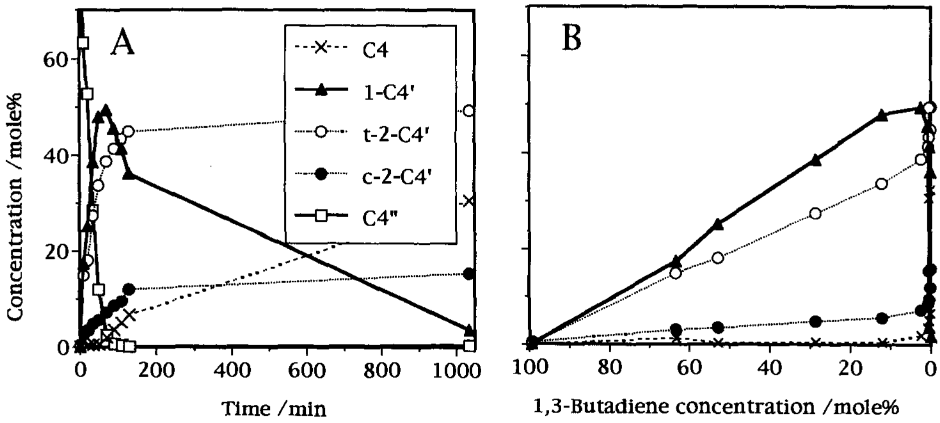


Fig. 1. Hydrogenation of 1,3-butadiene on 0.5Tl5Pd/Al_2O_3 reduced at 673 K: (A) time course; (B) concentration of products vs. 1,3-butadiene, where C4, 1-C4′, *t*-2-C4′, *c*-2-C4′, and C4″ show butane, 1-butene, trans-2-butene, cis-2-butene, and 1,3-butadiene, respectively.

Table 1
Selectivities of the primary products in the hydrogenation of 1,3-butadiene over Tl/Pd catalysts[a]

No.	Tl/Pd atomic ratio	Temperature (K)		Product selectivity (mol%)		
		reduction	reaction	1-butene	*t*-2-butene	*c*-2-butene
1	0	373	235-245	79	18	3
2	0.5	673	300	55	38	6
3	0.5[b]	673	300	57	39	2
4	0.7	673	300	55	38	7
5	1.0	673	300	34	56	10
6	2.0	673	373	12	72	16
7	2.0[b]	673	373	18	67	13
8	2 wt% Tl/Al_2O_3	673	473	21	56	23
9	2.0	300	300	61	34	5
10	2.0	323	323	49	43	8
11	2.0	373	373	13	61	17
12	2.0	473	373	11	72	17
13	2.0	673	373	12	72	16
14	2.0[c]	300	373	12	71	17

[a] Reaction mixture of 1,3-butadiene : $H_2 = 1 : 2$ (total pressure = 33 kPa) was used.

[b] Reaction mixture of 1,3-butadiene : cis-2-butane : $H_2 = 1 : 1 : 4$ (total pressure = 33 kPa) was used.

[c] Catalyst which has been reduced at 300 K, reacted at 473 K and oxidized at 573 K.

Fig. 2 shows the same type of plot as fig. 1B for the case of 2Tl5Pd/Al_2O_3 calcined at 673 K. By contrast to 0.5Tl5Pd/Al_2O_3, 2Tl5Pd/Al_2O_3 reduced at 673 K gave trans-2-butene as the main product (72%) and neither hydrogenation nor isomerization of butenes was observed after all the 1,3-butadiene was consumed at 423 K

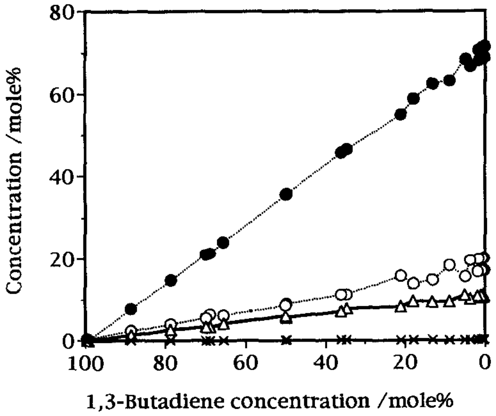
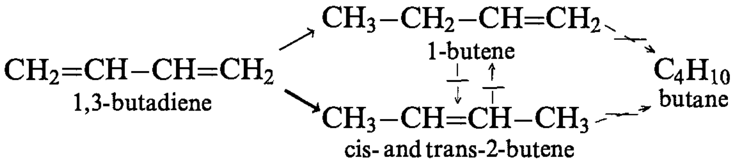


Fig. 2. Plot of concentration of products vs. 1,3-butadiene in the hydrogenation of 1,3-butadiene on 2Tl5Pd/Al_2O_3 reduced at 473–673 K; see fig. 1B for symbols.

(No. 6). The presence of cis-2-butene in the reaction mixture did not affect the selectivity (No. 7). The reaction route for $2Tl5Pd/Al_2O_3$ (type B) can be depicted as in the following scheme:

route for type B reaction



- - → at close to 100% conversion of 1,3-butadiene
—— no reaction

On all the catalysts examined, the same type of plot as in fig. 1B gave a straight line. The reactions on $5Pd/Al_2O_3$ (No. 1) and $0.7Tl5Pd/Al_2O_3$ (No. 4) belong to type A and the one on $1Tl5Pd/Al_2O_3$ (No. 5) stays in between types A and B. The reaction slowly proceeded on 2 wt% Tl/Al_2O_3 (No. 8) at 473 K with type B mechanism. It was found from these experiments in the hydrogenation of 1,3-butadiene on Tl-modified Pd catalysts reduced at 673 K that (1) the reactivities were decreasing with increasing Tl loading in the catalysts, (2) the main primary reaction products were 1-butene and trans-2-butene to 0–0.7 and 1–2 of the Tl loading in atomic ratio of Tl/Pd, respectively.

The variation of the product distribution in 1,3-butadiene hydrogenation also resulted from the pre-treatment temperatures of $2Tl5Pd/Al_2O_3$. As was shown in Nos. 9–14 in table 1, 1-butene formed mainly when the catalyst had been reduced at 300 K (No. 9), while trans-2-butene was a main product when it had been reduced at 373 K or more (Nos. 11–13). The change in the main product from 1-butene to trans-2-butene on Tl-modified Pd catalysts was accompanied by the decrease of reaction rate. The critical temperature was found at about 323 K (No. 10). Not only reduction temperature but also reaction or oxidation temperature does affect the results. As was shown in No. 14, a catalyst which had been reduced at 300 K, reacted at 473 K, oxidized at 573 K, re-reduced at 300 K, gave trans-2-butene as the main product (71%) at 373 K, where the reaction proceeded smoothly. The effects of pre-treatment temperature on selectivity and reactivity of the hydrogenation reaction may be interpreted in conjunction with facile migration of Tl or Pd on the catalyst surface at around 323 K to form a binary overlayer of Tl–Pd.

The TPR measurements applied to bimetallic catalysts can give information about the degree of association between the metals [7,8]. The TPR patterns on Tl-modified 5 wt% Pd/Al_2O_3 calcined at 673 K are shown in fig. 3. The TPR profile of 5 wt% Pd/Al_2O_3 gave a desorption peak at 345 K, which can be attributed to the decomposition of Pd hydride formed below 300 K. In fact, two unresolved hydrogen uptake peaks were observed below 280 K. These peaks should come from the

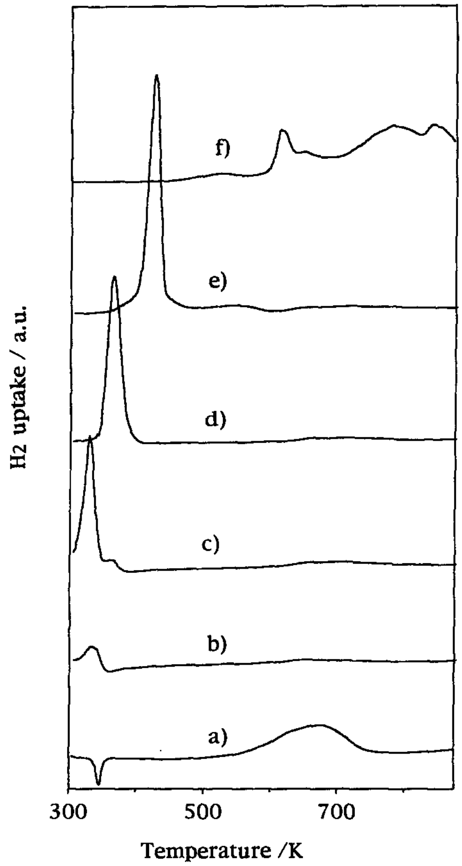


Fig. 3. TPR pattern of H_2 uptake vs. ramping temperature with the rate of 5 K/min on Tl-modified 5 wt% Pd/Al_2O_3 with Tl loading of (a) 0, (b) 0.2, (c) 0.5, (d) 1, and (f) 2, respectively, in Tl/Pd ratio after oxidation treatment at 673 K for 1 h.

reduction of Pd and from absorption of hydrogen in Pd to form Pd hydride. The negative peak became small on a sample with Tl/Pd = 0.2 and disappeared for samples with Tl/Pd$\geqslant$0.5. The TPR pattern of 2 wt% Tl/Al_2O_3 calcined at 673 K gave complex hydrogen uptake peaks, which could be attributed to the reduction of Tl nitrate or Tl oxides. As the Tl content increased to 0.5, 1, 2 in Tl/Pd atomic ratio, a new peak emerged whose temperature was observed at 327, 362, 423 K, respectively. The new peaks, which were not observed on 5Pd/Al_2O_3 and Tl/Al_2O_3, have been suggested [7,8] to be related to the reduction of Pd-metal oxidized species or to the occurrence of the alloy or intermetallic compounds. In contrast to the samples calcined at 673 K, 2Tl5Pd/Al_2O_3 that had been calcined in air at 373 K gave two H_2 uptake peaks of 364 and 489 K as depicted in fig. 4. The sample did not show a negative peak due to absorbed H_2. Neither 5Pd/Al_2O_3 nor Tl/Al_2O_3 gave the corresponding peaks and the peak temperature of reduction strongly related

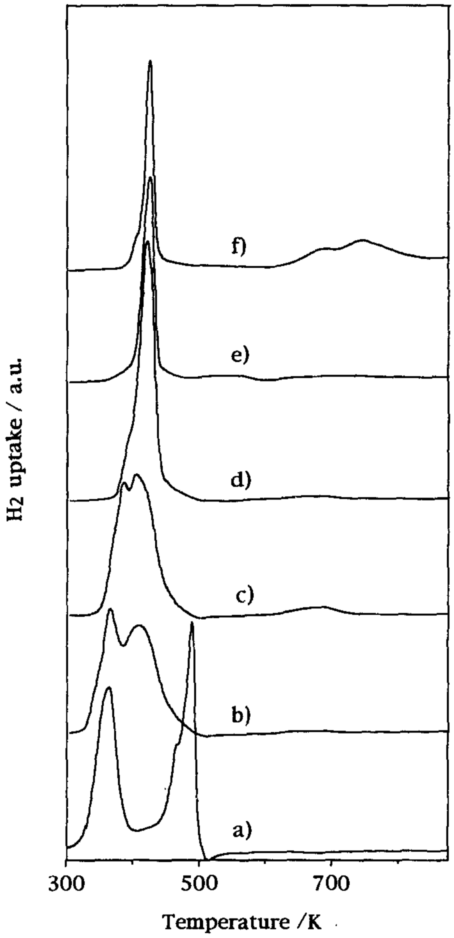


Fig. 4. TPR pattern of H_2 uptake vs. ramping temperature from 303 K to 870 K on $2Tl5Pd/Al_2O_3$ at different oxidation temperatures, (a) 373, (b) 473, (c) 523, (d) 573, (e) 673, and (f) 873 K, respectively.

with the Tl content after the calcination at 673 K. Accordingly, these peaks were proposed to be attributed to Pd- and Tl-rich binary compositions. The samples calcined at 473 and 523 K also gave two peaks, namely, at 364, 408 and 385, 402 K, respectively, but after calcination at 573 K, the two peaks were coalesced to one at 420 K. This suggests that sufficient mobility and miscibility of Tl and Pd proceeds to form Tl–Pd alloy or intermetallic phase at above 673 K of calcination temperature.

The XRD patterns of $5Pd/Al_2O_3$ and $0.2Tl5Pd/Al_2O_3$ show the presence of Pd and PdHx, while those of $0.5Tl5Pd/Al_2O_3$ and $1Tl5Pd/Al_2O_3$ give shifted Pd peaks, which suggest the formation of a Pd–Tl alloy. Increasing the Tl loading to 2 in Tl/Pd atomic ratio gives the XRD peaks, which have different crystal structure from Pd metal and can be attributed to Pd–Tl intermetallic compound(s) [5]. These XRD data were in consistence with the TPR data. The gap of transition temperatures deduced from 1,3-butadiene hydrogenation and from TPR may be accounted for by the difference of surface to bulk character.

4. Conclusion

These studies may provide the following conclusions:

(1) The selectivity and reactivity in the hydrogenation of 1,3-butadiene catalyzed by Tl-modified Pd catalysts vary not only with amounts of Tl loading but also with the reduction temperatures.

(2) TPR and XRD measurements showed the formation of Pd–Tl alloy and intermetallic compounds on the Tl-modified Pd catalysts by the calcination and H_2-reduction.

(3) The activity and selectivity controlling of the Tl-modified catalysts in 1,3-butadiene hydrogenation is proposed to be based on the decreasing of the ensemble size of Pd metal with Tl when forming the Tl–Pd alloy and intermetallic overlayer due to the facile mobility of Tl or Pd on the surface.

References

[1] C.H. Bartholemew, Catalysis 10 (1993) 41.
[2] R.T.K. Baker, E.B. Prestrige and G.B. McVicker, J. Catal. 89 (1984) 422.
[3] M. Ricci and M. Gillet, Z. Phys. D 19 (1991) 315.
[4] M. Che and C.O. Bennett, Adv. Catal. 36 (1989) 55.
[5] R. Ohnishi, W.-L. Wang and M. Ichikawa, Appl. Catal. A 113 (1994) 29.
[6] R. Ohnishi, H. Suzuki and M. Ichikawa, Chem. Lett. (1991) 841.
[7] F.B. Noronha, M. Schmal, M. Primet and R. Frety, Appl. Catal. 78 (1991) 125.
[8] A. Benedetti, G. Fagherazzi, F. Pinna, G. Rampazzo, M. Selva and G. Strukul, Catal. Lett. 10 (1991) 215.