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Effect of Hydrocarbonaceous Deposits on Competitive Hydrogenation of 1,3-Butadiene and Propene over Pd Catalyst

A. Sarkany

Institute of Isotope and Surface Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 77, H-1525 Budapest, Hungary
E-mail: sarkany@sunserv.kfki.hu

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Gas phase hydrogenation of 1,3-butadiene, propene, and mixtures of 1,3-butadiene and propene has been investigated over 0.05 wt% Pd/Al_2O_3 catalyst. The catalyst was deliberately poisoned by methane (513 K) or diene (473 K) and the effect of the hydrocarbonaceous materials was tested on the product selectivity and the rate of hydrogenation of diene–propene mixtures. It has been concluded that a large quantity of hydrocarbonaceous deposit decreases the surface fugacity of diene due to transport hinderance and in consequence enhances the over-hydrogenation of diene and permits the hydrogenation of propene in the presence of diene.

1. INTRODUCTION

Selective partial hydrogenation of 1,3-butadiene in C4 alkene cuts over Pd catalysts is an industrial process for production of high purity alkene streams (1). Systematic investigations have shown that *n*-butane, an unwanted product of hydrogenation, is produced (i) directly from diene, presumably via participation of intermediate carbenes (2, 3), and (ii) from saturation of *n*-butenes (1–5) in the presence of diene. In the latter process the difference in the strength of complexation of diene and alkene to Pd is a crucial factor in governing the partial hydrogenation selectivity (1–5). In recent studies testing the effect of deposits in hydrogenation of 1,3-butadiene we have observed increasing over-hydrogenation selectivity upon covering Pd and Pd–Ag catalysts by large amount of hydrocarbonaceous materials (6, 7). Increasing ethane formation selectivity was also reported in hydrogenation of acetylene–ethene mixtures over Pd-based catalysts (8–13). The tracer and kinetic studies indicated simultaneous participation of two or three different types of reaction site on the surface (9, 11, 13). Formation of various multiple-bonded so-called spectator species is almost inevitable in these hydrogenations (14, 15). Deposits are considered to participate in stabilization of reaction sites (14–16) and in altering hydrogen-transfer properties (17).

In the present paper we have investigated the competitive hydrogenation of 1,3-butadiene–propene mixtures on freshly reduced and deliberately poisoned Pd surfaces. The kinetic principle that determines the ratio of adsorption coefficients is well demonstrated (14, 15) and has already been applied to characterize butadiene–propene and 1-butene–propene pairs over Pt and Pd catalysts (16). The method seems to be sensitive enough to reveal small changes in the surface state of the catalysts (15, 16). Our objective is to check the effect of hydrocarbonaceous materials on the product selectivity and to clarify how the poisoning affects the competition between 1,3-butadiene and propene over 0.05 wt% Pd/Al_2O_3 catalyst of egg-shell type.

2. EXPERIMENTAL

The catalyst used in this study is of egg-shell type: 0.05 wt% Pd is supported on transient alumina (BET surface area = 34 m^2/g, pore volume = 0.38 cm^3/g, pore radius = 22 nm, 3 mm spheres). The depth of the impregnated shell is 0.032 mm in average. Two different levels of carbon poisoning were tested with the same pellets (52 mg catalyst). The amount of carbon was measured by TPO (1% O_2 in He, 50 K/min ramp). Catalyst A was prepared by treating reduced catalyst with methane at 513 K for 2 h. After TPO, Cat. A was reduced and a few experiments were performed on the regenerated sample (Cat. AR). Catalyst B is the diene poisoned sample: Cat. AR was aged in the batch reactor in the presence of 5.3 kPa 1,3-butadiene at 473 K for 8 hr.

Hydrogenation of 1,3-butadiene (BD), propene (Pr), and diene and propene mixtures has been tested in a batch reactor ($V = 0.165$ dm^3, recirculation rate 2.3 dm^3/min) described in previous papers (6, 7). The stability of the catalyst was repeatedly controlled using a reaction mixture consisting of 1.33 kPa BD, 4 kPa propene, and 2.66 kPa H_2 unless otherwise stated. Between experiments a standard regeneration treatment was performed (6); hydrocarbons were frozen out in liquid N_2 in a U tube located in the pumping system and 3.3 kPa H_2 (or D_2) was circulated for 20 min prior to the next experiment. The reactor was then separated from the pumping part, hydrocarbon and hydrogen

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were removed from the pumping part, and finally the hydrogen was evacuated from the reactor tube before a new experiment was begun.

Transformation of substrates was followed up to about 30% conversion of diene, measuring at least four distributions, including the initial one, as a function of time. Rate is shown as percentage of butadiene consumed/min (further on %/min) measured over 52 mg catalyst. The reaction mixture was analyzed at 294 K on a 8-m-long column packed with bis(methoxyethyl)adipate (BMEA). From the primary data, initial and subsequent rates of hydrocarbon consumption were calculated. The C_4 distribution was characterized by integral product selectivities: moles of product formed were divided by moles of diene consumed (6, 7).

3. RESULTS AND DISCUSSION

In Fig. 1, TPO spectra of the regenerated and reduced catalyst (Cat. AR, (curve 1), Cat. A (curve 2), and Cat. B (curve 3)) are presented (full line, O_2 consumption; dotted line, CO_2 evolution). The reduced sample (Cat. AR) shows only one broad peak (O_2 consumption) centered at 765 K which corresponds to the bulk oxidation of Pd particles. Over Cat. A the maximum rate of CO_2 formation appeared at 576 K, whereas over Cat. B one broad peak was detected with maximum at 800 K and a smaller peak at 610 K (please note that the sensitivity was decreased by a factor of 32). TPO spectra confirm that the carbon coverage on Cat. A and Cat. B is significantly different: the carbon loading is 0.017 and 3.4 mgC/gcat over Cat. A and Cat. B, respectively. The CO_2 formation at 576 K (curve 2) and 610 K (curve 3) can tentatively be attributed to oxidation of C_xH_y present on or at the vicinity of metal particles whereas the large broad peak at 800 K (see curve 3) probably represents oxidation of the deposits formed on the support sites or migrated from the metal sites onto the support sites.

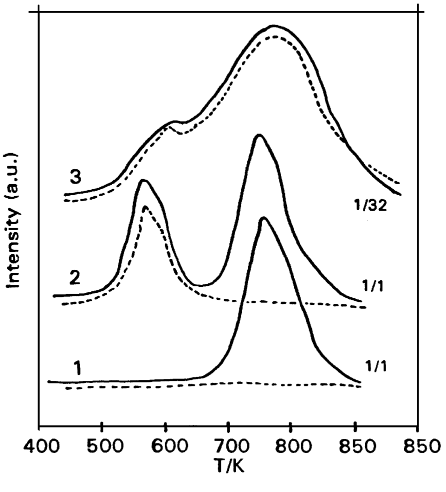

FIG. 1. TPO curves observed after methane (Cat. A) and butadiene (Cat. B) treatments (full lines, O_2 consumption; broken lines, CO_2 formation): 1-TPO of regenerated catalyst (Cat. AR); 2-TPO of Cat. A, and 3-TPO of Cat. B.

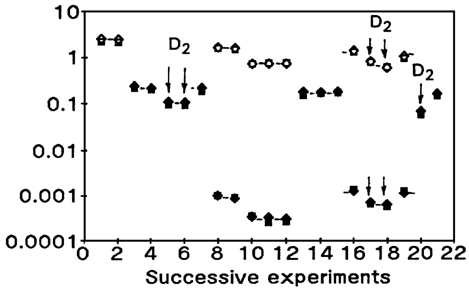

FIG. 2. Rate of 1,3-butadiene (open symbols) and propene (full symbols) consumption on Cat. A (T = 288 K, ◇ and ◆, initial rate; □ and ■, subsequent rate). Arrow, experiment in D_2.

Typical rate data on the hydrogenation of propene (4 kPa Pr, 2.66 kPa H_2) on Cat. A at 288 K in the absence and presence of 1,3-butadiene are shown in Fig. 2. After CH_4 treatment at 513 K for 2 h the activity, as indicated by successive experiments, is stable enough and the diene hydrogenation rate, R(BD), on average is 2.4%/min (exps. 1 and 2, 1.33 kPa BD, 2.6 kPa H_2) and the propene hydrogenation rate R(Pr) is 0.24%/min (exps. 3, 4, and 7, 3.99 kPa Pr, 2.6 kPa H_2), decreasing slightly in successive experiments (exps. 13, 14, 15, and 21). In deuterium (exps. 5, 6, and 20) the hydrogenation rate is slower; R^H/R^D for propene is 1.9. In the presence of 1.33 kPa 1,3-butadiene the propene hydrogenation rate (exps. 8 and 9) is less by more than two orders of magnitude (0.00089%/min). In 2.66 kPa BD (exps. 10, 11, 12) this rate is 0.00035–0.00031%/min. The R(Pr)/R(Pr,BD) ratio is about 280 and 730 in 1.33 and 2.66 kPa BD, respectively. Replacement of hydrogen with deuterium decreases the hydrogenation rate of both propene and butadiene (exps. 17 and 18). The R^H/R^D values for propene and diene hydrogenation (1.33 kPa BD) are 1.8 and 1.7, respectively (exps. 16–19).

A similar series of hydrogenation experiments over Cat. B at 301 K is presented in Fig. 3. The rate of propene

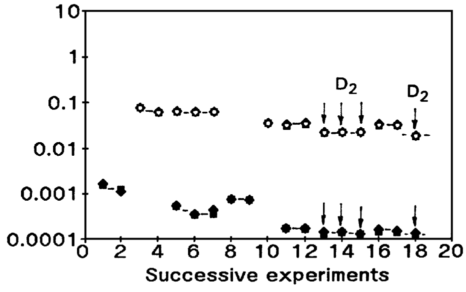

FIG. 3. Rate of 1,3-butadiene (open symbols) and propene (full symbols) consumption on Cat. B (T = 301 K, ◇ and ◆, initial rate; □ and ■, subsequent rate). Arrow, experiment in D_2.

TABLE 1

Initial Product Selectivity in Hydrogenation of 1,3-Butadiene (1.33 kPa BD and 2.66 kPa H_2)

Catalyst	$^{a}S_{nB}$	S_{1B}	S_{t2B}	S_{c2B}	1B/2B	t2B/c2B
Cat. A[b](1)	0.17	66.7	28.8	4.3	2.01	6.7
Cat. B (3)	8.61	47.3	35.6	8.5	1.07	4.2
Cat. AR (1)	0.04	68.2	27.5	4.3	2.14	6.4

[a] S_{nB}, S_{1B}, S_{t2B}, and S_{c2B} is the selectivity of *n*-butane, 1-butene, *trans*-2-butene, and *cis*-2-butene formation, respectively.

[b] Number of experiment.

(exps. 1, 2 and 8, 9) and diene hydrogenation (exps. 3 and 4, 1.33 kPa BD) due to the large amount of deposits is only 0.0015 and 0.075%/min, respectively, over this sample. The significant change in the working of the catalyst is indicated by the fact that in the presence of 1.33 kPa diene (exps. 5–7) the rate of propene hydrogenation is suppressed only from 0.0015 to 0.00044%/min at 303 K; i.e., $R(\mathrm{Pr})/R(\mathrm{Pr,BD})$ is 3.4. In 2.66 kPa BD (exps. 11, 12, 16, and 17) the ratio is 8.8. A few experiments were also performed replacing H_2 with D_2 (exps. 13–15 and 18): the isotope effect of hydrogenation is 1.5 for diene consumption but only 1.2 for propene in the simultaneous hydrogenations.

The product selectivity of diene hydrogenation is presented in Table 1. Over Cat. B the selectivity of *n*-butane formation (S_{nB}) is 8.6% whereas on a fresh sample S_{nB} is 0.04% at 298 K. Over Cat. A S_{nB} is 0.17%. There is also some change in the distribution of *n*-butenes: Over Cat. B low 1-butene/2-butenes ratios ($R_{1B}/R_{2B} = 1.1$) and low *trans*/*cis*-2-butene ratios ($R_{t2B}/R_{c2B} = 4.2$) were observed.

Comparison of Figs. 2 and 3 confirms that a large amount of hydrocarbonaceous deposits significantly alters the catalytic behaviour of Pd sites. The $R(\mathrm{Pr})/R(\mathrm{BD})$ values are significantly less over Cat. B than over Cat. A, suggesting that a large amount of deposit alters the competition of the two reactants. This behaviour is in agreement with observations on hydrogenation of acetylene–ethene "tail-end" mixtures: a gradual decline in ethene selectivity, reaching many times negative values, was observed during the time on stream experiments. ^{13}C and ^{14}C tagging experiments (9, 11) have confirmed that ethane produced comes predominantly from ethene and ageing facilitates formation of ethane from ethene even in the presence of acetylene.

The question that immediately arises is how to interpret the significant decrease of $R(\mathrm{Pr})/R(\mathrm{Pr,BD})$ ratios over Cat. B. Upon poisoning the catalyst the rate of propene hydrogenation is affected to a greater extent than that of butadiene. Over regenerated catalyst $R(\mathrm{Pr})/R(\mathrm{BD})$ is 0.5–0.7. As shown in Figs. 2 and 3, over Cat. A and Cat. B the $R(\mathrm{Pr})/R(\mathrm{BD})$ ratio is 0.1 and 0.02, respectively. Therefore, any assumption that upon poisoning special sites would be generated over which the propene complexation is stronger than the diene complexation is highly improbable. Moreover, the decreasing $R(\mathrm{Pr})/R(\mathrm{BD})$ does not support suggestions that additional alkene hydrogenation sites would be generated on the catalyst upon the formation of hydrocarbonaceous material.

In our opinion, in the interpretation of the results one has to consider the transport effect of the hydrocarbonaceous deposits over Cat. B. Over this sample the amount of deposit is 3.4 mg dep/gcat but the carbon concentration is higher in the 0.3-mm outer shell. Under the reported conditions some of the carbon dissolves in the bulk forming PdC_x ($x < 0.15$) (6, 13). A larger fraction, however, forms oligomers/polymers sitting on metal sites and on the support. Formation of oligomers/polymers requires either formation of a C–C bond between neighbouring adsorbed species (4, 8) or insertion of a C_4 unit into an existing Pd–C bond. The oligomers are likely to form a hydrocarbon film over the surface and cause restriction in entering the pores. As shown in Table 1, over Cat. B the selectivity of *n*-butane is higher by a factor of 215 than over regenerated catalyst (Cat. AR). The complete hydrogenation of 1,3-butadiene seems to indicate that on the working sites the surface fugacity of 1,3-butadiene is low, which can be attributed to transport hindrance (decrease of the effective diffusivity) caused by the presence of deposits. In the absence of sufficient diene concentration over the working sites, intermediate *n*-butenes are not displaced immediately by diene molecules; consequently there is a chance for complete hydrogenation. The longer residence time of *n*-butenes on the surface also explains the observed low values of 1-butene/2-butene and *trans*/*cis*-2-butene ratios on the highly poisoned Cat. B. The crucial point in this behaviour is that the hydrogen availability is affected to a lesser extent than the diene concentration over the sites. Apparently the hydrocarbonaceous material on the surface is more "permeable" for hydrogen than for hydrocarbons probably due to fast hydrogen diffusion. As a consequence of the low diene surface coverage the hydrogen concentration on the working surface increases which in turn influences the kinetics of hydrogen addition as observed in hydrogenation of acetylene (21) and ethene (22). The reaction order for BD is slightly negative (−0.12) over Cat. A (from experiments 8–12 in Fig. 2) whereas it is positive (0.2) over Cat. B (from experiments 5–7 and 10–12 in Fig. 3) indicating that under the given conditions the surface of Cat. B is not saturated with diene. The drastic decrease of diene fugacity over Cat. B also explains why propene molecules are able to find sites on the heavily poisoned surface and, therefore, the $R(\mathrm{Pr})/R(\mathrm{Pr,BD})$ ratio is significantly less over Cat. B than over Cat. A or freshly reduced catalyst. The effect of transport limitation is also supported by the significant decrease of the apparent activation energy of hydrogenation over Cat. B. There is no large difference between the apparent activation energies over Cat. A and freshly reduced

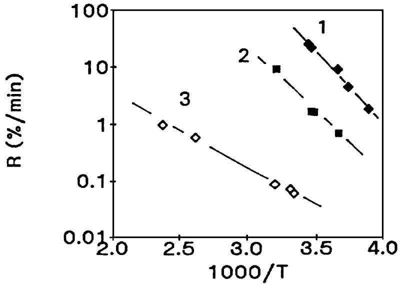

FIG. 4. Arrhenius plot of diene consumption (1.33 kPa BD, 2.66 kPa H_2): 1-regenerated catalyst (Cat. AR), 2-Cat. A, and 3-Cat. B.

sample as indicated in Fig. 4. The observed values of E are 48.1 and 51.1 $kJmol^{-1}$ over fresh sample and Cat. A, respectively but 25.3 $kJmol^{-1}$ over Cat. B. The observed isotope effect of hydrogen addition does not differ from values published for ethene (23) or acetylene (24) hydrogenations and it may allow one to suggest that addition of hydrogen to C_4X_7 and C_3X_7 ($X = \mathrm{H}$ or D) is the rate limiting step over Cat. A. Over Cat. B the $R^{\mathrm{H}}/R^{\mathrm{D}}$ values are smaller and for propene it is only 1.2. In the absence of further evidence this result may point to some compensation between kinetic and equilibrium hydrogen isotope effects (23).

To summarize this study, it has been shown that large amounts of hydrocarbonaceous materials increase the selectivity of complete hydrogenation and exerts a detrimental effect on the diene–alkene competition for the active sites. The results can be interpreted by the appearance of transport hinderance caused by the accumulation of deposits which decreases significantly the surface fugacity of the diene, rather than by formation of some special sites (9) and/or reverse spillover of hydrogen from the support to metal sites. The presented results permit us to conclude that the hydrocarbonaceous material affects the hydrocarbon transport to a larger extent than hydrogen. The enhancement of hydrogen availability on a fraction of working sites compensates for the activity loss caused by the decreasing diene coverage and results in over-hydrogenation. The decreasing effective diffusivity of acetylene in hydrogenation of acetylene–ethene mixtures over Pd catalysts provides a reasonable ground to explain the slow decrease of acetylene conversion and the increasing rate of ethane production in the time on stream experiments (10–13). Direct gravimetric measurements have already confirmed the very fast accumulation of oligomers in this reaction (12). Further work is needed to clarify the mechanism of deposit formation and to find a model consistent with the amount of deposit and its effect on the hydrogenation behaviour.

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REFERENCES

1. Müller, H. J., Kons, G., Herion, C., Meyer, G., Vicari, M., Freire-Erdbrügger, C., Flick, K., Polanek, P., and Laib, H., *in* "Proceedings, 9th International Symposium Large Chemical Plants, Antwerp, October 4–6, 1995."
2. Hub, S., and Touroude, R., *J. Catal.* **114**, 411 (1988).
3. Boitiaux, J. P., Cosyns, J., and Robert, E., *Appl. Catal.* **49**, 235 (1989).
4. Bond, G. C., and Wells, P. B., *Adv. Catal.* **15**, 92 (1964).
5. Derrien, M. L., *Stud. Surf. Sci. Catal.* **27**, 613 (1986).
6. Sarkany, A., *Appl. Catal. A* **165**, 87 (1997).
7. Sarkany, A., *Stud. Surf. Sci. Catal.* **101**, 111 (1997).
8. Sheridan, J., *J. Chem. Soc.* 470 (1945).
9. McGown, W. T., Kemball, C., Whan, D. A., and Scurrel, M. S., *J. Chem. Soc. Faraday Trans. I* **73**, 632 (1977).
10. Weiss, A. H., Gambir, B., LaPierre, R., and Bell, W., *Ind. Chem. Eng. Proc. Des. Dev.* **16**, 352 (1977).
11. Sarkany, A., Weiss, A. H., and Guczi, L., *Appl. Catal.* **10**, 369 (1984).
12. LeViness, S. C., Ph.D. Thesis, Rice University, Houston, Texas, 1989.
13. Borodzinski, A., and Golebiowski, A., *Langmuir* **13**, 883 (1997).
14. Al-Ammar, A. S., and Webb, G., *J. Chem. Soc. Faraday Trans. I* **74**, 195 (1978).
15. Al-Ammar, A. S., and Webb, G., *J. Chem. Soc. Faraday Trans. I* **74**, 657 (1978).
16. Jackson, S. D., and Casey, N. J., *J. Chem. Soc. Faraday Trans. I* **91**, 3269 (1995).
17. Thomson, S. J., and Webb, G., *J. Chem. Soc. Chem. Commun.* 139 (1976).
18. Rader, Ch. P., and Smith, H. A., *J. Am. Chem. Soc.* **84**, 1443 (1962).
19. Szymanski, R., Charcosset, H., Gallezot, P., Massardier, J., and Tournayan, L., *J. Catal.* **97**, 366 (1986).
20. Ouchaib, T., Massardier, J., and Renouprez, A., *J. Catal.* **119**, 517 (1989).
21. Moyes, R. B., Walker, D. W., Wells, P., Whan, D. A., and Irvine, E. A., *Appl. Catal.* **55**, L5 (1989).
22. Jackson, S. D., McLellan, G. D., Webb, G., Conyers, L., Keegan, M. B., Mather, S., Simpson, S., Wells, P. B., Whan, D. A., and Whyman, R., *J. Catal.* **162**, 10 (1996).
23. Ozaki, A., "Isotopic Studies of Heterogeneous Catalysis." Academic Press, New York, 1977.
24. Inonue, Y., and Yasumori, I., *J. Phys. Chem.* **75**, 880 (1971).