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The Catalytic Hydroboration of Ethylene with Diborane in the Gas Phase — The Acidity of Catalysts and the Reaction Activity —

Tsuneo Matsuda, Isao Seto,* and Toyosuke Tanaka
Faculty of Engineering, Saitama University, Shimoohkubo, Urawa, Saitama 338
**Bridgestone Tire Co. Ltd., Kyobashi, Chuo-ku, Tokyo 104*

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Synopsis. The catalytic hydroboration of ethylene with diborane to triethylborane in the gas phase was studied in the presence of various catalysts. The acidity of catalysts and the reaction activity were measured; the increase in the activity can be related to surface acidity of the catalysts.

The hydroboration of olefin in the liquid phase using diglyme (diethylene glycol dimethyl ether), tetrahydrofuran (THF), diethyl ether and so on as solvent was widely investigated.1) Very few investigations of the noncatalytic hydroboration in the gas phase have, however, been reported.2–5) We previously found that Pd–carbon was a active catalyst for the vapor-phase hydroboration of ethylene.6) In this paper the activity of various catalysts in the hydroboration of ethylene was investigated, and it was found that the surface acidity of catalysts is correlated with its activity.

Experimental

The reaction was carried out in a closed circulation apparatus equipped with two small traps in which the product was collected. One of the traps was cooled with a salt-ice bath during the reaction.

Diborane was produced by allowing $NaBH_4$ in a diglyme solution or $LiAlH_4$ in an ether solution to react with $BF_3 \cdot C_2H_5OC_2H_5$ at room temperature under a nitrogen atmosphere.7) The diborane was purified by freezing it with liquid nitrogen, by then pumping off any impurities, and finally by distilling it. The ethylene was also purified by low-temperature distillation. The catalysts used were Pd-carbon (Pd 3 wt.%), α- and γ-Al_2O_3 (kindly provided by Kawaken Fine Chemicals and the Tōkai Kōnetsu Co., Ltd.), active carbon, Ni-γ-Al_2O_3, and silica gel and its pretreated species with an acidic or alkaline medium. Before the reaction the catalysts were treated at 450 °C for 1 h under a vacuum (about 10^{-3} mmHg). The reaction conditions were as follows: molar ratio: 6 (C_2H_4; 4.58, B_2H_6; 0.758 mmol); catalyst used: 0.5 g; temperature: 50 °C, and time: 1 h. After the reaction, the residual gases in the apparatus were condensed by the liquid nitrogen into another trap containing THF, which was then isolated from the reactor system during the reaction, in order to recover the unreacted diborane. Then the dry nitrogen was admitted into the apparatus and the reaction vessel, and the traps in which the product had condensed were removed from the reactor system. Immediately the catalyst in the reaction vessel was washed with the purified ether several times in order to extract the reaction product adhering on the catalyst, after which the extract was added to the trap containing the product. The product thus collected was analyzed by gas chromatography, with a 10 wt% Silicone oil on Celite 545 column,8) and using toluene as the internal standard. The unreacted diborane in THF was converted to boric acid with water. The boric acid was then titrated with a sodium hydroxide solution in the presence of glycerol, using phenolphtalein as an indicator.

The surface acidity of the catalysts was determined by the measurement of the irreversibly adsorbed amount of ammonia at 50 °C.

Results and Discussion

The only hydroboration product of ethylene under the conditions described above was triethylborane. It has been reported that, in a high molar ratio of diborane to olefins, mono- and dialkylborane were produced in the gas phase without any catalyst,4) but in this study no such products were detected. The pressure changes during all the catalytic reactions were almost the same as in the previous paper;6) an induction period in the initial stage was observed in every case. The catalyst properties and the results of the hydroboration of ethylene on the various catalysts are summarized in Table 1. A good correlation between the catalytic activity (yield) and the acidity was found, as is indicated in Fig. 1.

The γ-Al_2O_3, both supported and non-supported, was active, and in the hydroboration with the Ni-γ-Al_2O_3 catalyst tributylborane was detected in a small yield as well as triethylborane. The tributylborane may be formed by the reaction of diborane and the butenes which are produced by the dimerization of ethylene, since Ni or NiO supported on a silica and (or) an alumina catalyst showed catalytic activity in the dimerization of ethylene.9) The addition of nickel

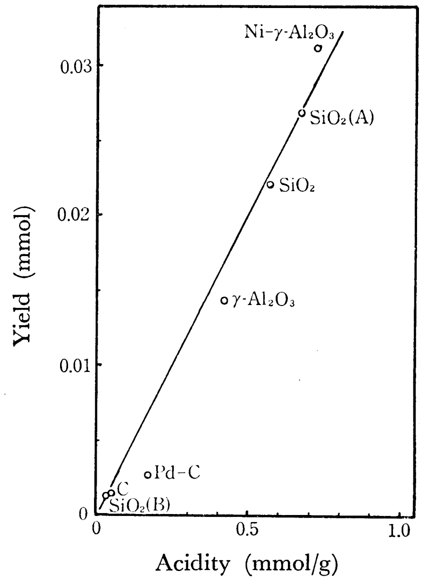

Fig. 1. A correlation of the yield and the acidity of the various catalysts.

TABLE 1. PROPERTIES OF CATALYSTS AND THIER CATALYTIC BEHAVIOR FOR HYDROBORATION OF ETHYLENE

Catalyst	Pd-carbon (Pd 3%)	Active carbon	α-Al_2O_3	Pd-α-Al_2O_3[a] (Pd 1%)	Pd-α-Al_2O_3[a] (Pd 3%)	γ-Al_2O_3	Ni-γ-Al_2O_3[b]	SiO_2[c]	SiO_2 (A)[d]	SiO_2 (B)[e]
Surface area[f] (m^2/g)	1030	1206	1.6	—	—	212	228	594	560	—
Acidity (mmol/g)	0.165	0.045	0	—	trace	0.427	0.725	0.567	0.674	0.035
Yield × 10 mmol[g]	0.354	0.167	0	trace	trace	1.45	3.15	2.33	2.69	0.160
(%)	4.7	2.2	—	—	—	19.1	41.6	30.7	35.5	2.1
Conversion[h] (%)	83.9	81.1	—	—	—	60.8	67.5	—	—	—
Selectivity[i] (%)	5.6	2.7	—	—	—	31.4	61.6	—	—	—

a) The α-Al_2O_3 was dipped in palladium chloride hydrochloric acid solution and then calcined at 400 °C for several hours in H_2 atmosphere. b) The catalyst containing 2.8 wt% Ni on γ-Al_2O_3 was prepared by the impregnation of γ-Al_2O_3 with $Ni(NO_3)_2$ solution and calcined at 400 °C for several hours in H_2 atmosphere. c) Commercial SiO_2 from Wakō Junyaku Co., Ltd. d) The silica gel in c) was boiled in 1M-HCl for 30 min and then washed with distillated water until no acid was detected. e) The silica gel in c) was treated in 1M-NaOH in stead of HCl by the same way as described in d). f) The surface area was determined by BET method at −196 °C with nitrogen. g) Percentage yield was calculated on the basis of both the amount of $B(C_2H_5)_3$ produced and the initial amount of diborane, $[B_2H_6]_0$. h) Conversion was calculated as the following equation; $\frac{[B_2H_6]_0-[B_2H_6]}{[B_2H_6]_0}\times 100$ $[B_2H_6]$; amount of unreacted diborane. i) $(\text{selectivity})=\frac{(\text{yield }\%)}{(\text{conversion})}\times 100$.

TABLE 2. THE DISTRIBUTION OF THE ACIDIC STRENGTH OF SOME CATALYST (unit; mequ./g)

Catalyst	p*K*a		
	below 6	6.8—4.0	4.0—−3.0
γ-Al_2O_3	0.082	0.225	0.038
SiO_2	0.383	0.157	0
SiO_2 (A)	0.536	0.338	0.134
SiO_2 (B)	0	0.064	0

to γ-Al_2O_3 increases the acidity by the interaction of the nickel with the support, as was also indicated by Aonuma *et al.*[10] In order to further ascertain the effect of the acidity on the catalytic activity, hydroboration with silica gel treated with acid or alkali was carried out. As is shown in Table 1 and Fig. 1, the acid-treated silica gel caused increases in the yield and the acidity. The percentage yield of the product with respect to the admitted amount of diborane at the initial stage are shown in Table 1. On the basis of the results of the titration of the boric acid, the conversion of diborane was calculated to be as is shown in Table 1.

The greater conversion on the Pd–C and active carbon than on the other catalysts may be ascribed to the large surface area of the former, much unreacted diborane being adsorbed.[6] This is probably the reason for the great discrepancy between the percentage yield and the conversion of diborane. As another reason, the reacted diborane calculated on the basis of the results of the titration does not always proceed to triethylborane, because a gas (perhaps H_2) uncondensable by liquid nitrogen, which may be due to the reaction of diborane with the hydroxylic surface of γ-Al_2O_3 and Ni–γ-Al_2O_3,[12] was detected. Because of the small surface area of α-Al_2O_3, the supported and non-supported α-Al_2O_3 would have little of either activity of acidity.

The distribution of the acidic strength of several catalysts was measured by the titration of the butylamine–benzene solution, using Netral Red ($pK_a=6.8$), 1-phenylazo-2-naphtylamine ($pK_a=4.0$), and dicinnamylideneacetone ($pK_a=-3.0$) as indicators.[11] Table 2 indicates the results of the distribution with respect to the strength of the acidity. As is shown in Table 2, relatively weak acidic sites seem to catalyze the hydroboration.

The hydroboration proceeds with the migration of the hydrogen atom in diborane to olefin and the B–C bond being newly constructed. It is known that diborane dissociatively absorbs on the catalyst surface.[6, 12] The acidic site on the catalysts seems to be related to the migration of the hydrogen of BH_3, by which the olefin atom can easily attack the boron atom.

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