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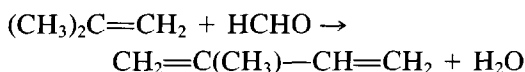
The Formation of Isoprene by Means of a Vapor-Phase Prins Reaction between Formaldehyde and Isobutene

INTRODUCTION

The condensation of aldehydes with olefins forms useful synthetic organic chemicals. This reaction, called the Prins reaction, has already been studied (1). Above all, the reaction of formaldehyde (HCHO) with isobutene is especially attractive as a route for obtaining isoprene, a raw material of synthetic rubber.

A two-stage process, condensation to form 4,4-dimethyl-*m*-dioxane in the presence of an aqueous sulfuric acid and its vapor-phase decomposition to isoprene using solid phosphoric-acid catalysts, was proposed by Hellin and Coussemant (2, 3). Their work was followed by the appearance of many patents.

On the other hand, the vapor-phase one-stage process has also been studied actively; there are numerous patents dealing with it.



The following solid acids are claimed to be effective for it; acidic clay, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{B}_2\text{O}_3\text{-WO}_3$, $\text{CaO-P}_2\text{O}_5$, $\text{MnO-P}_2\text{O}_5$, $\text{Co}_2\text{O}_3\text{-P}_2\text{O}_5$, $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3$, B_2O_3 , $\text{PbO-P}_2\text{O}_5$, Sb_2O_4 , $\text{Sb}_2\text{O}_4\text{-P}_2\text{O}_5$, Bi_2O_3 -based mixed oxides, and metal sulfates. However, Mitsutani (4) concluded, from a survey of the patent literature, that this reaction is not realizable as an industrial process because of the low space-time yield and because of the lack of any stability of catalytic activity. Besides the patent information, very few scientific reports have yet been published. Yashima *et al.* (5, 6), however, have studied the reaction with

$\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ and Maruyama *et al.* (7) have tested the activity of supported metal-sulfates.

Recently, it was found that a $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ (P/V atomic ratio = 1.06) catalyst consisting of vanadyl pyrophosphate, $(\text{VO})_2\text{P}_2\text{O}_7$, and exhibiting an excellent performance in the oxidation of *n*-butane to maleic anhydride, possesses an enhanced acidic property sufficient to activate paraffinic hydrocarbons and, at the same time, a certain extent of basic property (8). We can predict that this catalyst will also be effective for certain acid- or acid-base-catalyzed reactions.

In this study, attention was focused on the vapor-phase condensation of HCHO with isobutene to form isoprene. We first tested the catalytic behavior of various kinds of metal oxides, and then we studied the characteristic feature of this reaction by using the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ ($P/V = 1.06$) catalyst.

EXPERIMENTAL

Reaction procedures. The reaction was carried out with a continuous-flow system using tertiary butyl alcohol (TBA) as the starting material for isobutene. The reactor and the experimental procedures were almost the same as those employed in the preceding work (9). Nitrogen or air was fed in as the carrier gas or the diluent, and a mixture of TBA and 37% formalin was introduced into the preheating section of the reactor by means of a micro liquid-feeder. Unless otherwise indicated, the reaction conditions were: flow rate of nitrogen or air, 280 ml (at 20°C)/min (ca. 0.7

mol/h); feed rate of HCHO, 15.6 mmol/h; TBA/HCHO molar ratio, 3.16; amount of catalyst used, 20 g; temperature, 240°C. The effluent gas from the reactor was led into three chilled water-scrubbers to recover the water-soluble compounds. At the end of 1 h, the content of the water-scrubbers were collected (120 ml). The reaction products were analyzed by gas chromatographs; a 1-m column of molecular sieve 13X for CO; a 6-m column of propylene carbonate for CO₂, isobutene, and isoprene; a 2-m column of PEG 20 M at 70°C for aldehydes, ketones, alcohols, and methyl formate. HCHO was analyzed by means of iodometry (10).

Catalysts. The catalysts used in this study were the same as those used in the preceding work (9).

RESULTS

Comparison of the Catalytic Performances of Various Oxides

Since little information has been reported about the catalytic behavior of transition metal oxides for this condensation reaction, it seemed necessary to make a character sketch of the catalytic action. Therefore, several series of experiments were carried out in an air atmosphere using MoO₃-, WO₃-, and V₂O₅-based mixed oxides and heteropoly compounds. The reaction conditions were fixed as described under Experimental. It was found that almost all of the TBA is converted promptly into isobutene and water, even at the low temperature of 140°C, over every catalyst tested. The main product detected was isoprene. The formation of an appreciable amount of carbon oxides was observed only at the beginning of the reaction, except for the Mo-Sn, V-Ti, V-Sn, V-Fe, and V-Ni oxides. The formation of such by-products as methyl formate and acetone, as detected by gas chromatography, was too small to explain the deviation between the HCHO consumption and the isoprene yield. It thus seems likely that the deviation

is to be ascribed mainly to the formation of unidentified polymers.

MoO₃-based oxides. The yields of isoprene obtained with a series of MoO₃-based oxides are plotted as a function of the elapsed time of reaction in Fig. 1. The activity of the single MoO₃ and the binary oxides of Mo-P (9-1), Mo-Bi (5-5), Mo-Al (8-2), and Mo-Fe (7-3) is very low. While a relatively high yield of isoprene is obtained with the Mo-Fe (2-8), Mo-Ti (2-8), and Mo-V (8-2) oxides, though it markedly decreases with an increase in the elapsed time of reaction. The Mo-Sn (3-7) oxide was more active for the HCHO consumption than the Mo-Fe (2-8) oxide, but the main product was carbon oxides.

WO₃-based oxides. Figure 2 shows the results obtained with a series of WO₃-based oxides. Generally, the WO₃-based oxides perform better than the MoO₃-based oxides. The addition of an acidic oxide, such as P₂O₅, MoO₃, or V₂O₅, to WO₃ is not desirable, while that of a large amount of an amphoteric oxide, such as Fe₂O₃, SnO₂, TiO₂, or NiO, markedly improves the performance. The best results are obtained with the W-Fe (2-8) and W-Sn (3-7) oxides.

V₂O₅-based oxides. Figure 3 shows the results obtained with the V₂O₅-based oxides. The single V₂O₅ shows some degree of activity. The addition of an amphoteric

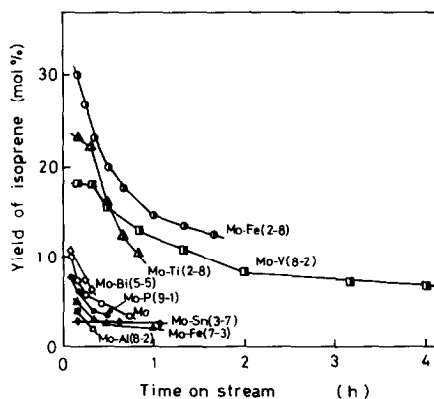


FIG. 1. Reaction with the MoO₃-based-oxide catalysts.

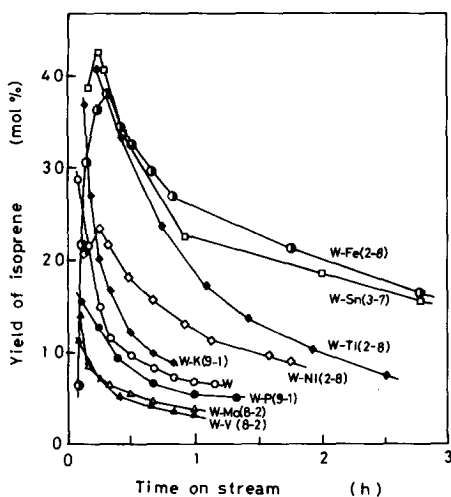


FIG. 2. Reaction with the WO_3 -based-oxide catalysts.

oxide to V_2O_5 enhances the formation of carbon oxides and lower the isoprene yield, unlike the case of the MoO_3 - and WO_3 -based oxides. P_2O_5 is the sole additive effective. The best results are obtained with the V_2O_5 - P_2O_5 ($P/V = 1.06$) catalyst.

V_2O_5 - P_2O_5 - M_nO_m ($V/P/M = 1/1.2/0.1$) oxides. In order to improve the yield of isoprene, attention was given to the modification of the V_2O_5 - P_2O_5 by adding a third component (M_nO_m), such as TeO_2 , Co_3O_4 , and ZrO_2 . It was found that only ZrO_2 shows a slightly improved performance.

Heteropoly compounds. The heteropoly compounds such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$, $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, $\text{Cs}_{2.5}\text{H}_{2.5}\text{PMo}_{10}\text{V}_2\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}$ were found to be ineffective as catalysts for this reaction; the yield was less than 2 mol% (based on the charged HCHO).

Effects of the Reaction Variables on the Yield of Isoprene

The study in the preceding section reveals that the best results for the formation of isoprene are obtained with the V_2O_5 - P_2O_5 and V_2O_5 - P_2O_5 - ZrO_2 catalysts. Thus, the characteristics of reaction were

studied by using the V_2O_5 - P_2O_5 ($P/V = 1.06$) catalyst.

Temperature and carrier gas. The reaction was conducted at different temperatures. With an elevation of temperature, the yield of isoprene increases, passes through a maximum at 240–260°C, and then decreases again. On the other hand, another series of experiments was conducted with a lower HCHO feed rate of 3.7 mmol/h using both air and nitrogen as the carrier gas, while fixing the other conditions as described under Experimental. The results are shown in Fig. 4. It is clear that nitrogen is better than air as the carrier gas and that there exists an optimum temperature which varies over the range 200–260°C, depending on the change in the reaction conditions. It should also be noted that the formation of carbon oxides is small, even in an air atmosphere.

Feed rate of HCHO. The reaction was performed in a nitrogen atmosphere at a fixed TBA/HCHO molar ratio of 6.83, while the feed rate of HCHO was changed from 1.9 to 7.0 mmol/h. The overall consumption of HCHO and the yield of isoprene (based on the charged HCHO) are

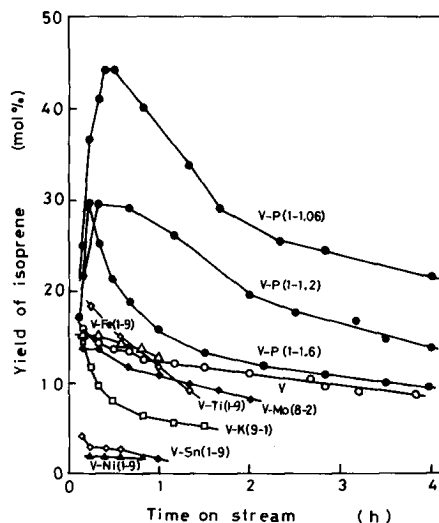


FIG. 3. Reaction with the V_2O_5 -based-oxide catalysts.

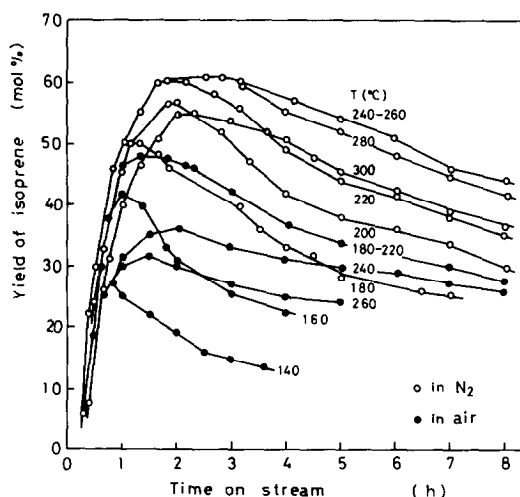


FIG. 4. Effects of the temperature and the carrier gas on the yield of isoprene.

shown in Fig. 5. The activity variation becomes rapid as the feed rate of HCHO increases.

TBA/HCHO ratio. The reaction was performed in a nitrogen atmosphere at a fixed HCHO feed rate of 7.0 mmol/h, the TBA/HCHO ratio was changed from 1.17 to 14.4. The results are shown in Fig. 6. The yield increases with an increase in the TBA/HCHO ratio.

Effects of the Reaction Variables on the Rate

The effects on the rate of isoprene formation was studied in a nitrogen atmosphere. Unless otherwise indicated, the feed rate of HCHO was fixed at 3.7 mmol/h. The data were taken about 2 h after the start of each run.

Contact time. The amount of catalyst used was varied from 0.5 to 20 g. The yield of isoprene increased steadily up to about 50 mol% with an increase in the contact time, indicating that the consecutive degradation of isoprene is small.

Temperature. The reaction was conducted using 2- to 40-g portions of the catalyst and by changing the temperature from 160 to 260°C. The rate of isoprene formation was calculated from the low-

level (<20 mol%) yield. The rate increased steadily with an elevation of temperature. The apparent activation energy, as calculated over the temperature range 160–200°C, is about 12 kcal/mol.

TBA concentration. The reaction was conducted using 4-g portion of the catalyst at a fixed HCHO concentration of 0.52 vol% and by changing the TBA concentration from 0.8 to 4.8 vol%. The results are shown in Fig. 7. The rate increases with the TBA concentration throughout this range of TBA concentrations.

HCHO concentration. The rate of isoprene formation at a fixed TBA concentration of 1.6 vol% and by changing the HCHO concentration from 0.075 to 1.55 vol% is shown in Fig. 8. The rate increases with the HCHO concentration up to 0.5 vol%, but it levels off with a further increase in the HCHO concentration.

Regeneration of the V_2O_5 - P_2O_5 Catalyst

The catalytic activity is regenerated completely by heat treatment at 350°C in a stream of air for 2 h. Moreover, the activity can also be regenerated to a great extent just by passing nitrogen gas through in

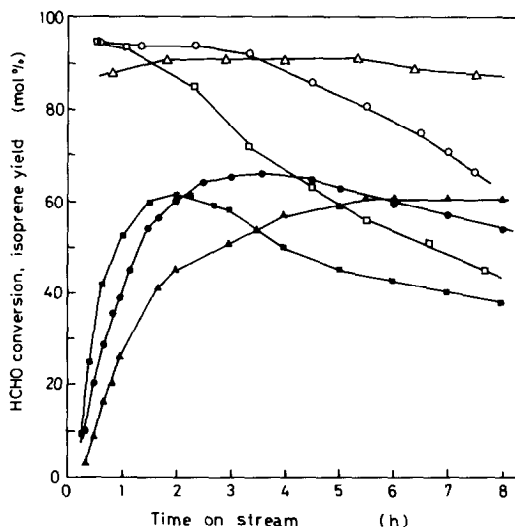


FIG. 5. Effect of the feed rate of HCHO on the yield of isoprene. Δ , \circ , \square , HCHO conversion; \blacktriangle , \bullet , \blacksquare , isoprene yield. HCHO feed rate: Δ , \blacktriangle , 1.8; \circ , \bullet , 3.7; \square , \blacksquare , 7.0 mmol/h. TBA/HCHO = 6.83.

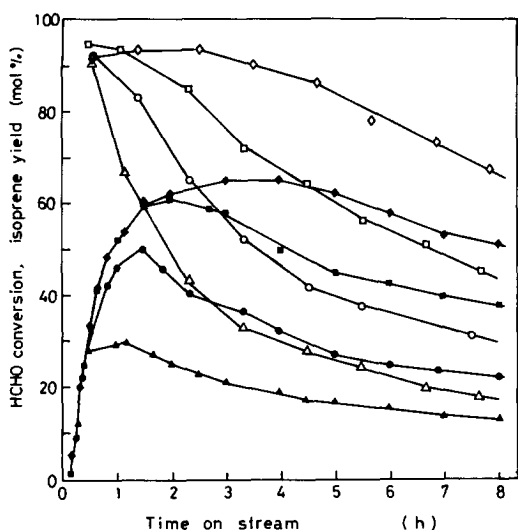


FIG. 6. Effect of the TBA/HCHO ratio on the yield of isoprene. Δ , \circ , \square , \diamond , HCHO conversion; \blacktriangle , \bullet , \blacksquare , \blacklozenge , isoprene yield. TBA/HCHO ratio: Δ , \blacktriangle , 1.17; \circ , \bullet , 3.16; \square , \blacksquare , 6.83; \diamond , \blacklozenge , 14.4. HCHO feed rate = 7.0 mmol/h.

place of the reactant-gas mixture at 280°C for 1 h.

DISCUSSION

Liquid acids such as sulfuric, phosphoric, and hydrochloric acid are generally employed as catalysts for the liquid-phase Prins reaction; therefore, it seems sure that the possession of an acidic property is indispensable for a solid catalyst in the vapor-phase reaction. Indeed, the solid catalysts proposed in the patent literature are acidic oxides (4).

However, it is interesting to note that the heteropoly compounds, which possess a much more eminent acidic property and a much more eminent catalytic activity for acid-catalyzed reactions than any other WO_3 - or MoO_3 -based oxides (11), are not effective as such catalysts. It certainly seems to be true, as has been pointed out (6), that catalysts possessing strong acidic sites are not effective and that there exists a certain acid strength just proper to catalyze the reaction.

The best results are obtained with the V_2O_5 - P_2O_5 ($P/V = 1.06$) catalyst, which

possesses an enhanced acidic property and, at the same time, a certain extent of the basic property (8). The next best results are obtained with the catalysts obtained by the combination of an acidic oxide, such as MoO_3 and WO_3 , with an amphoteric oxide, such as TiO_2 , SnO_2 , or Fe_2O_3 . It has been found (12) that these combinations often bring about the generation of both acidic and basic sites. These findings lead us to assume that the basic sites also play a certain role in producing isoprene; e.g., in the dehydration stage or in the desorption of isoprene. This view is also supported by the fact that the Mo-P and W-P oxides, which are assumed to be deficient in the basic property, are inactive for the reaction.

On the other hand, the main product was carbon oxides over the V-Ti, V-Sn, V-Fe, V-Ni, and Mo-Sn oxides. It has been found in the previous study (12) that HCHO tends to be converted to carbon oxides over relatively basic oxide catalysts. Therefore, the above-cited oxides seem to be too basic to be catalysts for this reaction.

Generally, the WO_3 -based oxides perform better than the corresponding MoO_3 -based oxides. This may be ascribed to the poor reducibility of WO_3 , because the cata-

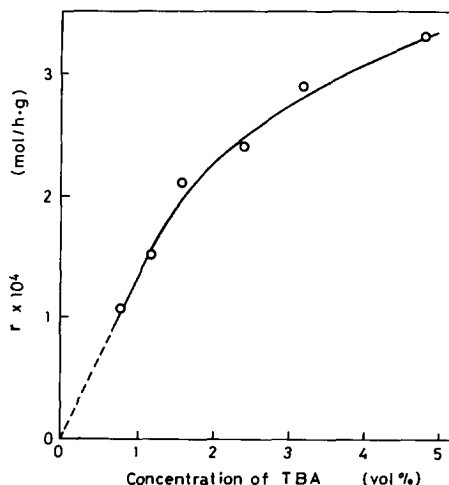


FIG. 7. Effect of the TBA concentration on the rate of isoprene formation.

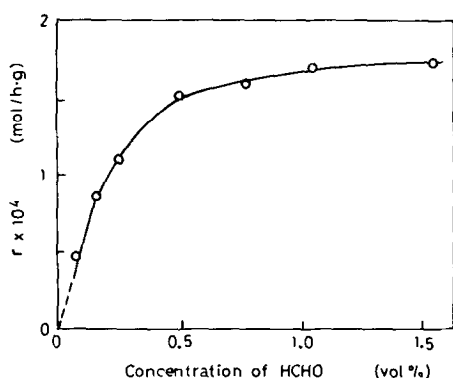


FIG. 8. Effect of the HCHO concentration on the rate of isoprene formation.

lysts suffer a reduction during the reaction, thus inducing a change in the acid-base property. The stability of the $V_2O_5-P_2O_5$ catalyst may also be ascribed, in part, to the unreducible property of P_2O_5 .

As may be seen in Figs. 5 and 6, the activity for the consumption of HCHO decreases steadily with the elapsed time of the reaction, while the yield of isoprene first increases, passes through a maximum, and then decreases. These findings are in accord with those reported for supported B_2O_3 (6) and sulfates (7). These results can be explained by assuming that the strong acidic sites, which are active for the consumption of HCHO and which lead the reaction to the formation of polymer compounds, are poisoned preferentially by the polymer products during the reaction.

It is to be noted that the activity of the $V_2O_5-P_2O_5$ catalyst can be regenerated to a great extent by the heat treatment in the absence of oxygen. It is likely that, at least in the case of the $V_2O_5-P_2O_5$ catalyst, the deactivation is not ascribed entirely to the reduction of catalyst.

It is also interesting to note that the poisoning action is promoted by the presence of gaseous oxygen (Fig. 4).

It is easily understandable that the poisoning action increases with an increase in the feed rate of HCHO (Fig. 5). However, as may be seen in Fig. 6, the poisoning action decreases with an increase in the

TBA/HCHO ratio, indicating that isobutene plays a role in depressing the poisoning action.

On the other hand, the deactivation of the $V_2O_5-P_2O_5$ is much less remarkable in the case of the condensation of HCHO with acetone (9), indicating that both isobutene and HCHO take part in the formation of the poisoning compounds. It may be envisaged as a possibility that the reaction of isobutene with more than 1 mol of HCHO leads to the formation of poisoning compounds.

The elevation of the temperature induces an increase in the rate of the overall reaction and, at the same time, in the deactivation as well. Therefore, the optimal temperature varies depending on the reaction conditions used. Under the conditions used in this study, it seems to be about 240 to 260°C.

As may be seen in Fig. 8, the rate levels off at the HCHO concentration of 0.5 vol%, while it increases steadily with an increase in the TBA concentration, even at a TBA concentration of 5 vol% (Fig. 7). This finding indicates that the presence of a large excess of isobutene with respect to HCHO is favorable in view of the increase in the rate of the reaction as well as in view of the depression of the deactivation.

Facility in regeneration is surely a great advantage of the $V_2O_5-P_2O_5$ catalyst. For example, the regeneration of $B_2O_3-SiO_2-Al_2O_3$ by burning the carbon deposit is accompanied by a risk of deactivation (6).

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*Research Laboratory of Resources
Utilization
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku
Yokohama 227, Japan*

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