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Stable Vapor-phase Catalytic Conversion of Pinacolone into 2,3-Dimethyl-1,3-butadiene

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In the vapor-phase synthesis of 2,3-dimethyl-1,3-butadiene from pinacolone over modified alumina catalysts, it was found that alumina modified with transition metals such as Co stabilized the conversion of pinacolone and produced 2,3-dimethyl-1,3-butadiene selectively under hydrogen flow conditions, whereas the catalytic activity of pure alumina was seriously deteriorated irrespective of its high initial activity.

2,3-Dimethyl-1,3-butadiene, abbreviated as DMB, is a useful chemical such as a synthetic rubber and a diene in Diels–Alder reactions. It is well known that ketones are synthesized in the pinacol rearrangement of vicinal diols: for example, 2,3-dimethyl-2,3-butanediol, so-called pinacol, is converted into 3,3-dimethyl-2-butanone, pinacolone, through dehydration. Homogeneous acids such as $SbCl_5$–$AgSbF_6$[1] and BF_3[2] catalyze the rearrangement. It is reported that the rearrangement proceeds under supercritical conditions without catalyst.[3] It is also reported that solid acids such as aluminum phosphate,[4,5] sulfated zirconia,[6] and zeolite[7] catalyze the rearrangement in the vapor phase. In the vapor-phase catalytic rearrangement, however, DMB can be produced as a by-product, into which pinacolone is transformed and dehydrated.[4,5]

It is reported that DMB is produced from pinacolone through migration of a methyl group of pinacolone and the following dehydration over alumina.[8–10] The selectivity to pinacolone is at most 77 mol %.[8] But it has some problems such as degradation of catalyst and the resulting low yield of DMB for a long operation. The catalyst deactivation prevents industrialization of the process. In acid-catalyzed reactions, the catalytic activity is often deactivated due to coke formation. Supported noble metals such as Pt often affect stabilization of catalytic activity in the acid-catalyzed reactions. In this paper, we developed an effective catalytic system for the conversion of pinacolone into DMB (Figure 1) using acid catalysts modified with transition metals, such as Co, Ni, Cu, Ag, and Rh.

Pinacolone, metal nitrates, and Rh/Al_2O_3 catalyst were purchased from Wako Pure Chemical Industries Ltd. ZrO_2 (RSC-HP) and TiO_2 (CS-750-24) were supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd. and Sakai Chemical Industry Co., respectively. SiO_2–Al_2O_3 (N632HN) was purchased from Nikki Chemical Co. Al_2O_3 (DC2282, specific surface area of 200 $m^2 g^{-1}$; other basic data are cited in the Supporting Information[11]) was supplied by Dia Catalyst. Supported catalysts were prepared by impregnating metal nitrate solution to a support, and water was evaporated at ambient pressure and ca. 70 °C by illuminating with a 350-W electric light bulb. The obtained solid was calcined at 500 °C for 3 h.

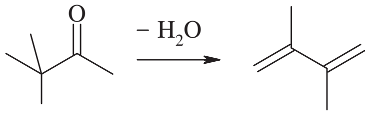

Figure 1. Conversion of pinacolone to DMB.

The catalytic reaction was performed in a fixed-bed down-flow glass tube reactor at atmospheric pressure in H_2 or N_2 flow of 30 $cm^3 min^{-1}$. Prior to the reaction, a catalyst was preheated in the carrier gas at a flow rate of 30 $cm^3 min^{-1}$ at 500 °C for 1 h. The effluent was collected in a liquid nitrogen trap at −196 °C every 1 h, and analyzed by FID-GC (GC-14A, Shimadzu) using a 30-m capillary column of TC-5 (GL Science, Japan). A GC-MS (QP5050A, Shimadzu) was used for identification of products in the effluent. A typical reaction was carried out under the conditions at 425 °C and $W/F = 0.265\ g\ h\ cm^{-3}$ where W and F are catalyst weight and reactant feed rate, respectively.

In our preliminary screening of catalyst, Al_2O_3 was found to be selective for the formation of DMB: pure Al_2O_3 catalyst showed an excellent selectivity to DMB of 96.2% (Table 1). But the catalytic activity of Al_2O_3 steeply decreased with time on stream (Figure 2) irrespective of carrier gas, either N_2 or H_2. After reaction the alumina catalyst turns black because of being covered by coke. Other catalysts such as SiO_2–Al_2O_3 and TiO_2 as well as Al_2O_3 showed deactivation, as shown in detail in the Supporting Information (Figure S1[11]). However, ZrO_2 showed an induction period in the initial stage of reaction.

Among the tested catalysts, Al_2O_3 was the most selective, so we modified Al_2O_3 with transition metals. Table 1 also shows the catalytic performance of several Al_2O_3 modified with

Table 1. Conversion of pinacolone over metal oxide supported on alumina and pure oxide catalysts[a]

Catalyst	(oxide content/wt %)	Conversion[b] /mol %	Selectivity/mol %[b]		
			DMB	DMBns	33DM1
Al_2O_3	(0)	65.3	96.2	3.2	0.2
SiO_2–Al_2O_3	(0)	55.7	66.7	10.3	2.1
ZrO_2	(0)	67.8	80.0	6.7	0.5
TiO_2	(0)	41.3	86.6	8.5	0.6
MnO_2/Al_2O_3	(2.5)	54.9	98.4	0.8	0
Fe_2O_3/Al_2O_3	(2.5)	77.3	97.7	2.1	0.2
Co_3O_4/Al_2O_3	(2.5)	87.7	96.6	3.3	0
NiO/Al_2O_3	(2.5)	81.2	91.9	7.1	0.4
CuO/Al_2O_3	(2.5)	91.8	85.8	11.9	0.9
Ag_2O/Al_2O_3	(2.5)	83.8	86.9	8.1	0.9
Rh/Al_2O_3	(0.5[c])	96.6	86.5	11.0	0.5

[a]Carrier gas, H_2; reaction temperature, 425 °C. [b]Average conversion in the initial 5 h; DMBns, average selectivity to the sum of 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and 2,3-dimethylbutane; 33DM1, 3,3-dimethyl-1-butene. [c]Rh metal content.

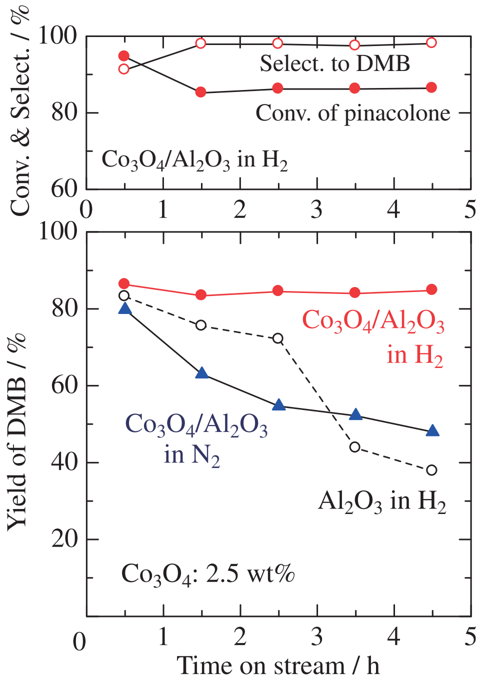

Figure 2. Change in the conversion of pinacolone over Co_3O_4/Al_2O_3 at 425 °C with time on stream.

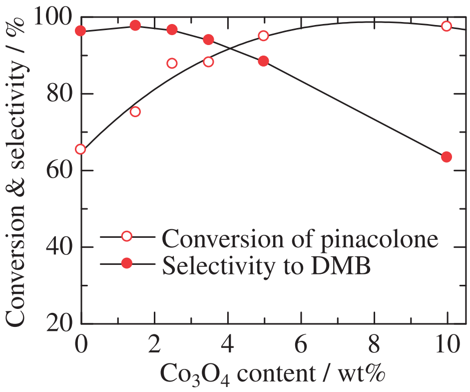

Figure 3. Influence of Co_3O_4 content in the Co_3O_4/Al_2O_3 catalyst on the average conversion of pinacolone at 425 °C.

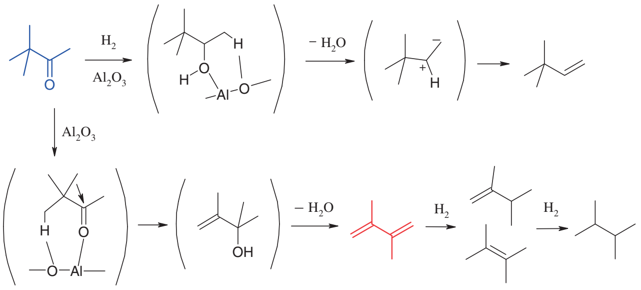

Figure 4. Possible reaction route in the reaction of pinacolone.

transition metals. Transition metals such as Mn, Fe, Ni, and Ag were not effective in stabilizing the catalytic activity: MnO_2 and Fe_2O_3 decreased the average conversion, and NiO and Ag_2O decreased the selectivity, while the conversion decreased with time on stream (Figure S2[11]).

In contrast, Rh, CuO, and Co_3O_4 were effective in the stabilization of catalytic activity. Commercial Rh/Al_2O_3 catalyst showed a stable conversion (Figure S3[11]). However, the selectivity to DMB slightly decreased because of the formation of dimethylbutenes through hydrogenation of DMB. CuO also stabilized the conversion (Figure S4[11]), whereas the selectivity to DMB decreased (Table S1[11]). Co_3O_4 showed the most stable conversion and high selectivity to DMB. The stable catalytic activity was realized in H_2 flow (Figure 2). In N_2 flow, however, the conversion steeply decreased with time on stream over Co_3O_4/Al_2O_3 as well as Al_2O_3. In addition, a change in carrier gas from H_2 to N_2 after catalyst reduction induced the degradation. This indicates that hydrogen is necessary to stabilize the catalyst activity.

Figure 3 shows the effect of Co_3O_4 content on the average conversion in the initial 5 h over the Co_3O_4/Al_2O_3 catalyst. The conversion of pinacolone increased with increasing Co_3O_4 content, whereas the selectivity to DMB decreased. Stable catalytic activity with the highest selectivity to DMB was obtained in the alumina-supported Co catalysts at Co_3O_4 contents of 2.5–3.5 wt %. Detailed selectivity of different Co_3O_4/Al_2O_3 catalysts is summarized in Table S2,[11] and the change in the conversion with time on stream is depicted in Figure S5.[11]

In a similar way to Co_3O_4, transition metals such as Cu, Ag, and Rh prevent degradation of catalytic activity of Al_2O_3 (Table 1). The metals, however, decreased the selectivity to DMB because of its hydrogenation ability. Most of the byproducts are hydrogenated products, as shown in the speculative reaction route of Figure 4.

Co_3O_4 is reducible in hydrogen flow at elevated temperatures, and the reducibility of Co_3O_4 during reduction has been reported:[12] the reduction of Co_3O_4 proceeds in two steps, (i) Co_3O_4 to CoO and (ii) CoO to Co. It is certain that the Co_3O_4/Al_2O_3 samples were partially reduced at the reaction temperature of 425 °C (Figure S6[11]). We speculate that Co_3O_4 in the Co_3O_4/Al_2O_3 catalyst is partially reduced to CoO in the working state and that the reduced CoO inhibits the catalyst degradation. Hydrogen with Co species probably acts as a remover of products from the catalyst surface to expose active sites on the alumina surface. Thus, the Co_3O_4-modified Al_2O_3 catalyst is used for this reaction for inhibition of catalyst degradation. A similar effect of hydrogen has been reported by Hattori in the isomerization of alkane.[13] We still need further study on the role of hydrogen.

It is concluded that vapor-phase pinacolone conversion to produce 2,3-dimethyl-1,3-butadiene can be stabilized in hydrogen flow over alumina modified with transition metals, especially with Co_3O_4, at 425 °C. The excellent catalytic performance without degradation is realized at an appropriate Co_3O_4 content, 2.5–3.5 wt %, whereas metal contents higher than 3.5 wt % induce hydrogenation ability to the catalyst and reduce the selectivity to DMB. Hydrogen with the partially reduced cobalt oxides such as CoO, which remove the produced DMB to prevent coke formation, is important to stabilize the catalytic activity of alumina.

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