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Formation of C_4-Hydrocarbons by Oxidative Methylation of Propylene with Methane over Various Metal Oxide Catalysts

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Various metal oxides were studied as a catalyst for formation of C_4-hydrocarbons by the reaction between methane and propylene in the presence of oxygen. La_2O_3 catalysts showed high activities for the C_4 formation. In the case of La_2O_3 catalyst modified with 3 wt% Na_2O, a much higher yield of C_4 (10.1%) was obtained.

Since Keller and Bhashin[1] reported the possibility of synthesis of C_2-hydrocarbons (C_2H_6+C_2H_4) by oxidative coupling of methane over various metal oxides, many researchers[2-8] are beginning to work in this field. Sofranko et al. have recently shown that in the case of methane-propylene in the absence of oxygen over manganese oxide on silica, butene is a primary product by way of methyl addition to propylene.[9] However, studies concerning the oxidative methylation of some olefins, aromatics, and nitriles containing a methyl group at α-position on the electron-accepting function group are not fully made. The oxidative methylation reported by Khcheyan et al. proceeds in a medium with excess methane in the presence of oxygen to give products with new C-C and C=C bonds.[10] It is well known that metal oxides and metal oxides modified with alkali metal oxides are effective catalysts for oxidative coupling of methane.[1-9] In this paper, effective metal oxide catalysts for the formation of C_4-hydrocarbons (1-C_4H_8, t-2-C_4H_8, c-2-C_4H_8, and 1,3-C_4H_6) by oxidative methylation of propylene were investigated, using a conventional flow method at atmospheric pressure.

The catalysts used here were prepared from various metal nitrates or metal carbonates, except for γ-Al_2O_3 and La_2O_3 catalysts. The catalysts supported on γ-Al_2O_3 or La_2O_3 were prepared by an impregnation method. Each catalyst was dried at 373 K and then calcined in air at 973 K for 2 h. Prior to the reaction, the pretreatment for the activation of catalyst was performed at 973 K for 0.5 h in a flow of nitrogen and oxygen, and then for 1.5 h in a stream of nitrogen alone. The reaction conditions were as follows; reaction temperature: T=923 K, partial pressure of methane: $P(CH_4)$=88.6 kPa, partial pressure of propylene: $P(C_3H_6)$=8.44 kPa, partial pressure of oxygen: $P(O_2)$=4.22 kPa, and W/F=4.67 g·h/mol. The products were analyzed by gas chromatography.

Table 1 shows the typical results of the reaction on various metal oxide catalysts. The yield was calculated on the basis of conversion of propylene to the each product. As is shown in Table 1, the La_2O_3 catalysts are much

Table 1. Catalytic Activity for Oxidative Methylation of Propylene at 923 K[a)]

Catalyst	Conversion/%			Yield/%[b)]		Distribution/%				
	CH_4	C_3H_6	O_2	CO_2 +CO	C_4-H.C.	1-C_4H_8	t-2-C_4H_8	c-2-C_4H_8	1,3-C_4H_6	n-C_4H_{10}
γ-Al_2O_3	7.5	33.5	56.3	3.49	1.28	46.5	15.1	15.4	23.0	-
10wt%CuO/γ-Al_2O_3	12.6	32.6	65.9	5.17	0.70	30.0	23.6	28.1	18.3	-
10wt%PbO/γ-Al_2O_3	6.2	29.2	60.9	5.77	1.20	28.6	15.5	21.9	34.0	-
10wt%Ag_2O/γ-Al_2O_3	4.6	32.0	52.5	4.22	1.09	22.7	18.1	20.0	39.2	-
10wt%Bi_2O_3/γ-Al_2O_3	15.0	61.5	49.5	8.12	3.21	24.4	11.9	11.9	47.7	4.1
30wt%La_2O_3/γ-Al_2O_3	18.4	34.2	57.3	4.97	2.20	33.7	14.6	11.5	40.2	-
La_2O_3	11.4	23.6	45.6	3.79	6.89	44.1	20.4	18.2	17.3	-
3wt%Na_2O/La_2O_3	8.7	29.4	79.6	4.50	10.1	55.2	15.7	13.9	15.2	-
8wt%Na_2O/La_2O_3	7.5	24.0	71.8	4.07	6.70	61.3	11.6	11.7	15.4	-

a) Data at 60 min. b) Calculated on the basis of propylene conversion; the rest was an yield of carbon deposit.

more effective for the reaction than the other catalysts. In addition, the La_2O_3 catalysts modified with Na_2O in the range of 1 to 5 wt% exhibited much more activity for C_4 formation than the La_2O_3 catalyst without Na_2O. However, further addition of Na_2O over 8 wt% resulted in a decrease in the yield of C_4. On the other hand, the γ-Al_2O_3, CuO/γ-Al_2O_3, PbO/γ-Al_2O_3, and Ag_2O/γ-Al_2O_3 catalysts were found to give remarkably lower yields of C_4 than the La_2O_3 catalysts. In the cases of Bi_2O_3/γ-Al_2O_3 and La_2O_3/γ-Al_2O_3 catalysts, the yields of C_4 were improved considerably, compared with the γ-Al_2O_3 catalyst. The distribution of C_4-hydrocarbons depends on the catalyst, as can be seen from Table 1. In addition, the formation of C_2-hydrocarbons was not observed in every case, because of relatively lower reaction temperature of 923 K.

The La_2O_3 catalyst with 3 wt% Na_2O gave a maximum C_4 yield of 10.1% and the yield remained almost constant for 2 h of reaction time, in spite of the formation of carbon deposit. From these facts, it can be said that developed studies on the oxidative methylation of propylene will be able to give much more yield of C_4-hydrocarbons than that described in this communication.

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