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Group 5A Metal Oxides as Promoters for Oxidative Coupling of Methane

Masami YAMAMURA,* Hideo OKADO, and Naohide TSUZUKI
JAPEX Research Center, Japan Petroleum Exploration Co., Ltd.,
1-2-1 Hamada, Chiba 260

Group 5A metal oxides were tested as promoters for oxidative coupling of methane. They were effective promoters for the coupling reaction, when mixed with 1A, 1A/2A, and 1A/3A oxide catalysts, respectively. Addition of Group 5A metal increased the activity of these catalysts.

Since the pioneer work by Keller and Bhasin,$^{1)}$ a number of catalysts for oxidative coupling of methane have been reported and reviewed.$^{2)}$ These are alkali-alkaline earth metal oxides, the compound oxides of lanthanide and actinide metals, and etc. The mixed oxides including Group 5A metals of the periodic table, however, have not been investigated systematically as catalysts for oxidative coupling of methane. The Group 5A metal oxides have been used as oxidation catalysts, for example, vanadium pentoxide in the oxidation of benzene to maleic anhydride. Although aliphatic hydrocarbons are oxidized to CO or CO_2 over Group 5A metal oxides because of their strong oxidation activity, it is thought that these metal oxides can be used as promoters for oxidative coupling of methane by controlling the amount of addition to existing catalysts. Especially the increase in catalytic activity is expected.

We have tested the effect of Group 5A metals as a promoter to the oxides of alkali metal, alkali-alkaline earth metals, lanthanum and of alkali-lanthanum metals, all well known as catalysts for oxidative coupling of methane.$^{2)}$

Catalysts were prepared by the following method using alkali metal carbonates, Group 3A metal oxides and Group 5A metal oxides. The mixture of these metal oxides was immersed to an aqueous solution of alkali metal carbonates. After the solution was evaporated, the powder was dried at 373-437 K, heated slowly to 1173 K, and calcined for 2 h.

The catalysts were tested using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure. The catalyst(1g) was packed in the center of Alumina reactor(9 mm i.d., 550 mm long). A CH_4/O_2(mole ratio= 90/10) gas mixture without a diluent was introduced to the reactor(flow rate=100 mlSTP/min). The reactor was heated to a reaction temperature within 30 min. Steady state results were recorded after 1 h.

The reaction products were analyzed with Shimadzu GC-8AT gas chromatograph using a Gaskuropack· 54 packed column for the separation of carbon dioxide and hydrocarbons and an active carbon packed column for the separation of oxygen and carbon monoxide. The conversion of methane, the selectivity and the yield of the products were calculated on the basis of carbon number of methane reacted.

Vanadium, niobium and tantalum were tested as Group 5A metals. Oxidative coupling of methane was carried out with the combination of one of these three metal oxides and another reported catalysts at 1023 K and/or 1073 K.

Table 1 shows the results of oxidative coupling of methane over Group 5A metal oxides alone, Na/5A and Na/Mg/5A mixed catalysts at 1073 K. Vanadium pentoxide could not be used in the reaction conditions because of it's low melting point(963 K). It was found that Group 5A metal oxides alone gave poor results.

Table 1. Oxidative coupling of methane over Nb_2O_5,Ta_2O_5,Na/5A,Na/Mg/5A
Temp=1073 K, CH_4/O_2=90/10 ml/min, Catalyst=1 g

	Conv./%		Selectivity/%					
	CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_3	C_{2+}
Nb_2O_5	9.0	81.5	57.3	19.4	10.0	12.3	1.0	23.3
Ta_2O_5	5.8	50.9	23.2	37.1	16.4	21.7	1.7	39.8
Na/Nb	12.0	91.4	15.7	38.8	25.4	16.5	3.6	45.5
Na/0.3Nb	9.2	61.1	5.8	32.1	26.6	27.4	8.1	62.1
Na/0.3V	13.6	82.6	12.1	26.7	38.5	18.7	4.0	61.2
Na/0.3Ta	9.2	60.2	14.6	15.9	37.5	25.3	6.7	69.5
Na/Mg	6.9	43.8	13.6	18.6	28.4	34.3	5.1	67.8
Na/Mg/0.3V	14.2	97.9	0.6	26.2	38.8	27.8	6.5	73.1
Na/Mg/0.3Nb	15.0	98.4	2.2	29.9	35.2	26.2	6.5	67.9
Na/Mg/0.3Ta	12.7	97.2	2.2	29.5	41.0	22.2	5.2	68.4

When niobium oxide was admixed with sodium carbonate at atomic ratio of 1:1, both of activity and C_{2+} selectivity increased as shown in Table 1. However, the selectivity was still less than 50%. The decrease of the amount of niobium oxide to the atomic ratio of 0.3 against sodium (designated as Na/0.3Nb) resulted in higher selectivity to C_{2+} hydrocarbon, but the activity decreased to the level of niobium oxide alone. In the case of vanadium, both activity and selectivity increased to a high level. Another alkali metals, Li and K, were also tested. Li/0.3Nb gave the best results in activity(16.2%) and C_2+ selectivity(79.3%) at 1023 K. The C_2+ yield was about 13%. On the other hand, potassium gave relatively poor results.

Although Na/MgO was reported as an effective catalyst for oxidative coupling of methane,[3)] it showed only 6.9% of methane conversion under our reaction conditions as shown in Table 1, probably because of higher CH_4/O_2 ratio and higher reactant pressure. Addition of vanadium with atomic ratio of 0.3 to Na/Mg resulted in a remarkable increase of methane and oxygen conversions as well as C_2+ selectivity. Both of conversions were also increased by adding niobium oxide. Na/Mg/0.3Ta showed almost the same C_2+ selectivity as that of Na/Mg/0.3Nb, but methane conversion was lower.

From the results described above, Group 5A metal oxides can be good promoters to 1A and 2A oxide catalysts for oxidative coupling of methane. As expected, the increase in catalytic activity was observed.

Lanthanum oxide itself is known to have high catalytic activity and high selectivity for oxidative coupling of methane.[4)] The results of the coupling reaction over La_2O_3 alone, La/5A and Na/La/5A mixed catalysts at 1023 K are shown in Table 2. Lanthanum oxide gave methane conversion of 15.0% and C_2+ selectivity of 63.2% in the reaction conditions. The activity and C_2+ selectivity for the niobium added lanthanum oxide did not exceed those of lanthanum oxide alone. For instance, addition of 0.3Nb gave the same results as lanthanum oxide itself, but vanadium oxide significantly decreased the selectivity to only about 30%. Therefore in the case of lanthanum oxide, addition of Group 5A metal oxides showed no improvement. These results indicate the addition of Group 5A metal oxides is not necessarily effective, especially when catalyst itself has high activity.

Table 2. Oxidative coupling of methane over La_2O_3,La/5A,Na/La/5A
Temp=1023 K, CH_4/O_2=90/10 ml/min, Catalyst=1 g

	Conv./%		Selectivity/%					
	CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_3	C_2+
La_2O_3	15.0	99.0	8.9	27.9	30.2	27.0	6.0	63.2
La/0.3Nb	13.2	97.1	8.1	27.1	28.1	32.6	4.1	64.8
La/0.3V	11.4	98.4	18.6	49.6	12.2	19.2	0.7	32.1
La/0.3Ta	13.2	98.1	10.5	39.1	21.0	26.5	2.9	50.4
Na/La	8.2	45.4	6.3	18.7	31.0	39.8	4.2	75.0
Na/La/0.2Nb	15.1	96.7	1.9	21.3	38.4	32.4	5.7	76.5
Na/La/0.3Nb	16.0	97.3	1.5	24.4	38.7	27.5	7.9	74.1
Na/La/0.3V	16.0	83.5	3.5	27.1	32.6	29.1	7.7	69.4
Na/La/0.3Ta	18.3	98.1	1.6	29.5	38.1	23.1	7.7	68.9

When sodium was added to lanthanum oxide with atomic ratio of 1:1, the C_2+ selectivity increased remarkably. However, the considerable decrease of the activity was observed. By adding small amounts of niobium oxide to Na/La catalyst, the activity increased up to the same level as that of lanthanum oxide alone without decrease in the selectivity. Addition of vanadium oxide or tantalum oxide to Na/La catalyst decreased the selectivity but increased the conversion, thus improved the C_2+ yield.

It is concluded that Group 5A metal oxides are effective promoters for oxidative coupling of methane especially in combination with alkali metals. The Group 5A metals improve the activity rather than the C_2+ selectivity, whereas alkali metals improve the selectivity. Group 5A metal is supposed to act as a promoter by controlling the basic sites of the catalysts.

The XRD patterns of Group 5A added catalysts were measured. Besides the oxides of each metal, complex metal oxides were observed, such as Na_3NbO_4 in Na/0.3Nb and La_3NbO_7 in Na/La/0.3Nb catalyst.

Na/La/0.3Ta catalyst had very low surface area of 1.02 m^2/g. The surface areas of another catalysts are supposed to be the same order. As Aika *et al.* have reported, it seems that a large surface area is not necessarily an important factor for catalytic activity and C_2+ selectivity in oxidative coupling of methane.3)

As oxidative coupling of methane is usually carried out in severe conditions, the stability of a catalyst is an important asset with the activity and the selectivity. It is expected that the catalysts promoted by Group 5A metal oxides have longer catalytic life time. Actually, Na/0.3V and Na/La/0.2Nb catalysts have shown no decrease in the catalytic activity and the selectivity more than 100 h. On the contrary, the life time of Li doped catalysts are known to be relatively short, because of the vaporization of Li at the reaction conditions.5) The life time of Li/0.3Nb or Li/La/0.3Nb which gave high activity and C2+ selectivity was also short.

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