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Active and Selective Catalysts in Oxidative Coupling of Methane. Nickel Oxides with Salts of Alkali Metals

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Methane is the major component of natural gas and is primarily used as a fuel. The abundance of methane makes it a raw material of great synthetic importance. However, because of the high stability of methane it must first be processed through a steam reforming step in any route to the desired chemicals. Obviously, direct conversion of methane to useful chemicals by partial oxidation and oxidative dehydrogenation would be a very desirable process.

We have looked for active and selective catalysts in the synthesis of C_2 hydrocarbons ($C_2H_4 + C_2H_6$) by partial oxidation of methane [1–4]. Among the catalysts tested, the oxides of first transition elements, such as NiO, TiO_2, Mn_2O_3, and ZnO containing lithium chloride, were useful catalysts in the selective synthesis of ethylene from methane [5]. In this communication, we report the effects of various alkali salt additives on oxidative coupling of methane over nickel oxide.

The NiO with various alkali salts were prepared by the impregnation method using aqueous solutions of the salts. The content of the alkali metals was adjusted to 20 mol% for each catalyst. The catalysts were pretreated in air at 973 K for 2 h before the experiments. The test of the catalysts were carried out using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure using helium as a carrier gas. The reaction conditions were as follows: $T = 1023$ K, $P(CH_4) = 5.1$ kPa, $P(CH_4)/P(O_2) = 2/1$, weight of catalyst = 1.00 g, and $W/F = 600$ g l^{-1} s.

Table I shows the effects of adding different lithium salts, NaCl and CsCl to NiO on the conversions of methane and oxygen, the selectivities of C_2H_4 and C_2H_6, the C_2 yield ($C_2H_4 + C_2H_6$), and the C_2H_4 yield observed at a time on stream of 20 min. The selectivities of C_2H_4 and C_2H_6 were defined as the percentages of C_2H_4 and C_2H_6, respectively, in the carbon containing products (C_2H_6, C_2H_4, CO, and CO_2) on the basis of the mole fraction of carbon atoms. The results for NiO alone (first row) show that no C_2 compounds were produced; *i.e.*, only deep oxidation of methane to CO_2 occurred. The addition of the lithium salts, NaCl and CsCl to NiO showed remarkable enhancing effects on the formations of C_2 compounds. The C_2 yields for the LiCl/NiO and LiBr/NiO were greater than 16%. It is noteworthy that the additives LiCl and LiBr enhance the formation of C_2H_4 selectively. The ratio C_2H_4/C_2H_6 in C_2 products observed for LiCl/NiO and LiBr/NiO are 3.6 and 14.8, respectively. This is desirable since the further oxidative dehydrogenation process for the C_2H_6 in C_2 products may not be required for the synthesis of C_2H_4. The yields of C_2H_4 for LiCl/NiO and LiBr/NiO in Table I are quite high (14.5 and 15.2%, respectively) and are comparable to the results obtained for $LiCl/Sm_2O_3$ catalyst [3].

The NiO without alkali metals showed high catalytic activity in the deep oxidation of methane (Table I). The catalytic activity of NiO was depressed strongly by adding any of the alkali salts to the oxides, but the activity for oxidative coupling of methane was increased remarkably as described earlier. These observations suggest that alkali metals poison the active sites which cause the burning of methane or of the C_2 compounds produced and create new active sites which are effective to dehydrogenation and coupling of methane. It is believed that

TABLE I. Effects of Alkali Salts on Partial Oxidation of CH_4 over NiO

Catalyst	CH_4-conversion (%)	O_2-conversion (%)	C_2H_4-selectivity (%)	C_2H_6-selectivity (%)	C_2-yield (%)	C_2H_4-yield (%)
NiO	29.9	81	0	0	0	0
LiCl/NiO	25.9	57	56.2	15.6	18.6	14.5
LiBr/NiO	35.1	94	43.4	2.9	16.2	15.2
LiF/NiO	20.5	90	12.9	12.9	5.3	2.6
LiOH/NiO	25.8	68	23.4	27.9	13.2	6.0
$LiNO_3$/NiO	26.1	75	23.8	32.0	14.6	6.2
Li_2CO_3/NiO	25.9	70	26.5	22.4	12.7	6.9
NaCl/NiO	17.9	44	20.2	14.5	6.2	3.6
CsCl/NiO	9.3	16	26.3	36.8	5.9	2.5

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the latter reaction is initiated by the abstraction of H from CH_4 to form CH_3 radicals [6]. The subsequent oxidative dehydrogenation of C_2H_6 produces C_2H_4 [4, 6, 7]. The active sites generated on NiO by adding alkali metals must be effective for the abstraction of H from CH_4. Alternatively, the sites may form oxygen species, such as O^-, which are reactive to the oxidative abstraction of H from CH_4 [6].

The specific increase in the yield of C_2H_4 observed for LiBr and LiCl can be ascribed to the enhancement in oxidative dehydrogenation of C_2H_6 which has been produced by the coupling of the CH_3 radicals. It is known that Cl radicals catalyze the formation of C_2H_4 from methane in the gas phase [8]. The C_2H_4 is formed as follows:

$$Cl\cdot + C_2H_6 \longrightarrow HCl + C_2H_5\cdot \qquad (1)$$

$$C_2H_5\cdot \longrightarrow C_2H_4 + H\cdot \qquad (2)$$

The LiCl and LiBr must play a role in supplying Br and Cl radicals. Dissociation enthalpies of lithium halides are of the order LiF > LiCl > LiBr [9], which indicates that the bond dissociation energies of Li–X decrease according to the same order. Although the mechanism of release of halogens from the alkali halides is not known, the release must be easy as LiBr > LiCl > LiF. This idea explains the observation that the ratio C_2H_4/C_2H_6 in C_2 products for the lithium halides/NiO increases as LiBr/NiO > LiCl/NiO > LiF/NiO.

The alkali salts shown in Table I can not be stable under the reaction conditions; *i.e.*, they may partly decompose, evaporate, react with methane and oxygen, or produce mixed oxides with NiO. We are carrying out further studies on these points and will describe the details soon.

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