

Partial Oxidation of Methane Over Rare Earth Metal Oxides Using N_2O and O_2 as Oxidants

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We have previously reported that rare earth metal oxides are selective catalysts in oxidative coupling of methane using oxygen as an oxidant at a low pressure of oxygen (0.4 kPa) and at low $P(O_2)/P(CH_4)$ ratio (0.022) [1]. However, when partial pressure of oxygen or $P(O_2)/P(CH_4)$ ratio increases, the selectivity to C_2 -compounds ($C_2H_6 + C_2H_4$) decreases [2].

The observation by Liu *et al.* [3, 4] indicated that partial oxidation of methane forming methanol and formaldehyde could be achieved with high selectivity by the use of N_2O as an oxidant. Shepelev and Ione [5] reported that aromatic products can be formed by partial oxidation of methane with N_2O over ZSM-5 type catalysts. Thus, N_2O may also be a favorable oxidant for oxidative coupling of methane.

In this communication we describe oxidative coupling of methane over seven rare earth metal oxides using N_2O as an oxidant. The results of the reactions using N_2O and O_2 at relatively high partial pressures of oxidants will be compared.

The rare earth metal oxides used were all reagent grade (purity > 99.9%) in the form of powder obtained from Asahi Chemical Industry Co. The experiments were carried out using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure. The partial pressures of CH_4 and oxidants (O_2 or N_2O) at the inlet of the reactor were 48.8 and 10.5 kPa, respectively.

Figure 1 shows the conversions of methane and the oxidants over seven rare-earth metal oxides at 823, 873 and 923 K for all the catalysts. When O_2 is used as the oxidant, there is not much difference in the catalytic activities of the oxides for activation of methane. This is true also when N_2O is used as the oxidant. The conversions of O_2 at 823 K observed for the rare earth metal oxides, except for CeO_2 , were one to two orders of magnitude greater than those of N_2O . These observations show that the reactivity of O_2 for the oxidation of CH_4 is much higher than that of N_2O for most of the rare earth metal oxides tested. Figure 2 shows the selectivities

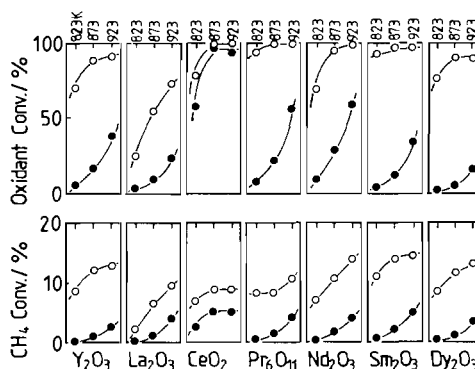


Fig. 1. Conversions of methane and oxidants in partial oxidation of methane over rare earth metal oxides at 823, 873 and 923 K. Weight of catalysts = 0.50 g, $W/F = 1.0 \text{ g cm}^{-3}$ s. Oxidants used: \bullet —, N_2O ; \circ —, O_2 .

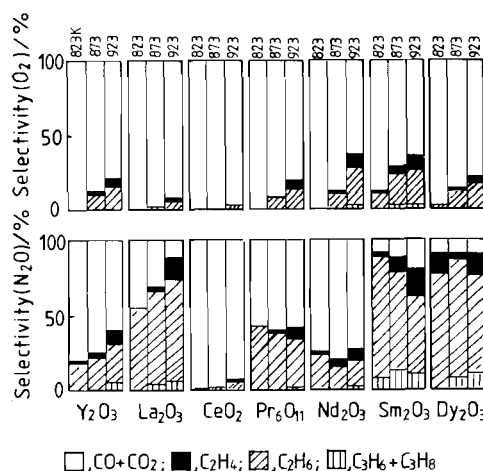


Fig. 2. Products distributions (selectivities) in partial oxidation of methane. Oxidants used: upper row, O_2 ; lower row, N_2O .

to $CO + CO_2$, C_2H_4 , C_2H_6 and C_3 -compounds ($C_3H_6 + C_3H_8$). The selectivities are defined as the percentage of converted methane reacted to the above products. When O_2 is used as the oxidant, since the partial pressure of oxygen and the ratio $P(O_2)/P(CH_4)$ are relatively high compared to the previous experimental conditions [1], the selectivities to the coupling products (C_2 - and C_3 -compounds) are less than 40% at 923 K. However, the highest selectivity observed for Sm_2O_3 [1] was confirmed also in the present experiments.

As can be seen in Fig. 2, the selectivities to the coupling products are quite high (>80%) over La_2O_3 , Sm_2O_3 and Dy_2O_3 when N_2O is used as oxidant. However, CeO_2 mainly catalyzed deep oxidation of methane with very low selectivities to the coupling products irrespective of the kind of oxidants. In

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general, the selectivity in the formation of the coupling products increases sharply with increasing temperatures when O_2 is used as the oxidant. In contrast with this, when N_2O is used, the temperature effect on the selectivity is not so appreciable especially for Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 and Dy_2O_3 . Thus, N_2O is a peculiar oxidant, enhancing selective coupling of methane at lower temperatures. For example, the selectivities to the coupling products at 823 K are almost zero for Y_2O_3 , La_2O_3 , Pr_6O_{11} and Nd_2O_3 when O_2 is used as oxidant. However, in the case of N_2O , the selectivities are 15, 51, 45 and 25% for Y_2O_3 , La_2O_3 , Pr_2O_3 and Nd_2O_3 , respectively. The selectivities observed for Sm_2O_3 and Dy_2O_3 using N_2O as the oxidant were as high as 90% at 823 K.

As described above, there are great differences in the kinetic features for the oxidative coupling of methane when N_2O and O_2 are used as oxidants. These observations strongly suggest that the oxygen species responsible for the reactions are different between the reoxidants. Alternatively, the rate-determining step in the reactions may be quite different. Details on these points will be published later.

In conclusion, oxidative coupling of methane using N_2O as the oxidant proceeded selectively over La_2O_3 , Sm_2O_3 and Dy_2O_3 even at the experimental conditions of high $P(\text{oxidant})/P(\text{CH}_4)$ ratio (= 0.21) and high partial pressure of oxidant (10.5 kPa), but the reaction with O_2 produced the coupling compounds with low selectivities. The favorable effect of N_2O on the selectivities to the coupling compounds under the same experimental conditions was especially remarkable at low temperatures (823 K). In contrast to this, the reaction with oxygen needed higher temperatures than 923 K to increase the selectivities.

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