CHEMISTRY LETTERS, pp. 499 - 500, 1985.

THE CATALYSTS ACTIVE AND SELECTIVE IN OXIDATIVE COUPLING OF METHANE

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Active and selective catalysts in oxidative coupling of methane were looked for over many metal oxides (25 oxides). In general, the oxides of rare earth elements showed higher C_2-selectivities than 75%. Among the metal oxides tested, Sm_2O_3 was the most active and selective catalyst in the formation of C_2-compounds (selectivity 93%).

Methane, one possible raw meterial, is the most abundant component of natural gas. Oxidative dehydrogenation and subsequent coupling of methane to ethane and ethylene ($CH_4+O_2 \rightarrow C_2H_6$, C_2H_4, CO_2, H_2O) is of an attractive attempt to use the methane as a precursor for ethylene. Keller and Bhasin[1)] reported that the catalysts containing the oxides of Pb, Bi, Sn, Sb, Tl, Cd, or Mn were the most active catalysts for the formation of C_2-compounds ($C_2H_4+C_2H_6$) with selectivities of $\lesssim$50%. Hinsen et al.[2,3)] reported that the PbO supported by SiO_2 was the best with respect to the C_2-selectivity which reached 72%, but its catalytic activity was low. As far as we know, this was the highest C_2-selectivity ever reported. In this communication, we will describe the results of screening for the catalysts which exhibit better catalytic activity and selectivity of C_2-compounds.

The experiments were carried out using a conventional flow system under atmospheric pressure. The experimental conditions were as follows; T=973 K, $P^o_{O_2}$(pressure of oxygen at the entrance of the reactor)=0.4 kPa, $P^o_{CH_4}$=18.2 kPa, P_{He}=82.5 kPa. The selectivity of C_2-compounds is defined as the percentage of converted methane reacted to C_2H_6 and C_2H_4.

Various rare earth metal oxides, PbO, Bi_2O_3, SnO_2, Ga_2O_3, GeO_2, In_2O_3, ZnO, CaO, and CdO without any carriers have been tested for activity and selectivity of C_2-compounds. The products were only C_2H_6, C_2H_4, CO_2, and H_2O. No other products such as C_3- or C_4-hydrocarbons, aldehydes, or alcohols were observed. The results are shown in Figs. 1-a and 1-b, respectively. Figure 1-a shows that the catalytic activity in the formation of C_2-compounds ($C_2H_6+C_2H_4$) is the largest for Sm_2O_3. The oxides tested can be put in order of their catalytic activities per unit surface area in the formation of C_2-compounds as follows; Sm_2O_3>PbO>Bi_2O_3, Ho_2O_3>Gd_2O_3>Er_2O_3>Tm_2O_3, Yb_2O_3, Y_2O_3>La_2O_3, Nd_2O_3, Eu_2O_3, Dy_2O_3, Lu_2O_3, CaO>ZnO>PrO_x, TbO_x>CeO_2, Sc_2O_3, GeO_2, In_2O_3, SnO_2. Figure 1-b shows that although the C_2-selectivity of PbO is fairly large (47%), there are many metal oxides giving better C_2-selectivities, i.e., Bi_2O_3, GeO_2, CdO, CaO, and the oxides of rare earth elements. The C_2-selectivities of the rare earth metal oxides are all larger than 75% for the reacted methane except those of CeO_2, PrO_x, and TbO_x (x may be in between 1.50 and 1.71).

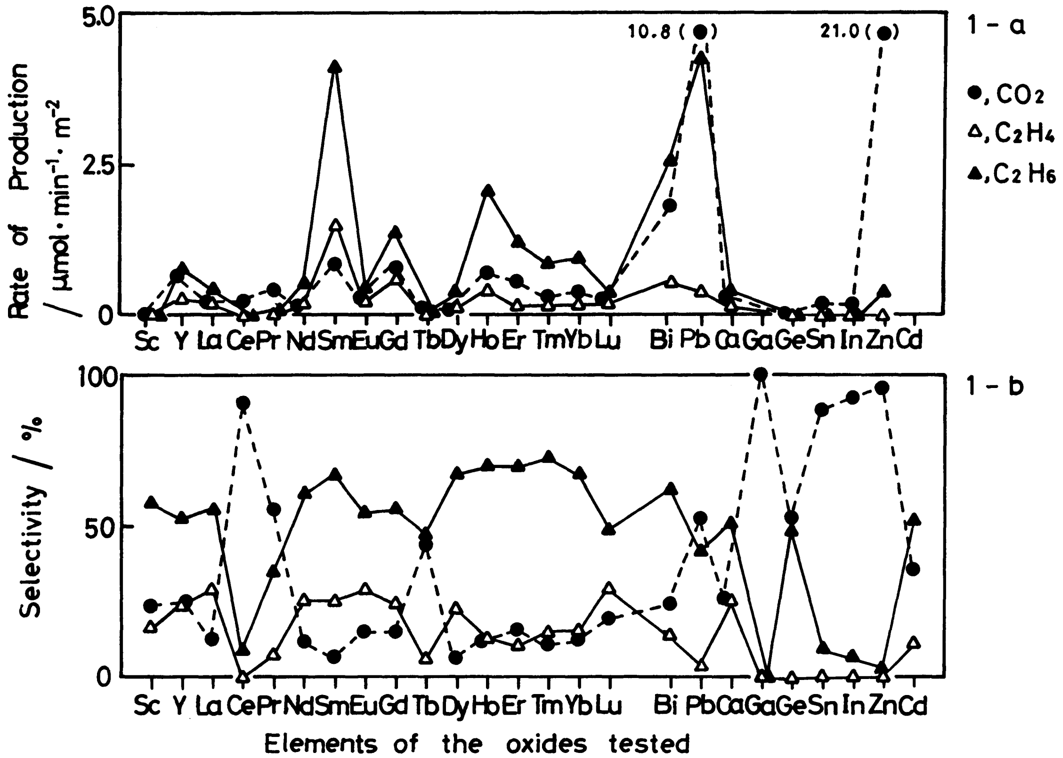

Fig. 1. 1-a: Catalytic activities of the oxides. 1-b: Selectivities.

Except the latter three oxides, the oxides of lanthanide including lanthanum showed especially high C_2-selectivities (>80%). The selectivities of the Sm_2O_3 and Dy_2O_3 reached 93% which is the highest value ever reported. The conversion of oxygen for the Sm_2O_3 and Dy_2O_3 (W/F=0.002 g s ml^{-1}) were 53 and 84%, respectively. According to Hinsen et al.[3], the oxygen conversion under their experimental conditions (T=1013 K, $P^o_{O_2}$=7 kPa, $P^o_{CH_4}$=70 kPa, W/F=1.55 g s ml^{-1}) was 22.7% for the PbO/SiO_2. Although no direct comparison among the activities of the catalysts is possible because of large difference in reaction conditions, higher oxygen conversion observed for the Sm_2O_3 and Dy_2O_3 in this work under much lower W/F compared to that of Hinsen et al. may indicate that the activities of these catalysts are better than that of PbO/SiO_2.

In conclusion, the highest selectivity and catalytic activity of the Sm_2O_3 in the formation of C_2-compounds suggest that this oxide is the most promising catalyst for oxidative coupling of methane. Ho_2O_3, Gd_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Y_2O_3, and Bi_2O_3 are also good catalysts on the basis of both activity and selectivity in the formation of C_2-compounds.

References

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(Received January 16, 1985)