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Oxidative coupling of methane over sodium-doped CaO catalysts prepared by the sol-gel method

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Abstract

Sodium-doped calcium oxide (Na/CaO) catalysts prepared by the sol-gel method (SGM) show relatively high performance for oxidative coupling of methane (OCM) compared with that prepared by impregnation method (IM). The difference between the performance of these catalysts for OCM seems to come from the difference in morphology and TPD profiles of these catalysts.

1. Introduction

Many metal oxides have been reported as catalysts for OCM since the first investigation by Keller and Bhasin [1]. For instance, Na/CaO is known to be a good catalyst [2]. Recently, we have also found that various natural calcium compounds (NCC), such as shells, give a high performance for OCM, and concluded that a high performance of NCC catalyst is due to morphology and the high concentration of sodium on the surface of NCC [3]. On the other hand, it has been reported that alkali metal promoted zirconia prepared by sol-gel method shows a noticeably increase of activity for OCM [4]. For the purpose of developing "Shell like catalyst" from reagents with a high performance, we have tried to prepare Na/CaO catalysts by sol-gel method, which can construct size-controlled micropores in metal oxides by using organic ligands as pore-forming agents.

2. Experimental

Na/CaO catalysts were prepared with varying the concentration of sodium in the starting materials from 0 to 10 mol% by the sol-gel method (SGM) described in the literature [5].

The catalysts (powder, 1 g) were tested using a fixed-bed reactor at 1023–1093 K under atmospheric pressure. A gas mixture of CH_4/O_2 (mole ratio = 9) without a diluent was introduced into the reactor with a flow rate of 100 N ml/min. The reaction products were analyzed with a gas chromatograph.

CO_2 temperature-programmed desorption (TPD) profiles of catalysts were measured using a TPD apparatus with an on-line Q-mass spectrometer.

3. Results and discussion

OCM was carried out using 7.5 mol% Na/CaO (SGM) under the above reaction conditions. Both

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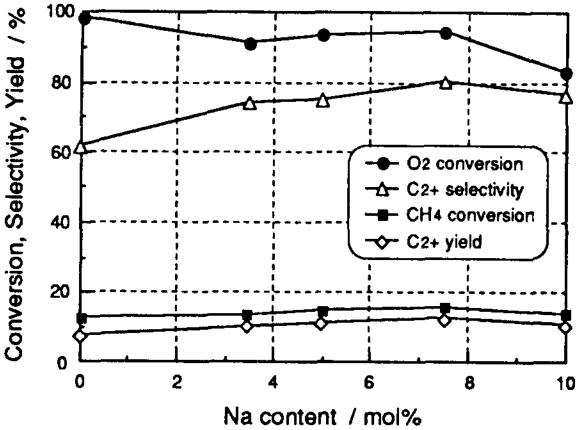

Fig. 1. Oxidative coupling of methane over Na/CaO catalysts (SGM) at 1063 K.

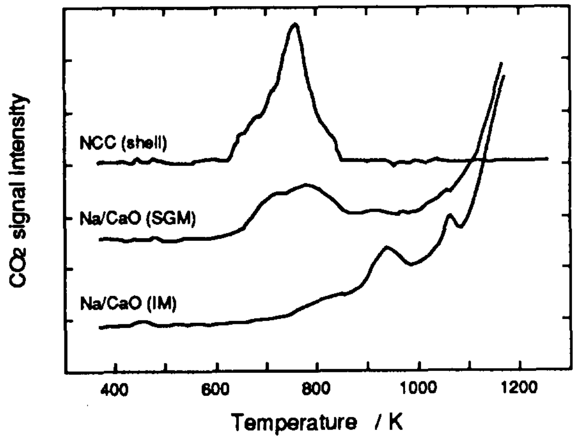

Fig. 2. TPD profiles of NCC, 7.5 mol% Na/CaO (SGM, IM).

of methane conversion and C_2+ selectivity increased with the rise of reaction temperature to 1063 K, but decreased beyond 1063 K.

Fig. 1 shows the changes in methane conversion, oxygen conversion, C_2+ selectivity and C_2+ yield at 1063 K over Na/CaO (SGM) catalysts as a function of sodium content (mol.%). The maximum values of methane conversion of 15.9% and C_2+ selectivity of 80.2% were obtained at the sodium content of 7.5 mol%. On the other hand, the methane conversion and the C_2+ selectivity for 7.5 mol% Na/CaO by a conventional impregnated method (IM) were 14.4% and 74.0%, and the maximum values of those for NCC [4] were 17.5% and 82.9%, respectively. It was found that the catalytic performance for 7.5 mol% Na/CaO (SGM) was higher than that for another one (IM), but still low compared with that for NCC.

Fig. 2 shows CO_2-TPD profiles of Na/CaO (SGM), Na/CaO (IM) and NCC. The CO_2-TPD peaks at near 750 K, which seem to be created by the interaction between Na_2O and CaO, are observed for NCC and 7.5 mol% Na/CaO (SGM). The latter peaks are smaller than the former peaks, while no peak for 7.5 mol% Na/CaO (IM). Also, the peak over 1000 K due to Na_2CO_3 is observed for 7.5 mol% Na/CaO (SGM) as well as another one (IM). However, such peak is not observed for NCC, the reason of which is due to a lower content of sodium, < 1 mol%. It is suggested that the peaks near 750 K are to some extent correlated with their catalytic performance.

From these results, it is concluded that Na/CaO (SGM) is more excellent than Na/CaO (IM) because of its morphology formed by using organic ligands for preparation and the existence of TPD peaks near 750 K, and further improvement of the method of preparing the catalyst is necessary to achieve the higher catalytic performance comparable to that of NCC.

4. Acknowledgements

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5. References

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