FARADAY COMMUNICATIONS

Microwave Effects on the Oxidative Coupling of Methane over Proton Conductive Catalysts

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The oxidative coupling of methane over proton conductive catalysts irradiated by microwaves is reported. Compared with a conventional heating mode, the temperature of the catalytic bed is lower with microwave irradiation and there is a change in both the product selectivity and in the product species formed. We believe this is to be the first reported change in product species using microwave energy in a catalytic reaction.

The use of microwave radiation to stimulate heterogeneous catalytic reactions has provided some remarkable results. Three efficient solvent-free reaction techniques have been developed.[1–4] Seyfield *et al.*[5] reported that the isomerization of hexanes over a Pt/Al_2O_3 catalyst in the presence of a microwave electromagnetic field resulted in a change in selectivity. This communication is, we believe, the first to report that oxidative coupling of methane (OCM) over $SrCe_{0.95}Yb_{0.05}O_3$ and $BaCe_{0.93}La_{0.07}O_3$, which are known to be good proton conductors,[6,7] in the presence of a microwave electromagnetic field results in a change in both the product species and the product selectivities.

$SrCe_{0.95}Yb_{0.05}O_3$ and $BaCe_{0.93}La_{0.07}O_3$ were prepared by solid-state reaction of the oxides (CeO_2, Yb_2O_3, La_2O_3) or the carbonates ($SrCO_3$, $BaCO_3$). The raw materials, in powder form, were mixed and calcined at 1300 °C for 8 h in air. The calcined oxides were finely ground and pelleted and heated under the same conditions. Powder X-ray diffraction showed that they had a single structure, confirmed to be perovskite type.

The OCM reaction was carried out at atmospheric pressure in a down-flow fixed-bed quartz tube (5 mm id) packed with the catalyst (particle size: 40–60 mesh). The catalytic bed can be heated either by conventional heating or by microwave radiation. (*a*) Conventional heating: The reactor was kept in a vertical tubular furnace. The reactor temperature (controlled by a temperature controller) was measured by a thermocouple located in the catalyst bed. (*b*) Microwave radiation: The part of the tube packed with catalysts was kept in a TE_{103} single-mode cavity, perpendicular to the broad wall of the waveguide and parallel to the direction of the electric field. The temperature of the catalytic bed (controlled by adjusting the microwave power and plunger) was measured by an infrared pyrometer (conventional measurement by the metallic thermocouples is not suitable here owing to the interference of the electromagnetic field with the metallic thermocouples). A microwave source with power 0–600 W, continuously adjustable, operating at a frequency of 2450 MHz was used for the experiment. The useful power for heating the sample was varied between 100 and 150 W during the experiment. The microwave power was varied so as to maintain the temperature at the required pre-set value.

Experimental conditions for these two modes were as follows: the amount of catalyst: 0.5 g; flow rate of gases: CH_4, 40 ml min^{-1}; O_2, 10 ml min^{-1}; He, 40 ml min^{-1}. The reactor effluent gases were analysed by gas chromatography.

The results are presented in Fig. 1 and 2. Obviously, under microwave radiation, the temperture of the catalytic bed is much lower than in the conventional heating mode. This is due to a 'hot-spot effect'. Microwave radiation could pass from a 'hot spot' generated by localized coupling of microwave energy to point defects or a weak surface bond, and this 'hot spot' stimulates the reaction to occur. Under microwave radiation the products from the OCM over the proton conductive catalysts were CO, CO_2, C_2H_2, C_2H_4, C_2H_6, H_2 and H_2O, but with conventional heating the products from the OCM over the same catalysts were CO, CO_2, C_2H_4, C_2H_6,

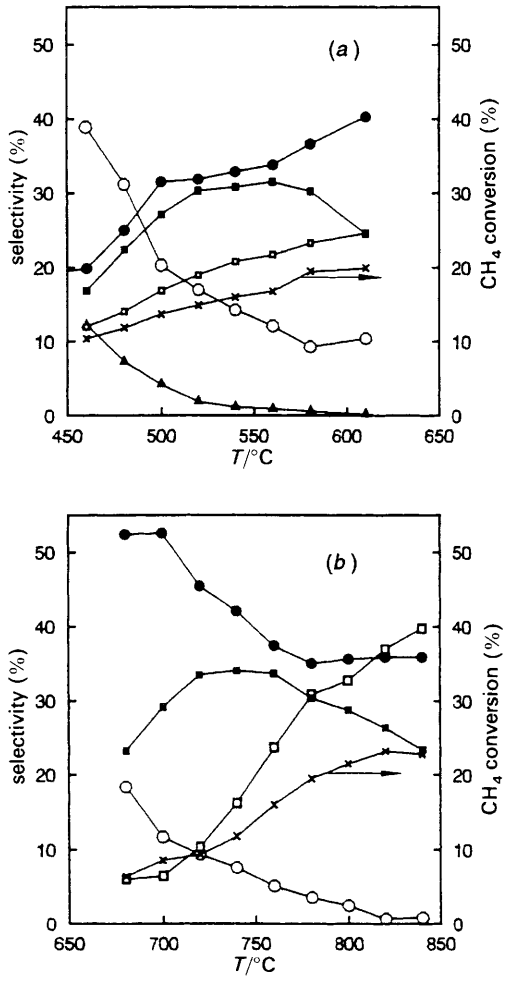

Fig. 1 Effect of temperature on methane conversion and product selectivities over $SrCe_{0.95}Yb_{0.05}O_3$ under the conditions described in the text. ×, methane conversion; ■, ethane selectivity; □, ethylene selectivity; ○, CO selectivity; ●, CO_2 selectivity; ▲, C_2H_2 selectivity. (*a*) Microwave radiation, (*b*) conventional heating.

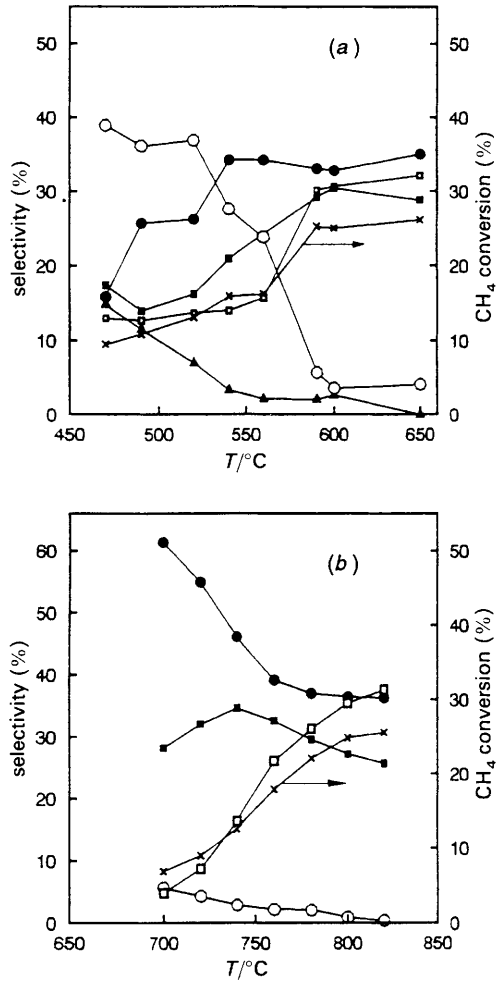

Fig. 2 Effect of temperature on methane conversion and product selectivities over $BaCe_{0.93}La_{0.07}O_3$ under the conditions described in the text. ×, methane conversion; ■, ethane selectivity; □, ethylene selectivity; ○, CO selectivity; ●, CO_2 selectivity; ▲, C_2H_2 selectivity. (*a*) Microwave radiation, (*b*) conventional heating.

H_2 and H_2O only. This OCM over proton conductive catalysts in the presence of microwaves results in the formation of C_2H_2. This is due to localized discharge. Localized discharge is a special phenomena that occurs with some catalysts in a microwave electromagnetic field.

References

1 D. Villemin and B. Labiad, *Synth. Commun.*, 1992, **22**, 2043.
2 A. Loupy, G. Bram and J. Sansoulet, *New J. Chem.*, 1992, **16**, 233.
3 D. Villemin, B. Labiad and A. Loupy, *Synth. Commun.*, 1993, **23**, 419.
4 G. Bram, A. Loupy and D. Villemin, in *Solid Supports and Catalysts in Organic Synthesis*, ed. K. Smith, Ellis Horwood, Chichester, 1992, p. 302.
5 L. Seyfried, F. Garin, G. Maire, J. M. Thiebaut and G. Roussy, *J. Catal.*, 1994, **148**, 281.
6 H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics*, 1981, **3/4**, 359.
7 H. Iwahara, H. Uchida, K. Ono and K. Ogaki, *J. Electrochem. Soc.*, 1988, **135**, 529.

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