# Synthetic Kentrolite as a Catalyst for the Selective Oxidation of Methane to $C_2$-Hydrocarbons

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A new family of catalysts for the oxidative coupling of methane to ethene and ethane based on $Pb_2Mn_2Si_2O_9$ (kentrolite) is reported.

In the quest[1—10] for catalysts capable of sustaining the oxidation of methane to more useful products, it has emerged that, not surprisingly, the structure of the catalyst plays a key role. Many different categories of solids show greater or lesser degrees of activity and selectivity, the rock-salt structure and the analogous Suzuki phases,[2] as well as the Keggin ion structure[8] being two prominent ones, depending upon whether the oxidant is $O_2$ or $N_2O$. In the search for new families of effective catalysts we took advantage of previous work, especially that of Baerns *et al.*,[1] who showed that the oxides of both Pb and Mn, when supported on silica, are promising catalysts.

By exploring the synergy displayed by the oxides of Pb and Mn supported together on silica, we have found that very good catalysts are formed. Their performance rivals that of the best catalysts hitherto reported. Detailed *X*-ray powder diffractometric analysis shows that, invariably, the most active catalyst preparations are those rich in the synthetic variant of the rare silicate mineral, kentrolite, $Pb_2Mn_2Si_2O_9$.[11] In some of the preparations, the active catalyst, formed as described below, also tended to contain the following phases: barisylite $[Pb_8Mn(Si_2O_7)_3]$, bixbyite $(Mn_2O_3)$, and cristobalite $(SiO_2)$. But in all cases the active catalyst consisted predominantly of synthetic kentrolite, the powder diffractogram characteristic of the catalyst changing very little even after some 20 h continuous use in a stream of $CH_4$–$O_2$ (see Figure 2) at 700 °C.

A typical preparation of the supported 'mixed oxide' catalyst entails slow addition of an aqueous solution of $Pb(NO_3)_2$ to dry silica gel (100—120 mesh) until the pores are filled with liquid. After evaporation of the water at *ca.* 100 °C, the solid is further impregnated twice with an aqueous solution of $Mn(NO_3)_2$. The resulting material is calcined in air at 300 °C for 1 h, then at 800 °C for 15 h. Synthetic kentrolite catalysts can be made by grinding stoicheiometric amounts of solid $Pb(NO_3)_2$ and $SiO_2$, then adding the mixture to an appropriate amount of 2.30 M aqueous solution of $Mn(NO_3)_2$. After stirring and evaporating the water at *ca.* 100 °C, the resulting mixture is calcined in air for 1 h at 300 °C and 15 h at 800 °C.

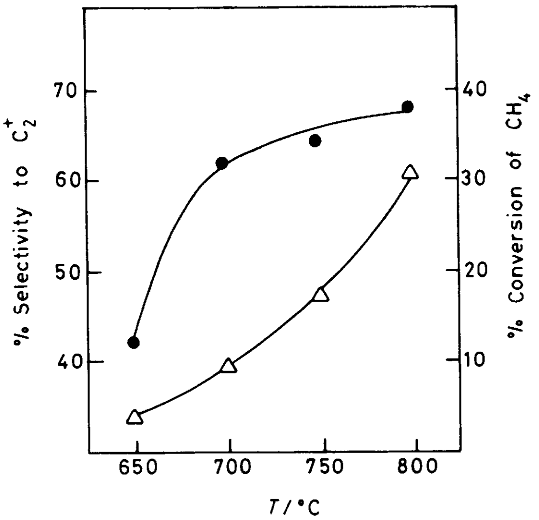

**Figure 1.** Variation of catalytic activity (△; expressed in percentage conversion of methane) and selectivity to ethene and ethane (●) of $Pb_2Mn_2Si_2O_9$–$SiO_2$ preparations as a function of temperature (GHSV = 1300 $h^{-1}$; $O_2$ : $CH_4$ ratio 0.13 : 1).

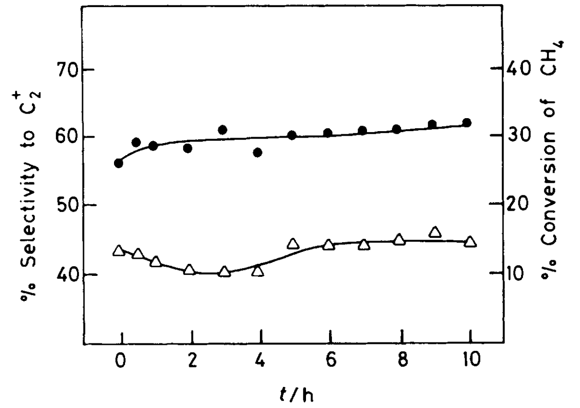

**Figure 2.** Variation of conversion (△) and selectivity (●) over a $Pb_2Mn_2Si_2O_9$–$SiO_2$ catalyst as a function of time. (Conditions as for Figure 1.)

Catalyst performance was assessed by using a test reactor, made of fused quartz [20 mm i.d.; 1.5 mm bed of catalyst (about 0.30 g) placed on a bed of 30—40 mesh quartz powder]. $N_2$ gas was used as a diluent; total pressure 1 bar, $O_2$–$CH_4$ ratio generally fixed at 0.125, other values ranging from 0.004 to 0.426 also used; gas hourly space volumes (GHSV) of 680 and 2900 $h^{-1}$; temperatures in the range 650—800 °C; products analysed by gas chromatography.

Typical plots showing activities and selectivities for a synthetic kentrolite preparation are shown in Figures 1 and 2. It is noteworthy that both the degree of conversion and selectivity to $C_2$ are substantial and do not diminish with time. At a GHSV of 680 $h^{-1}$, the conversion at 700 °C is a factor of about three higher than that at 2900 $h^{-1}$ and the selectivity to $C_2$ is approximately 45%.

At present, the mode of action of the silicate catalyst is obscure: it is not clear whether oxygen is sacrificially removed[12] from the solid or whether minority phases (crystalline or non-crystalline) at the hot catalyst surface are implicated. One significant fact is that B.E.T. (Brunauer–Emmett–Teller) areas are very low (*ca.* 1 $m^2$ $g^{-1}$). It is possible that these questions may be resolved in the course of studies (now underway) using isomorphous analogues such as $Pb_2Fe_2Si_2O_9$.

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