Methane Deuterium Exchange on Graphite–Potassium Lamellar Compounds

By Masaru Ichikawa and Kohei Kawase
(*Sagami Chemical Research Centre, Ohnuma, Sagamihara, Kanagawa-ken, Japan*)
and Kenzi Tamaru*
(*Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan*)

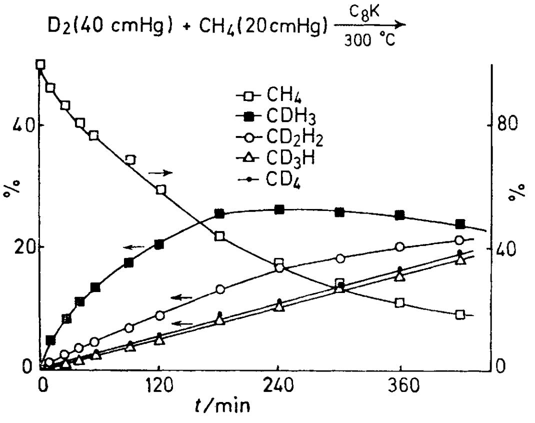
Summary A step-wise hydrogen exchange between deuterium and paraffins, such as methane, takes place over graphite–potassium lamellar compounds at *ca.* 300 °C.

A recent investigation demonstrated that graphite–alkali metal lamellar compounds such as C_8K and $C_{24}K$, like transition metals, are catalysts for the synthesis of ammonia, and for the hydrogenation of carbon monoxide, olefins, and acetylenic compounds.[1]

We report here that graphite–potassium lamellar compounds sorb a considerable amount of methane and deuterium.

Two lamellar graphite compounds (golden C_8K and deep blue $C_{24}K$) were prepared, using Rüdorf's methods, by the reaction of pure graphite with stoicheiometric amounts of distilled potassium metal *in vacuo* at 320 and 350 °C respectively. 5·0 g of the lamellar compound was placed in a U-shaped glass reaction vessel; the total volume of the closed circulating system was *ca.* 350 cm³. Methane (40 cmHg; 99·9%) was admitted over the C_8K and $C_{24}K$ powders; the same amount (*ca.* 4 cm³), was adsorbed by both, and deuterium was adsorbed up to the saturation value. On saturation at 300 °C, the compositions were estimated to be $C_8KD_{0\cdot7}$ and $C_{24}KD_{0\cdot15}$ respectively. It was also found that the desorption of methane and deuterium was slow at the reaction temperatures.

When a mixture of CH_4 (20—40 cmHg) and D_2 (20—40 cmHg) was circulated at a rate of 140 cm³ min⁻¹ over the lamellar compounds at temperatures of 100 and 350 °C, deuteriated methanes such as CH_3D and CH_2D_2 were formed reversibly (Figure). The variation in the proportion of methane followed first-order kinetics. In all the experiments an equimolar mixture of methane and deuterium was admitted to the reaction system, and the relative amounts of methanes were determined at intervals by mass spectrometry. The activation energies of the exchange reaction between 150 and 350 °C were estimated to be 14—13 kcal mol^{-1} over the C_8K and $C_{24}K$ and the exchange rate [$V(CH_3D)$ cm^3 h^{-1} mole^{-1}] was more than twice as large over $C_{24}K$ as that over C_8K at 300 °C. Dehydrogenation to the corresponding olefins and self-hydrogenolysis to methane also occurred at 300 °C.



Figure

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[1] *E.g.* K. Tamaru, *Adv. Catalysis*, **1964**, **20**, 327; *Catalysis Rev.*, 1970, **4**, 161.