Catalytic Hydrogenation of Benzene by Lamellar Compounds C_8K and $C_{24}K$

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Summary Graphite–potassium (C_8K and $C_{24}K$) lamellar compounds behave as catalysts, similar to transition-metal catalysts, for the hydrogenation of benzene to cyclohexane in high yields.

LAMELLAR compounds such as C_8K and $C_{24}K$, have been shown to act, like transition metals, as catalysts in the hydrogenation of carbon monoxide, olefins, and acetylenic compounds.[1] We now report that benzene is also hydro-

genated to cyclohexane in high yield by graphite–potassium lamellar compounds.

Two lamellar compounds, C_8K (golden) and $C_{24}K$ (deep blue), were prepared by treating pure graphite† with stoicheiometric amounts of distilled potassium metal‡ *in vacuo* at 300 °C and 350 °C, respectively. C_8K and $C_{24}K$ (*ca.* 2·6 g) were treated with 0·2 mol of benzene in a 300 ml autoclave without contact with oxygen or moisture.§ When the reaction was initiated under 100 Kg cm^{-2} pressure of hydrogen between 50° and 300 °C, the total pressure decreased over several hours and temperature was kept above 200 °C.

Cyclohexane was selectively (above 98%) produced in a yield of 80—90% at 250 °C in 2 h without any gaseous or polymer products (see Table). $C_{24}K$ exhibited much higher catalytic activity for the benzene hydrogenation than C_8K under the similar reaction conditions. The catalysts made of potassium and active carbon (surface area, 890 $m^2 g^{-1}$) have only a small catalytic activity although potassium was dispersed over the entire carbon surface. The maximum yield of cyclohexane was obtained at temperatures over 250 °C with $C_{24}K$ as catalyst. There was almost no hydrogenation below a hydrogen pressure of 10 kg cm^{-2}. On increasing the molar ratio of hydrogen: benzene to $> 3{\cdot}0$, the yield of cyclohexane reached almost 100% in 2 h at 250 °C under 100 kg cm^{-2} pressure of H_2. Alkylbenzenes such as toluene and propylbenzene were also hydrogenated to the corresponding cyclohexane derivatives in the presence of $C_{24}K$ at 100 atm of H_2 and 200 °C, but their dealkylation reaction took place to produce methane and cyclohexane as by-products.

TABLE. *Hydrogenation of benzene in the presence of graphite–potassium lamellar compounds and other catalysts*

Catalyst (g)	Benzene (mol)	H_2 (kg cm^{-2})	Temp (°C)	Time (h)	Yield (%)	Selectivity to cyclohexane (%)
C_8K(0·022 mols)	0·2	100	250	5	60·8	99·8
	0·2	150	250	5	79·7	99·6
$C_{24}K$ (0·006 mols)	0·2	97	250	2	86	99·9
K–C[a]	0·2	100	250	5	37	99·9
$C_{24}Li$ (0·006 mols)	0·2	100	250	5	14·1	99·9
K[b]	0·2	100	250	5	2·7	87[c]
$C_{24}K$ (0·006 mols)	0·2	103	50	5	0·2	—
	0·2	100	150	5	21·5	99·9
	0·2	100	300	5	57	99·9
	0·2	48	250	5	6·7	99·9
	0·2	72	250	5	35	99·9
	0·2	136	250	2	80	99·9
	Toluene				methylcyclohexane	
	0·4	100	250	5	8·1	39
	0·4	100	150	5	1·2	92
	Propylbenzene				propylcyclohexane	
	0·13	95	200	5	49	98·6

[a] Active carbon (2·0 g) was treated with K(0·3 g) in a sealed tube at 300 °C for 20 h; [b] potassium metal was dispersed in benzene [c] cyclohexene: 0·3%; [d] by-product; benzene, cyclohexane, and methane.

The standard catalytic activity of $C_{24}K$ (i.e. activity per unit surface area) for the hydrogenation of benzene was almost equal to that of the activated Raney–Ni and of platinum at lower pressures 10—100 kg cm^{-2} and temperatures 150—250 °C. C_8K and $C_{24}K$ have a surface area of less than 10 $m^2 g^{-1}$. This is the first observation that the non-transition metal catalysts such graphite–potassium lamellar compounds exhibit a marked activity for the hydrogenation of benzene under mild conditions.

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† The graphite (from Union Carbide Co.) contains less than 5 p.p.m. of Fe, Al, and Si as ash.

‡ Potassium metal (from Merck Reagent Co.) was of 99·9% purity with Na, Ca, Fe, and Mg as impurities being less than 0·01%.

§ These lamellar compounds are unstable in air, water vapour, acids, etc., and must be used with care in a dry-box. When hydrogen gas was preadsorbed sufficiently, the complexes were comparatively stable in the ordinary procedures.

[1] K. Tamaru, *Catalysis Rev.*, 1970, **4**, 161.