Methanation of CO over Alkali Metal–Carbon Catalysts

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Activated carbon-supported alkali metals catalyse the methanation of CO above 750 K in the order Cs > Rb > K > Na ; H_2S is not a poison.

Alkali metals are known to be effective catalysts for the gasification of coal and carbon by H_2O and CO_2,[1,2] the main products being CO–H_2 and CO, respectively. In the EXXON catalytic coal gasification process, where potassium is used as catalyst, methane formation is an essential feature.[3] It has been suggested that not only the gasification but also the methane formation is a result of a catalytic action of the potassium, but no direct evidence has been published for this. In other processes methane formation from CO–H_2 mixtures involves a separate step. The metallic catalysts used, *e.g.* Ni,[4] however, are readily poisoned by traces of H_2S, which is nearly always present in synthesis gas from fossil fuels. Sulphur-tolerant catalysts would constitute a considerable process improvement.

Here, we present the results of a preliminary investigation that show that all alkali metals on activated carbon catalyse the methanation of CO. Moreover, these catalysts are not poisoned by H_2S.

The catalysts were prepared by pore volume impregnation of an activated carbon (Norit RX extra, $0.25 < d_p < 0.59$ mm, specific surface area 800 m^2/g, ash yield 5 wt%) with an aqueous solution of an alkali metal carbonate (Merck CP), followed by slowly evaporating the water at 323 K and drying at 400 K. The carbon/metal atomic ratio was 51.8. The experiments were carried out in a quartz fixed-bed flow reactor, using catalyst samples with a carbon content of 360 mg. CO and H_2 (Matheson CP, purified over molecular sieves and a Cu–Al_2O_3 catalyst) were passed over the catalyst at a flow rate of 60 µmol/s each, at a total pressure of 0.3 MPa. The product gas was analysed by gas chromatography. The measurements were started at 673 K and subsequently the temperature was increased by 50 K, followed by an isothermal period of 5 min during which the products were analysed. The temperature was then increased by 50 K again, and the process repeated up to 1073 K. Pseudo-steady state activities were measured in separate experiments at 873 K.

Table 1. Turnover frequency (T.O.F.) of the different alkali metals for methanation at different pressures. Total pressure 0.3 MPa, CO–H_2 ratio 1. (– indicates no catalytic activity, + indicates activity measured at different conditions).

		T.O.F./10^{-4} mol CH_4 s^{-1} (mol CO)$^{-1}$				
Alkali metal	T/K	773	823	873	923	973
Na		–	+	0.3	1.2	3.0
K		+	0.5	1.9	4.5	8.5
Rb		+	+	2.0	5.0	9.0
Cs		+	+	4.0	9.0	13.0

The results in Table 1 show that alkali metals on a carbon support catalyse the methanation above 750 K. The activity increases with increasing atomic number: Na < K < Rb < Cs. The same order is found for the catalysed CO_2 gasification.[5] Besides methane, carbon dioxide was formed in 2—7 times larger amounts than methane; obviously CO disproportionates according to reaction (1). This phenomenon, also observed in pure CO over these catalysts, is to be expected since the alkali metals catalyse the CO_2 gasification, which is the reverse reaction.

$$2\,CO \rightarrow C + CO_2 \qquad (1)$$

When the CO flow is stopped, methane is still produced, although at a 2—3 times lower level. This is not the case for a sample which has not 'seen' CO. Apparently, the carbon produced by the disproportionation (1) is more active than the carbon support itself.[2] This active carbon probably reacts further to give methane. In this respect it should be mentioned that, using caesium as a catalyst, the rate of methane formation at 873 K is about three times higher than the rate of CO_2 gasification of the carbon support. At present it is unclear if the alkali metal catalyses this hydrogenation of the deposited carbon.

Below 973 K the activity slowly reached a steady state level, whereas above this temperature the activity decreased continuously. We have shown[5] that the alkali metals are in an oxidised form during gasification. So, apart from the carbon deposition, a reduction of the oxidic catalyst might be responsible for this decrease, especially at higher temperatures.

Repeated injection of 250 μl of H_2S in the CO–H_2 feed did not change the CH_4 and CO_2 production, whereas when the CO was removed from the feed, the methane production immediately stopped after injection of H_2S. Addition of CO to the feed again restored the original activity. Apparently, an oxygen-containing species must be present to prevent poisoning by H_2S. Further research into the methanation mechanism is in progress.

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