

Reaction Sequence for the Alkylation of Alkenes with Methane

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Methane addition to alkenes is demonstrated to occur over transition metal catalysts to give modest yields.

Dissociative methane adsorption onto a transition metal has a low sticking coefficient. Under mild conditions alkenes have a very high reactivity with respect to transition metal surfaces. Mainly for these reasons direct homologation of alkenes with methane, catalysed by transition metals has not yet been realized, while indirect conversion routes have very low selectivities.^{1,2} Using solid superacids under mild conditions, methane has been shown to add to ethylene selectively, as long as a high methane:ethylene ratio is used in order to suppress ethylene oligomerization.³

Here we report homologation of alkenes with dissociatively pre-adsorbed methane catalysed by group VIII transition metals.

Fig. 1 shows a reaction sequence in which methane is dissociatively adsorbed to a previously reduced transition metal catalyst ($T_{\text{red}} = 823 \text{ K}$, $p_{\text{H}_2} = 10 \text{ kPa}$) at 723 K. After methane deposition the catalyst is quickly cooled in a helium flow to prevent 'ageing' of the surface carbon. In a second step an alkene is co-adsorbed onto the methane treated catalyst ($T_{\text{ads}} = 323 \text{ K}$). Then the system is exposed to hydrogen ($p_{\text{H}_2} = 10 \text{ kPa}$, flow = 22.4 ml min^{-1} at 323 K) and hydrocarbons desorb. Reaction gases were analysed with GC and with GC-MS. ^{13}C -Labelled methane (99% ^{13}C , Cambridge Isotopes) as well as non-labelled CH_4 were used. The catalysts studied are a 5 wt% Ru (metal particle size = 5.5 nm) and a 10% Co (8.5 nm) prepared by incipient wetness impregnation on Grace 332 type silica ($300 \text{ m}^2 \text{ g}^{-1}$).

During the hydrogenation step equimolar amounts of adsorbed C_1 of methane and alkene react, both with an initial

surface coverage of about 10% (based on CO chemisorption measurements). These low carbon surface coverages consist mainly of reactive carbidic carbon.⁴ The products formed during the hydrogenation at 323 K, of the surface carbonaceous species generated from methane adsorption (from a pulse of $6.7 \mu\text{mol}$ at 723 K) and propylene (3 pulses of $1.4 \mu\text{mol}$ at 323 K) are shown in Fig. 2. About 60% of the methane adsorbed. From propylene $1.8 \mu\text{mol}$ adsorbed after methane adsorption and $0.9 \mu\text{mol}$ without methane pre-adsorption.

Surface carbonaceous species produced from methane dissociation can be hydrogenated partially to C_2^+ hydrocarbons.⁴ However, most of it is converted back into methane. When propylene is co-adsorbed methane formation is reduced

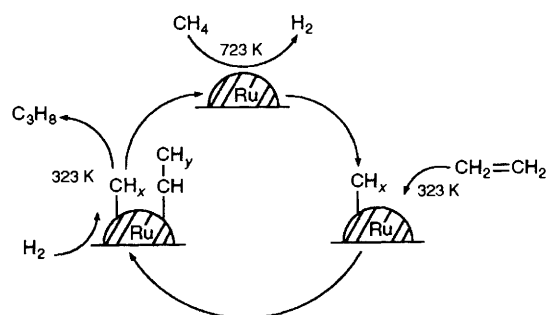


Fig. 1 Reaction cycle for the conversion of methane with an alkene to a higher homologue on ruthenium

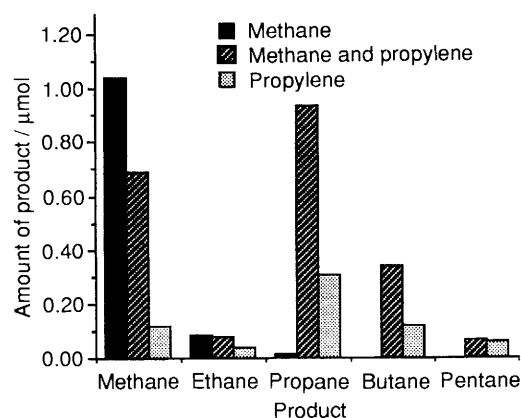


Fig. 2 Product spectrum from hydrogenating surface intermediates from methane and propylene at 323 K, $p_{\text{H}_2} = 10$ kPa on the cobalt catalyst. A comparison is given with the results obtained by separate methane and propylene adsorption.

and butane formation is increased. This may be indicative of a reaction between carbon from methane and adsorbed propylene to butane. As is shown in a separate propylene adsorption experiment, propylene disproportionation leads to ethane and butane. The appearance of pentane indicates also consecutive homologation of adsorbed butene by C_1 surface intermediates produced by hydrogenolysis. When only propylene is adsorbed on the reduced catalyst propane desorption is observed due to autohydrogenation. When methane is pre-adsorbed, more C_3 fragments stay on the catalyst due to partial hydrogenation of the C_1 fragments.

In order to distinguish disproportionation from the incorporation of carbon from methane, experiments were performed with ^{13}C -labelled CH_4 . The percentage of the reaction products, formed at 323 K and 10 kPa H_2 , consisting of one ^{13}C atom from methane and ^{12}C atoms from pre-adsorbed ethylene or propylene, are shown in Table 1.

Table 1 shows that methane is incorporated in the reaction products. From fragment mass spectra it was concluded that the ^{13}C atom appeared as the primary carbon atom in the product molecules propane and butane. Since nearly half of the homologated product molecules are due to self homologation, the reactivity of surface carbon from methane is very similar to that of surface carbon generated by hydrogenolysis of the alkenes. This agrees with a conclusion by Rodriguez *et al.*,^{5,6} that the rate of hydrogenolysis and self homologation are similar, indicating a related mechanism. The absence of labelled ^{13}C in propane in the reaction with propylene, indicate that butane is not formed according to the metathesis

Table 1 Percentage yield of the reaction products propane and butane consisting of one ^{13}C atom from methane and ^{12}C atoms from ethylene and propylene, respectively

Reaction	Catalyst	
	5% Ru/SiO ₂	10% Co/SiO ₂
$^{13}\text{CH}_4 + \text{C}_2\text{H}_4 \rightarrow ^{13}\text{C}^{12}\text{C}_2\text{H}_8$	60%	62%
$^{13}\text{CH}_4 + \text{C}_3\text{H}_6 \rightarrow ^{13}\text{C}^{12}\text{C}_3\text{H}_{10}$	45%	73%

reaction. The mechanism of carbon-carbon bond formation between the adsorbed carbonaceous surface species is closely related to that occurring in the Fischer-Tropsch reaction in which also mainly linear products are formed (ratio i : n butane = 0.04). This conclusion supports the findings of Tanaka *et al.*^{7,8} who indicated that the intermediates involved in the Fischer-Tropsch reaction and metathesis are different.

The propane overall yield for the reaction of $^{13}\text{CH}_4$ with adsorbed ethylene is 2.8% on the basis of pulsed methane and 4.5% on the basis of ethylene on ruthenium. The yield on the methane basis is about three times higher than that in superacid-catalysed alkylation.³

Incorporation of pre-adsorbed methane into an alkene to produce a higher alkane is demonstrated to occur over heterogeneous transition metal catalysts. The comparable rates between disproportionation and incorporation of methane indicate that the C_1 intermediates involved are similar.

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