

Homologation of Ethene over Supported Tungsten Oxide; Abnormal Formation of Branched Products

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Homologation of ethene takes place over supported tungsten oxides to give propene and isobutene; inclusion of hydrogen promotes both homologation and metathesis.

Several mechanisms for carbon-carbon bond formation in Fischer-Tropsch synthesis have been proposed.¹⁻⁴ In view of the importance of the control of selectivity in Fischer-Tropsch synthesis, it is important to investigate the process of olefin homologation. Recently Brady and Pettit⁵ reported a close similarity in the hydrocarbon reaction products of CO and H₂ on the one hand and CH₂N₂ on the other over several transition-metal surfaces. We report the results of experiments on the homologation of ethene indicating that the carbon-carbon bond formation may proceed *via* polymerization of 'carbenes and alkyl groups' on the surfaces of WO₃-TiO₂ and WO₃-ZrO₂.

The supported tungsten oxide (5 mol %) catalysts were prepared by impregnating TiO₂, ZrO₂, Al₂O₃, and SiO₂ with an aqueous solution of ammonium paratungstate. The resultant catalysts were calcined in air for several hours.⁶ Reactions were carried out at 473 K in a closed recirculation reactor with an internal volume of 354 ml. Prior to reaction, catalysts were evacuated at 773 K, followed by reduction with 66–133 kPa of hydrogen at the same temperature. Typical reaction mixtures contained 66 kPa of ethene and hydrogen.

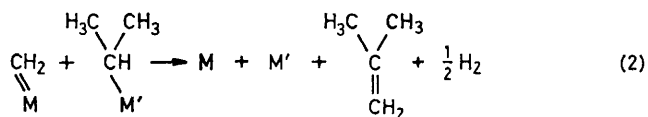
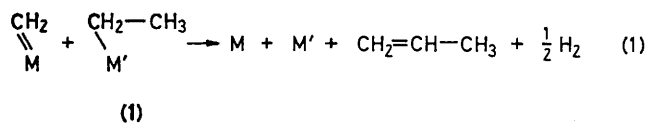
The main results are shown in Table 1 and notable features are as follows. (i) Inclusion of hydrogen increased the rate of homologation considerably but the reaction order with respect to hydrogen was low (*ca.* 0.2). Without hydrogen, the rate of homologation was slow and self-hydrogenation of

Table 1. Hydrogenation and homologation of ethene over supported tungsten oxide catalysts.

Catalyst	Yield, % ^a				
	Ethane	Propene	Propane	Butene	Butane
WO ₃ /TiO ₂	8.7	7.5	tr.	1.1 ^c	0
WO ₃ /TiO ₂ ^b	tr.	0.6	0	tr.	0
WO ₃ /ZrO ₂	31.5	9.2	0.5	1.8	0
WO ₃ /Al ₂ O ₃	0.1	0.7	0	0	0
WO ₃ /SiO ₂	3.7	0	0	0	0
WO ₃	0	0	0	0	0

^a mol % after 30 min reaction (tr. = trace). ^b Reaction without hydrogen. ^c Composition: but-1-ene (0%), isobutene (98%), *trans*-but-2-ene (tr.), *cis*-but-2-ene (2%).

ethene took place. (ii) TiO₂ and ZrO₂ were effective as supports, but WO₃ itself was inactive. (iii) Hydrogenation took place as well as homologation. Selectivity to homologation was high over the catalyst supported on Al₂O₃, though the activity was low. The SiO₂-supported catalyst was specific for hydrogenation; no homologation took place. Over a TiO₂-supported catalyst, a higher pressure of ethene and a lower pressure of hydrogen resulted in a higher yield of homologation products. High yields of hydrogenated products over ZrO₂-supported catalysts may arise from the support itself, since ZrO₂ showed some activity for hydrogenation of olefins.⁷ (iv) Homologation



products were mostly propene and butene. Pentene was formed only at high conversion. Hydrogenated products were ethane and propane; butane was not formed. (v) The butene formed was almost exclusively isobutene. This is in marked contrast with the distribution of butene isomers synthesized by metathesis of propene at 373 K.⁸ Similarly the pentene formed at high conversion was almost exclusively the branched isomer. (vi) Addition of hydrogen during the course of metathesis of propene over WO_3 supported on TiO_2 at 373 K enhanced the reaction rate several times. High rates of metathesis were also observed when hydrogen was included in the initial propene reagent.

The products of the conversion of ethene over supported WO_3 indicate a role for a single carbon entity. The effects of added hydrogen further suggest the involvement of an alkyl intermediate. One possible interpretation of the production of propene is a sequential insertion of a methylene group into an alkyl intermediate [equation (1)] as Pettit proposed in the $\text{CH}_2\text{N}_2\text{-H}_2$ reaction over supported metal catalysts.⁵ A similar chain-growth scheme has been considered previously by Sachtler in the Fischer-Tropsch reaction.² Although the production of branched products in Fischer-Tropsch synthesis is considered¹ to be a result of the isomerization of α -olefin products, it would still be possible for branched products to originate from successive insertions of CH_2 into the $\text{M}'\text{-C}$ bond of isoalkyl intermediates [equation (2)]; however, the origin of isoalkyl species is uncertain.

Recently, the homologation of ethene on supported iron clusters and of alkanes over metal films was reported by Basset *et al.*⁸ and by Rooney *et al.*,⁹ respectively. They suggested the formation of a metallacyclobutane as a possible intermediate. The production of propene and isobutene may proceed *via* metallacyclobutane intermediates by a combination of CH_2 and alkyl fragments. In self-hydrogenation of ethene, the formation of the ethyl intermediate (1) is also possible. The homologation took place slowly under these conditions.

We suggest that alkyl intermediates play a significant role in homologation and metathesis. A possible interconversion between alkyl and carbene intermediates in many alkene reactions has already been postulated.¹⁰

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