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SELECTIVE TRANSFORMATION OF ETHANOL INTO PROPENE ON COBALT CATALYSTS

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On Co/Al_2O_3 catalysts, ethanol can be converted into higher hydrocarbons if dehydration is avoided by adding water. There is good selectivity for olefins with a propene concentration of up to 35 percent of the products. Transformation of ^{13}C enriched ethanol shows that the methyl group of the alcohol molecule participates mainly in the chain growth.

It has been recently found that methanol behaves as a syngas on typical Fischer–Tropsch catalysts, namely cobalt deposited on alumina [1,2] or metallic cobalt prepared by chemical reduction [3]. To understand better the behaviour of alcohols on this type of catalyst, we have studied the transformation on cobalt supported catalysts of the homologous C_2 alcohol.

On this type of metallic catalyst deposited on an acidic support, pure ethanol can undergo three types of reactions, namely dehydration into ether and/or into olefin, dehydrogenation into aldehyde and condensation into higher hydrocarbons. While it is not possible to dissociate the last two reactions, as is the case with methanol [2], dehydration can be avoided by adding water to the feed. This effect is shown in fig. 1 where the conversion of a $C_2H_5OH–H_2O$ mixture is plotted versus the water content for catalytic runs carried out at 473 K on 2 g of metallic cobalt deposited on GFS alumina [4]. With methanol [2] dehydration becomes negligible for water contents above 30 percent (vol./vol.). Under these conditions the conversion of ethanol increases and at the same time hydrocarbons and carbon monoxide appear in the reaction products. For the various water contents, the repartition of hydrocarbons is summarized in fig. 2. Whatever the water content, the C_3^+ cut obeys the Schultz-Flory law (fig. 3) and the probability of chain growth decreases when the water content increases.

As shown in fig. 4 where the repartition of hydrocarbons is plotted versus the number of carbon atoms in the chain (starting mixture $C_2H_5–OH : H_2O = 60 : 40$ vol./vol.) the selectivity (expressed as mass carbon balance) for olefins is very

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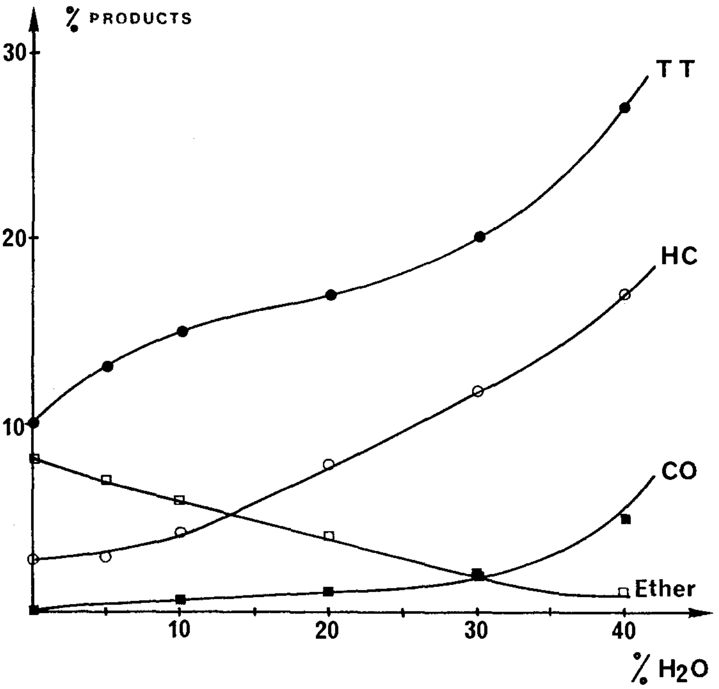
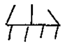


Fig. 1. Influence of the water content in the feed on the activity (TT) and the selectivity of ethanol transformation (2g Co/Al_2O_3 GFS catalyst, 473 K).

good (60 percent), the main hydrocarbon being propene which represents roughly 35 percent by weight of the total products for a conversion of ethanol of 28 percent.

As is the case with syngas [2], except for C_1 and C_2 hydrocarbons, the repartition of hydrocarbons obeys the Schultz–Flory law: this can be explained by the complete decomposition of the alcohol molecule into C_1 surface species such as alkyl CH_3 , carbene CH_2 , carbyne CH  groups or surface carbon atoms and hydrogen. These surface groups, according to certain authors [5,6] are the key species in the synthesis of hydrocarbons starting from carbon monoxide and hydrogen. Another possibility is the dehydrogenation of ethanol into ethanal:

$CH_3\text{-}CH_2OH \rightarrow CH_3\text{-}CHO + H_2$.

Ethanal, in turn, can decompose to form methane and carbon monoxide: the latter is present in the reaction products. In this case, at the catalyst surface there is a complex mixture of ethanol, CO and H_2 that can behave as a syngas to which ethanol tracer has been added [7]; the result would be a chain growth starting from C_2 species formed from ethanol. In order to define the possible mechanism of the formation of higher hydrocarbons, we studied the conversion of pure ethanol enriched in ^{13}C on the carbon atom linked to the alcohol function. Propene was trapped at the reactor outlet in the form of dibromo 1-2, propane

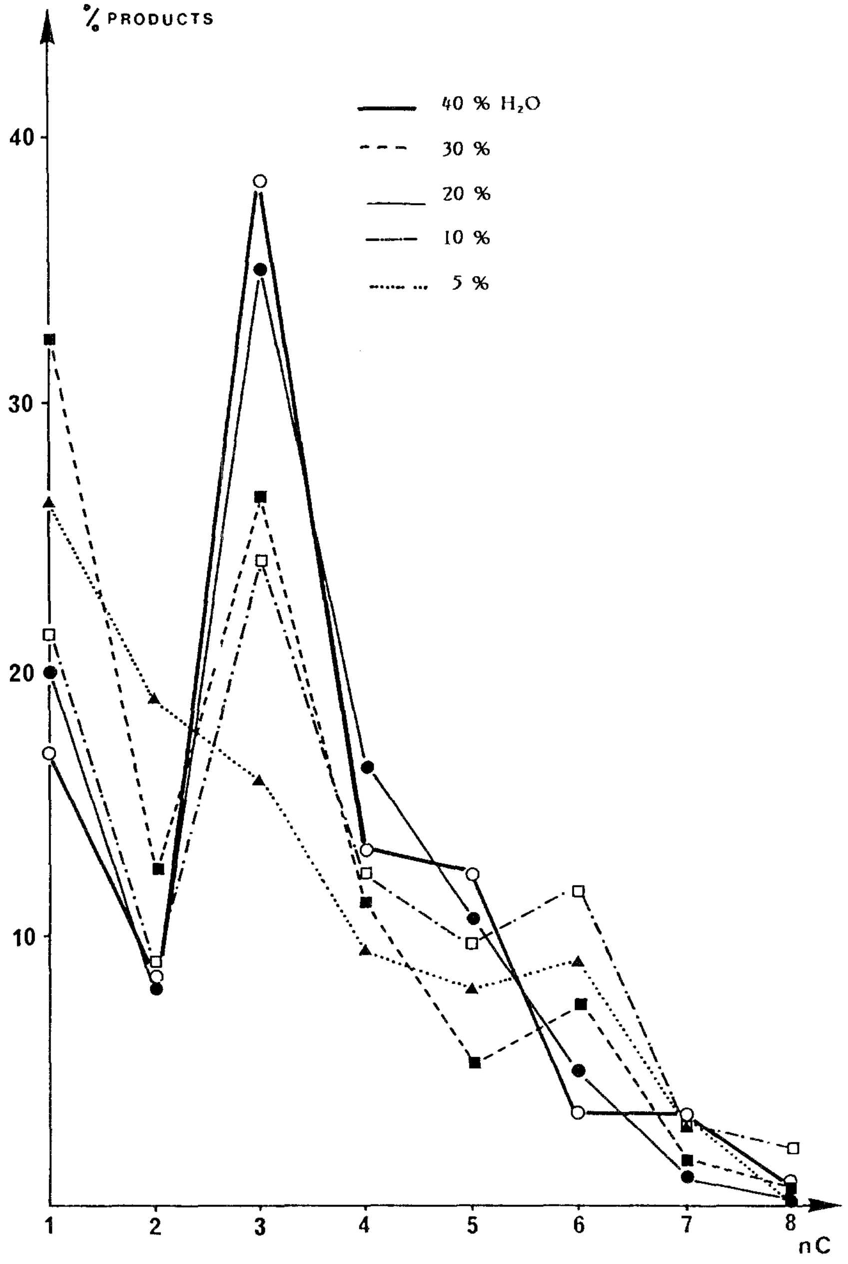


Fig. 2. Hydrocarbons repartition for various water contents in the feed.
(conditions same as for fig. 1).

[7]. The ^{13}C NMR spectra obtained with natural isotopic abundance and with enriched alcohol are shown in fig. 5. Peak height ratios are given in table 1.

It is evident that the main labelled carbon atom is the C_2 atom and to a lesser extent the C_1 atom. This result excludes a total breakdown of the ethanol

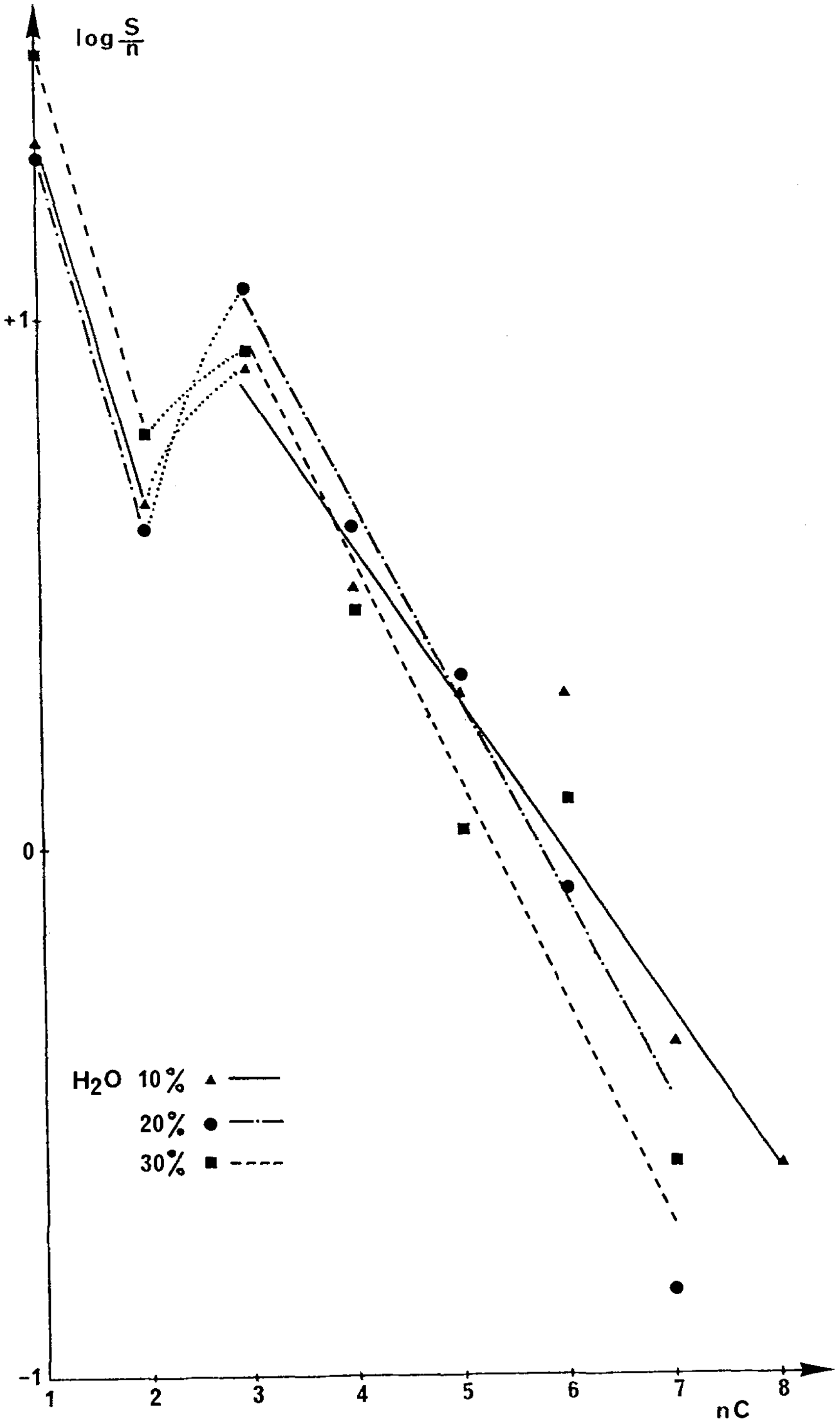


Fig. 3. Schulz–Flory plots for various water contents (conditions the same as in fig. 1). Slope values give a chain growth probability of 0.5 (10% H_2O), 0.42 (20% H_2O) and 0.39 (30% H_2O).

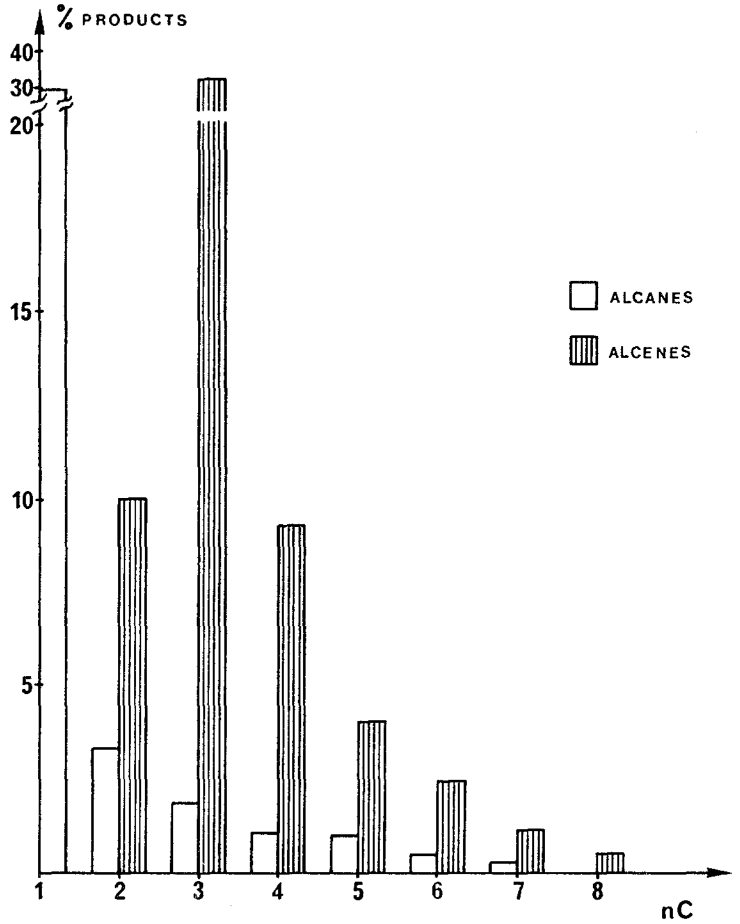


Fig. 4. Repartition of hydrocarbons obtained with a feed C_2H_5–OH : H_2O = 60 : 40 (2g Co/Al_2O_3 GFS, 473 K, conversion 28%).

molecule since, in this case the various C atoms in propene would be randomly labelled. Given that the initial participation of the alcohol molecule is obvious, it is to be noted that the C_1 atom of propene could come either from one of the two

Table 1
^{13}C NMR results expressed as peak height ratios for

$$\underset{C_3}{\underset{\downarrow}{CH_3}}-\underset{C_2}{\underset{\downarrow}{CHBr}}-\underset{C_1}{\underset{\downarrow}{CH_2Br}}$$

	Reference	Enriched
C_3/C_2	2.64	0.47
C_3/C_1	1.65	1.08
C_2/C_1	0.65	2.33

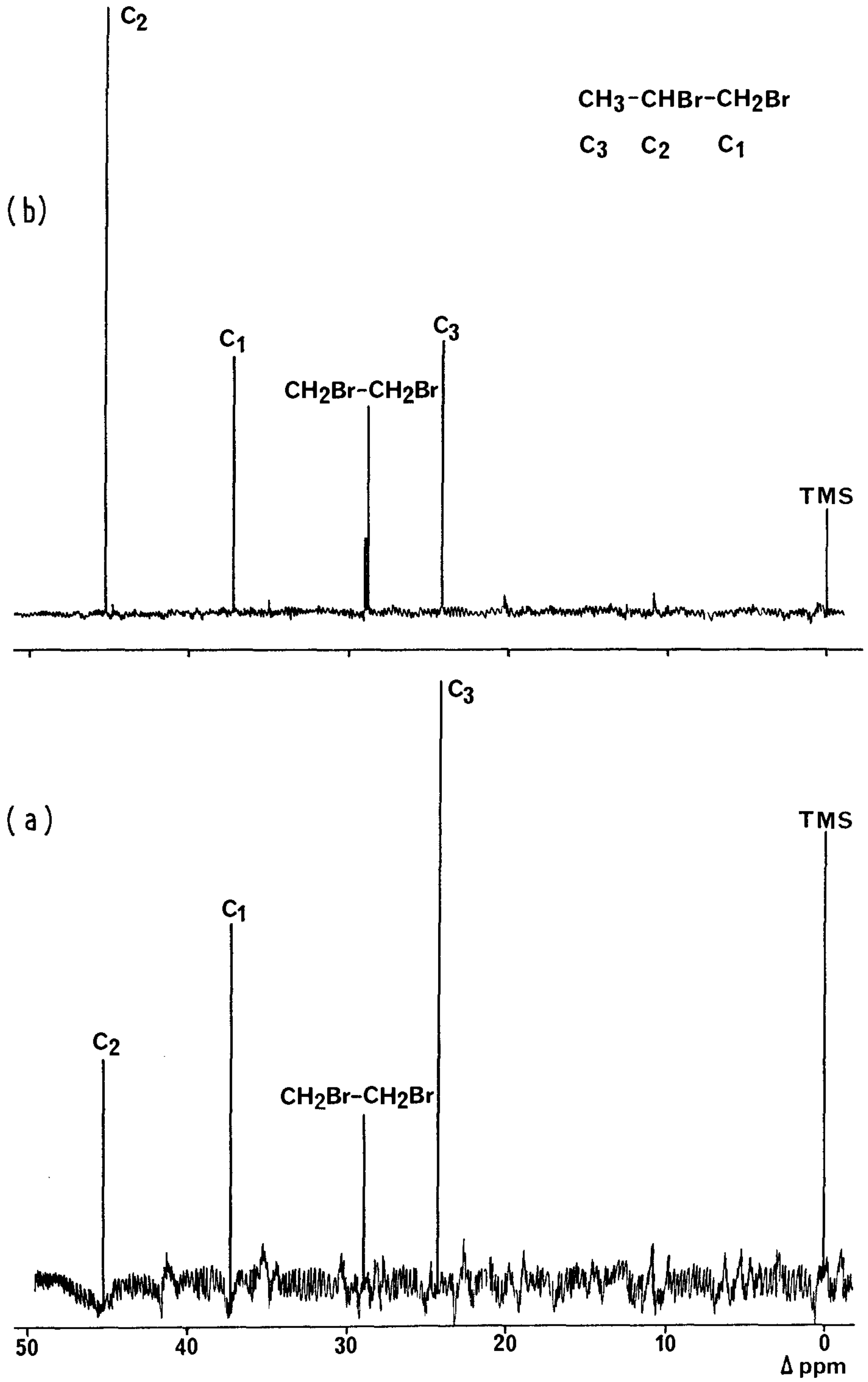
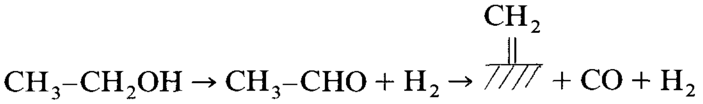


Fig. 5. ^{13}C NMR spectra of $CH_3-CHBr-CH_2Br$ obtained from propene with C_2H_5OH (a): natural abundance (b): ^{13}C enriched $CH_3-^{13}C\ H_2OH$.

indistinguishable C atoms of the alcohol molecule or from one in particular. According to the ^{13}C NMR intensities, it can be concluded that the C_1 atom of propene results preferentially from the CH_3 group of alcohol at 75 percent. For this, are two possible explanations at least:

(i) part of the alcohol is decomposed on the surface leading to CH_2 species and carbon monoxide:

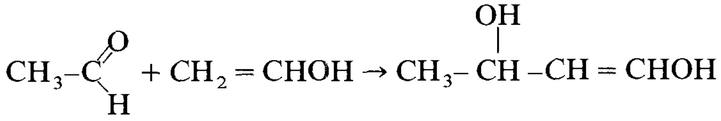


$$CH_3\text{-}CH_2OH \rightarrow CH_3\text{-}CHO + H_2 \rightarrow \overset{CH_2}{\overset{\|}{////}} + CO + H_2$$

these latter surface species being incorporated by a chain growth process initiated from C_2 adsorbed species.

(ii) there is some alcolic condensation followed by decarboxylation:

$$2CH_3\text{-}CH_2OH \rightarrow 2CH_3\text{-}CHO$$



$$CH_3\text{-}C\overset{O}{\underset{H}{\langle}} + CH_2 = CHOH \rightarrow CH_3\text{-}\overset{OH}{\overset{|}{CH}}\text{-}CH = CHOH$$

$$\rightarrow CH_3\text{-}CH = CH_2 + CO + H_2O$$

Further experiments are in progress to clarify these points.

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