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COBALT CATALYSTS FOR THE PRODUCTION OF ALCOHOLS IN THE F.T. SYNTHESIS

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A cobalt catalyst is prepared by reduction of a cobalt salt on cobalt oxide used as a support. The selectivity of the Fischer-Tropsch synthesis is thus changed and the production of alcohols is observed.

Since the first experiments in Fischer-Tropsch catalysis, metallic cobalt has been reported to produce mainly n-alkanes in a wide range of molecular weights: the catalyst is usually supported and it is used in gas phase. The reduction of a cobalt salt by an alkylaluminum followed by the decomposition of the resulting complex and further hydrolysis gives rise to another type of cobalt-alumina catalysts which may be used as a slurry in a high boiling solvent in order to produce a cut of light hydrocarbons which contains large amount of olefins [1]. The production of alcohols was never observed: this may be due to the lack of adsorbed undissociated CO which must be incorporated in the growing C-C chain in order to produce oxygenated compounds [2]. The formation of the C-C chain involves some species arising from the dissociation of CO: these species have been reported to occur on metallic sites.

In a first stage, a cobalt oxide-alumina support is prepared by coprecipitation of cobalt and aluminum nitrates with sodium carbonate ($\mathrm{pH} = 9$, $T\,^\circ\mathrm{C} = 50$). The precipitate is then washed, filtered and dried at 120 °C.

Afterwards it is calcined at 300 °C, under an atmosphere of N_2 for 4 hours. XRD powder patterns show the presence of a spinel phase $CoAl_2O_4$ not fully crystallized. Similar results have been reported by Marchi [4] for Co-Cu-Al mixed oxides: according to their data the cobalt is in the octahedral sites of a non-stoechiometric spinel $CoAl_2O_4$.

In a second step, a slurry of this oxide in dry benzene is treated at room temperature with a solution of $AlEt_3$ in the same solvent: the addition of this solution is stopped as soon as there is no more evolution of the ethane which is

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* This paper is dedicated to the late Professor Paul Canesson.

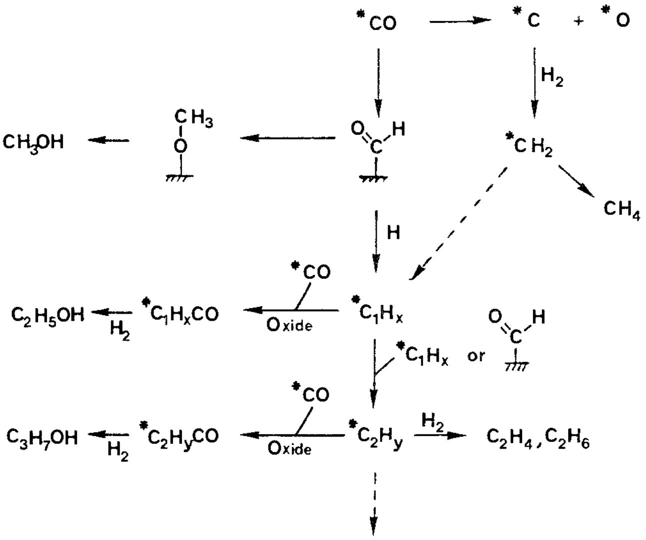
Table 1
Activity and selectivities for (Co/Al_2O_3), Reaction conditions 200 ° C, 40 bars, $H_2/Co = 2$ (molar), 24 → 240 h on stream.

CO conversion	(%)	40.2
Products selectivities (%)	CO_2	3.6
	Hydrocarb.	96.4
	Alcohols	–
Hydrocarbons distribution (%)	C_1	23.6
	C_2	4.4
	C_3	9.1
	C_4	8.2
	C_5	9.9
	C_6	10.4
	C_7	11.1
	C_8	10.2
	C_9	7.7
	C_{10}	5.4
Olefins selectivity	(%)	16.7

produced by the reaction of the alkyl compound with the surface –OH groups. Finally, the alkyl groups still present are used for the reduction of a solution of $Co(acac)_2$, the amount of which is calculated in order to create as much metallic cobalt as cobalt oxide present in the support ($Co^0 : Co^{2+} = 1:1$). The solid turns to a black colour.

Table 2
[8] Activity and selectivities for (Co^0/Co^{2+}) Al catalyst, Reaction conditions = 225 ° C, 40 bars, $H_2/Co = 2$ (molar), 19 h on stream.

CO conversion	(%)	41.3	
Products selectivities (%)	CO_2	52.5	
	Hydrocarb.	27.4	
	Alcohols	20.1	
		Hydrocarbons	Alcohols
Distributions (%)	C_1	40.5	1.5
	C_2	14.3	57.5
	C_3	20.7	23.5
	C_4	8.8	12.1
	C_5	8.5	4.2
	C_6	4.4	1.2
	C_7	2.1	–
	C_8	0.7	–
Olefins selectivity		75.1	



Scheme 1.

The temperature is progressively increased under a stream of syngas ($CO : H_2 = 1 : 2$). The benzene is distilled while a high boiling solvent (Santotherm 66) is introduced. As soon as a temperature of 200 °C is reached, the F.T. synthesis starts and the water which is produced in situ is used for the hydrolysis of the aluminum salts. The final state of the catalyst is cobalt-alumina supported on $CoAl_2O_4$.

The tables 1 and 2 present the data of two runs in rather similar conditions. The first catalyst is a cobalt-alumina prepared from $Co(acac)_2$ and $AlEt_3$ (1), the other is the present one (2).

It is obvious that the formation of the alcohols is favoured by the association between the metal and its oxide; moreover it is noteworthy that C_2, C_3, C_4 alcohols are the most important.

This result is in accordance with the reaction mechanisms which have been postulated by many authors [5–7] and scheme 1 takes into account the possibility to use CH_x surface species and CO to produce hydrocarbons and/or alcohols.

The CO insertion would appear on oxidized sites and the formation of hydrogenated intermediates on metallic centers.

Thus the production of alcohols from syngas on cobalt catalysts can be possible if a close association is realized between metallic cobalt and cobalt oxide which is known to adsorb CO undissociatively [3].

References

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[8] The high percentage of CO_2 is a consequence of the working temperature which favours the dismutation of CO. A larger amount of cobalt on the support would give rise to a more active catalyst and thus the possibility to work at a lower temperature.