Selective Production of Alkenes and Alcohols on Cobalt Catalysts in the Liquid Phase

Michel Simon,[a] André Mortreux,[a] Francis Petit,*[a] Dominique Vanhove,[b] and Michel Blanchard[c]

[a] *Laboratoire de Chimie Organique Appliquée, U.A. C.N.R.S. 402, ENSC. LILLE, USTL, B.P. 108, 59652 Villeneuve D'Ascq Cédex, France*

[b] *Laboratoire de Catalyse Organique, L.A. C.N.R.S. 231, E.S.C.I. LYON, 43, Bd. du 11 Novembre 1918, 69622 Villeurbanne Cédex, France*

[c] *Laboratoire de Catalyse, U.A. C.N.R.S. 350, 40, Avenue du Recteur Pineau, 86022 Poitiers Cédex, France*

Syngas (CO–H_2, 1 : 1) conversion on a Ziegler-type cobalt slurry in the liquid phase produces under pressure with good activity a narrow range of light hydrocarbons, essentially alkenes, as well as oxygenated compounds, mainly alcohols in the C_1—C_4 range.

During the last decade, there has been increasing interest in the selective synthesis of alkenes and alcohols from syngas (CO–H_2, 1:1), a new route which could replace their production from petroleum. In this context, we have already developed a cobalt-based catalytic system, from which a narrow range of hydrocarbons (mainly terminal alkenes) could be synthesized in the liquid phase at 200 °C under atmospheric pressure, with selectivities as high as 75% for the C_2—C_6 range.[1,2] Under such conditions, the reactions were slow however, although the catalyst lifetime was very high.†

We report now the application of such a catalyst for the same reaction under more drastic conditions, which appears to give not only hydrocarbons, in which a larger range of alkenes is obtained (C_2—C_8), but also a small amount of oxygenated products, consisting mainly of C_1—C_4 linear alcohols. The cobalt catalyst was prepared according to a method already described and summarized in equation (1).

$$\mathrm{Co(acac)_2 + AlEt_3 \longrightarrow Catalyst} \qquad (1)$$

Conditions: i, buta-1,3-diene, C_6H_6; ii, *o,o'*-terphenyl, CO–H_2 (1:1); Hacac = pentane-2,4-dione.

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† One of these catalysts has been used for 6 months without noticeable decline in activity, with an average turnover number 5×10^{-4} h^{-1}.

Table 1. Catalytic results for the $Co(acac)_2$–$AlEt_3$–butadiene preformed catalyst.[a]

Expt. no.	2	5	7	9	12	13	16	18	19	21	22	23
T/°C	190	220	240	250	250	250	250	250	250	250	250	250
P/atm	50	50	50	50	50	50	25	100	50	50	50	50
H_2/CO	1	1	1	1	1	1	1	1	1	0.5	3	1
t/min	240	240	240	5	60	120	60	60	60	60	60	60
Conv. CO, %[b]	12.4	51.4	71.6	7.6	47.6	49.5	37.0	23.2	30.8	14.5	78.6	24.1
Selectivity for hydrocarbons[c]	90.7	73.7	44.6	92.8	57.0	64.2	80.5	76.5	87.9	87.2	98.4	92.6
C_1	66.5	38.1	42.4	36.0	34.9	38.6	51.1	45.4	47.9	45.1	72.8	51.3
C_2—C_8 alkanes	22.3	27.9	32.0	32.7	35.6	32.7	27.2	34.5	28.6	25.3	27.1	28.1
C_2—C_8 alkenes	11.2	34.0	25.6	31.3	29.5	28.7	21.7	20.1	23.5	29.6	0.1	20.6
Selectivity for oxy-products	9.3	5.9	1.7	7.2	3.3	6.7	8.5	3.7	5.3	9.1	0.9	7.4
MeOH	8.7	17.2	19.4	37.2	21.8	29.7	32.1	34.3	45.9	35.2	18.4	31.9
EtOH[d]	33.6	45.3	36.0	37.8	28.4	37.2	38.8	40.1	37.0	39.4	63.6	44.5
Pr^nOH	8.6	13.5	13.6	12.2	9.3	14.1	13.6	13.9	10.8	13.1	13.6	16.1
Bu^nOH	0.9	6.9	6.5	3.1	4.9	7.7	5.6	3.6	—	—	—	—
Selectivity for CO_2	0	20.4	53.7	0	39.7	29.1	11.0	19.8	6.8	3.7	0.7	0

[a] Catalyst: $Co(acac)_2$ (8.5 mmol), $AlEt_3$ (7.5 mmol), butadiene (35 mmol), *o,o′*-terphenyl (50 g). [b] [(CO consumed)/(initial CO)] × 100. [c] All selectivities are expressed in C_1 units, *S*(hydrocarbon) + *S*(oxy-products) + $S(CO_2)$ = 100% of recovered C_1 unit. The carbon balance was estimated using an external standard. [d] The balance of 100% is Me_2CO and MeCHO.

Table 2. C_1 unit percentage of oxygenated products as a function of reaction time.[a]

t/min	5	15	30	120	240
MeOH	37.2	37.7	43.5	29.7	29.7
EtOH	37.8	36.3	34.2	37.2	37.3
Pr^nOH[b]	12.2	13.5	16.6	14.1	14.8
Bu^nOH[b]	3.1	7.7	4.6	7.7	7.1
MeCHO	5.9	2.8	Trace	6.1	5.2
Me_2CO	3.8	2.0	1.1	5.2	6.0

[a] Batch reactions; *T* 250 °C; *P* (initial) 50 atm; $H_2:CO$, 1 : 1. [b] Traces of propan-2-ol and butan-2-ol were also detected in each reaction.

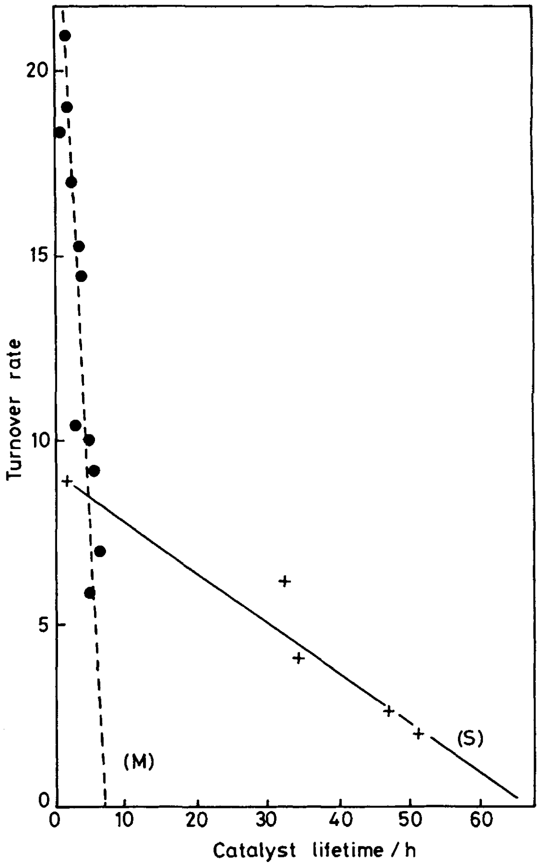

Figure 1. Average turnover rate [mol CO (g-atom Co)$^{-1}$h^{-1}] during several runs over the same catalysts. Curve (M): $Co(acac)_2$–$LiAlH_4$–THF–tetralin; *P* (initial) 14 atm at 20 °C; $H_2:CO$, 1 : 1; *T* 260 °C; batch reaction time 30 min. Curve (S): $Co(acac)_2$–$AlEt_3$–butadiene–*o,o′*-terphenyl; *P* (initial) 50 atm at 250 °C; $H_2:CO$, 1 : 1; *T* 250 °C; batch reaction time 60 min.

The catalyst was introduced into an autoclave as a solution in benzene, with *o,o′*-terphenyl. Benzene and most of the byproducts of the catalyst preparation were eliminated by warming slowly to 200 °C under a stream of syngas, which was continued for 8 h. The mixture in *o,o′*-terphenyl was then allowed to react with syngas (50 atm initial pressure) at 250 °C in a batch reaction. The consumption of CO–H_2 under such conditions is three orders of magnitude higher than those previously found under the milder conditions [*ca.* 1 (compared with 10^{-3}) mol CO (g-atom Co)$^{-1}$ h^{-1}].

Furthermore, it appears that the addition of butadiene is essential to obtain both good selectivities and stability of this catalyst.‡ Indeed, Mitsudo and co-workers[3] have found under similar conditions that reduction of $Co(acac)_2$ with lithium aluminium hydride in the presence of tetrahydrofuran (THF) gave the same kind of catalyst, although the range of hydrocarbons they obtained was larger than ours with added butadiene.

Figure 1 compares the behaviour of such catalysts after several runs; it is clear that catalyst M [$Co(acac)_2$–$LiAlH_4$–THF] has better activity than catalyst S [$Co(acac)_2$–$AlEt_3$–butadiene], but under standard conditions (250 °C; 50 atm; CO–H_2, 1 : 1; batch reaction; 1 h), the turnover rate with catalyst M declines drastically after several successive runs. In contrast, the curve for catalyst S, which shows the results obtained with the same catalyst at several times within a large series of experiments, during which reactions have been conducted for 50 h, clearly demonstrates that catalyst S has a better stability.

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‡ The role of butadiene in this catalyst synthesis is still an open question. However, during the preparation of the catalyst, one observes initially in benzene that the reduction of the cobalt salt gives a homogeneous solution which is transformed further in *o,o′*-terphenyl into a slurry at higher temperatures. Magnetic studies on the resulting powder after reaction have shown that the presence of butadiene enhances the production of small particles (average size 40 Å) whereas larger aggregates (>120 Å) are preferentially obtained when butadiene is absent.

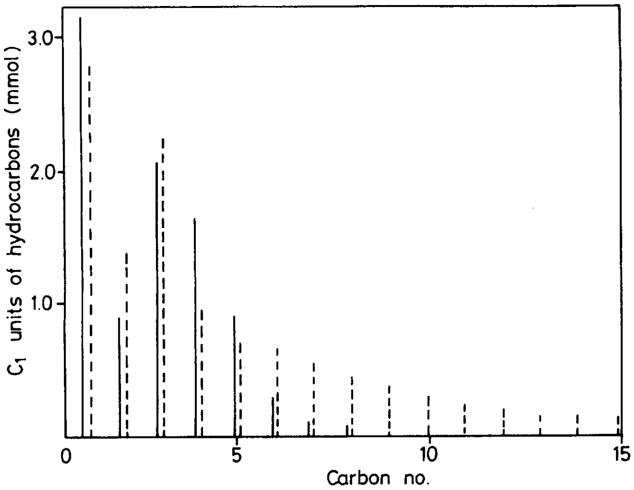

Figure 2. Comparative hydrocarbon distribution from CO–H_2 catalytic transformation over different cobalt catalysts under identical conditions (as in Figure 1): full line: catalyst S; dotted line: catalyst M.

An additional interesting feature is the difference between the range of hydrocarbons obtained under identical conditions with the two catalysts; in spite of the severe reaction conditions, the S catalyst (from butadiene) gave only hydrocarbons in the C_1—C_8 range, whereas experiments with catalyst M confirm that a Schulz–Flory-type distribution of hydrocarbons is obtained (Figure 2).

The stability of the catalyst allowed several experiments to be performed on the same catalyst sample and some typical results are given in Table 1; factors such as temperature, pressure, reaction time, and H_2–CO ratio were varied. As previously described,[1] the selectivity for alkenes is strongly dependent upon the H_2–CO ratio. Furthermore, in contrast with the results obtained at atmospheric pressure and lower temperatures, in every case, oxygenated compounds, essentially alcohols, were formed. Although the extent of their production is rather low (*ca.* 1—10% selectivity depending on the reaction conditions and H_2–CO ratio), their synthesis seems to be enhanced at rather low conversion, but we have been unable to find any relationship between the alkene–alcohol ratio and the reaction time, the oxygenated compounds as well as the alkenes being formed even at very low conversion. A similar conclusion can be drawn from a careful analysis of the internal selectivities in oxygenated products (Table 2). It is clear that the internal selectivities do not depend upon the conversion level, so that all these compounds must be produced by parallel reactions, along with the hydrocarbons.§

It is noteworthy that this alcohol production on a cobalt catalyst in the absence of any promotor reveals a particular behaviour of our catalytic system as compared to conventional cobalt–thoria–magnesia supported catalysts, for which the extent of alcohol production is <1% at temperatures up to 200 °C.[4] Indeed, alcohol synthesis from syngas with cobalt catalyst has been described in patents with copper as cocatalyst,[5] or even under homogeneous conditions at higher pressure and lower temperature.[6] Whether or not the participation of the solvent in this particular synthesis is responsible for the selective production of light alkenes and/or the selectivity in oxygenated products is still an open question, for which further experiments are in progress.

Received, 2nd April 1985; Com. 449

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§ A significant increase or decrease in C_{2+} alcohols (*vs.* reaction time) would have been conclusive evidence for the possibility of either alcohol production from alkenes, or decomposition of alcohols to alkenes. However, the presence of acetaldehyde in the reaction mixture is consistent with the probable production of higher alcohols by a homologation process from methanol, as shown by D. R. Fahey (*J. Am. Chem. Soc.*, 1981, **103**, 131).