

Selective synthesis of isobutanol by means of the Guerbet reaction Part 1. Methanol/*n*-propanol condensation by using copper based catalytic systems

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Abstract

The synthesis of isobutanol (*i*BuOH) from mixtures of methanol (MeOH) and *n*-propanol (PrOH), via the Guerbet reaction, has been studied. Heterogeneous copper based catalytic systems, in combination with soluble sodium methoxide (MeONa) as basic component, were employed. In particular, copper-Raney and copper chromite were tested as metal components. The effect of the relative amount of MeONa with respect to the copper component as well as of PrOH was investigated. The influence of reaction parameters such as temperature, reaction environment (type of gas and its pressure) and composition of the MeOH/PrOH mixture used as feed was also evaluated.

In all cases, independently from the type of copper derivative used, the selectivity to *i*BuOH was nearly complete. Moreover, an increase of the temperature in the 180–220 °C range caused a remarkable improvement of PrOH conversion and productivity to *i*BuOH.

The replacement of H₂ atmosphere by N₂ caused a significant improvement of catalyst productivity. When the experiments were performed under CO/H₂ atmosphere the catalyst activity was similar to that obtained under H₂. The catalysts based on copper chromite showed, under the same reaction conditions, higher activities (about one order of magnitude) as compared with those obtained by using copper-Raney based catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Isobutanol; Guerbet reaction; Alcohols condensation; Copper catalysts

1. Introduction

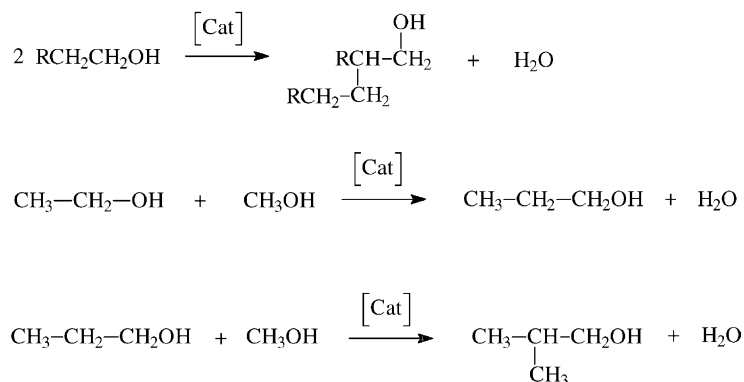
In the recent years a growing research interest has been devoted to the synthesis of isobutanol which represents a potential gasoline additive and a precursor for obtaining isobutene, in turn converted to methyl *tert*-butyl ether (MTBE) or to isooctane (via isobutene

dimerization and successive hydrogenation) when MTBE will be no more desired as gasoline additive, as for example in California. In particular, a largely explored approach is the direct synthesis from CO and H₂ [1–7]. However, this process, named higher alcohols synthesis (HAS), usually performed under drastic conditions (100–300 atm and 350–500 °C) by heterogeneous catalysts, allows one to obtain isobutanol with rather low selectivity and productivity [8]. An alternative approach was the two-step process [3,9],

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Scheme 1.

where in the first stage methanol and a mixture of higher alcohols are obtained from syngas at low temperature with modified methanol catalysts and in the second stage the mixture is converted to an isobutanol-rich product with high temperature methanol catalysts. With this approach an increased overall yield of isobutanol was obtained although the high temperature of the second stage caused selectivity problems and undesired retro-conversion of methanol to syngas. In the first stage a typical methanol/ethanol/*n*-propanol/isobutanol mixture composition of about 10/1/1/1 molar ratios was obtained. In this context, with the aim to realize a synthetic process able to give isobutanol with better performances, preserving the advantages of the two-step processes but limiting the drawbacks of the second stage, we have decided to investigate the conversion to isobutanol of the alcohol mixture from the first stage through a lower temperature route as the Guerbet reaction (Scheme 1). Therefore, excess methanol in the HAS mixture could be reacted with *n*-propanol to afford the target alcohol. Indeed, the reaction discovered by Guerbet in 1899 represents a cross condensation between alcohols promoted by a bifunctional catalyst, containing both a base function as well as a dehydrogenating/hydrogenating metal species.

Veibel and Nielsen [10] proposed that the mechanism of the Guerbet reaction is based essentially on three subsequent steps involving (i) dehydrogenation of the alcohols to the corresponding aldehydes, (ii) the aldol condensation of the obtained aldehydes, (iii) the hydrogenation of the unsaturated condensation products to the higher alcohol through different

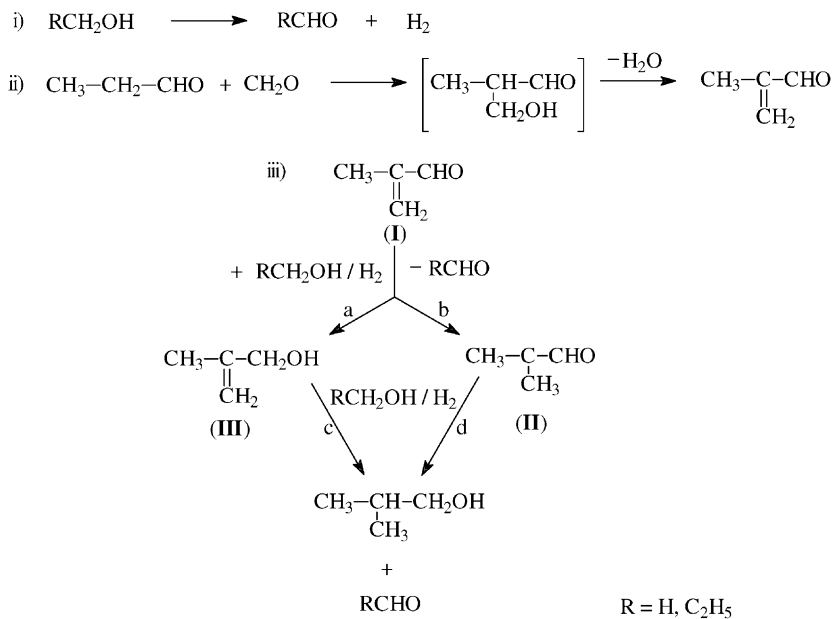
intermediates, thus giving rise to a chain process which is represented in Scheme 2 for the methanol/*n*-propanol mixture.

In addition to the above reactions the aldehydes, in the presence of a base, may give dimerization products according to the Cannizzaro reaction (formation of the corresponding alcohols and carboxylic acids), particularly at high temperatures (150–300 °C). However, at lower temperatures this reaction plays a minor role, particularly if the formed water is continuously removed from the reaction medium.

On the basis of the research work carried out by Nielsen some considerations may be drawn.

- The Guerbet reaction may proceed in the presence of a base without any use of a metal catalyst, however the addition of a metal, such as Ni-Raney, largely improves the productivity to the Guerbet alcohol.
- Dehydrogenation of the alcohol is easier when the hydrogen may be transferred to an acceptor compound, thus avoiding to load the catalyst.
- At rather low temperatures (130–140 °C) the slowest kinetic step of the reaction is represented by the alcohol dehydrogenation, whereas at higher temperatures (160–180 °C) the aldol condensation is the rate determining step. Studies at high temperatures confirmed this last result [11].

The condensation, in vapor phase at 362 °C on a fixed bed of a basic oxide (MgO resulted the best catalyst, as compared with CaO and ZnO), of methanol with a primary alcohol, having a methyl or methylene group in β position with respect to the hydroxy group,



Scheme 2.

was characterized by the formation of a carbon–carbon bond on the 2-position of the higher alcohol to give a 2-methylsubstituted Guerbet alcohol [12,13], as represented in Scheme 1 for the *n*-propanol/methanol mixture.

Moreover, working with deuterated methanol, it was proved that during the reaction the obtained carbonyl compounds are adsorbed together with the alcohols on the MgO catalytic surface and a rapid hydride transfer occurs between the adsorbed species thus giving rise to the formation of the Guerbet alcohol. The reaction was proved to proceed through the formation of α,β -unsaturated carbonyl compounds and allyl alcohols, as represented in Scheme 2, hydrogen transfer from methanol to the above unsaturated species being the main process. However, it is known that for this kind of reaction, different catalysts can provide different mechanistic pathways [14].

It is noteworthy that methanol and *n*-propanol react to give isobutanol as main product, because this does not give further condensation reactions, at least under the reaction conditions adopted, due to its high steric hindrance and to the presence of only one hydrogen in α -position to the methylol group.

The use of transition metals belonging to the VIII group, particularly rhodium, in combination with a

base allowed to perform the Guerbet reaction below 140 °C and at room pressure [15].

Moreover, the use of the Rh/C system as heterogeneous catalyst for the Guerbet reaction of *n*-butanol in combination with the corresponding alkoxide allowed to clarify mechanistic aspects of the reaction [15]. In particular, it was ascertained that the dehydrogenation step of the alcohol to the corresponding aldehyde (step i, Scheme 2) requires the catalysis of both alkoxide and the transition metal. The unsaturated aldehyde (I) may be reduced to the Guerbet alcohol by means of two pathways, (routes b–d and a–c, Scheme 2) through the intermediates II and III, respectively, the former being promoted only by the alkoxide and the latter by both alkoxide and transition metal.

Although complexes of different transition metals (Rh, Ru, Ir, Pt and Pd) have been used as homogeneous catalysts for the Guerbet reaction [16,17], heterogeneous catalysts (Ni-Raney, Ni/kieselguhr, Ru/C, Pd/C, etc.) displayed a much higher activity [18], due to the instability of the former systems, easily reduced by the alkoxide to the corresponding metal.

Taking into account that for the production of isobutanol from syngas and more recently for the synthesis of the same alcohol from methanol and *n*-propanol heterogeneous catalysts based on copper chromite [3]

and on Cu–Mg–CeO_x [4,7,19] have been claimed, the present paper deals with the investigation of the Guerbet reaction for the selective synthesis of isobutanol starting from the methanol/*n*-propanol model mixture by using heterogeneous copper catalysts combined with sodium methoxide as basic component. In particular, the effect of the nature of copper derivative and its relative amount with respect to both the basic component and *n*-propanol as well as the influence of reaction conditions, in terms of temperature, gas environment (H₂, CO, N₂) and methanol/*n*-propanol molar ratio, will be studied in order to improve and optimize the productivity and selectivity to isobutanol.

2. Experimental

2.1. Materials

Methanol (Prolabo) and *n*-propanol (Carlo Erba) were dried by distillation under dry argon after refluxing for 6 h on magnesium methoxide, according to the Lund and Bjerrum method [20]. *n*-Propanal (Aldrich) was distilled and stored under dry argon.

Sodium methoxide (MeONa) (Aldrich) was used as received and stored under dry argon.

Cu-Raney (Aldrich), commercialized as a slurry in water (50%), was dried under vacuum at room temperature, then it was activated prior to the use in a mechanically stirred Parr reactor in the presence of methanol at 180 °C for 4 h under 80 atm of H₂.

Cu 1955-P catalyst (Engelhard), a commercial copper chromite having the following composition in wt.%: Cu (36.0), Cr (33.0), Mn (3.0), was activated following the same procedure as described for Cu-Raney.

2.2. Catalytic experiments for the condensation of methanol with *n*-propanol

A 300 ml Parr reactor, equipped with a mechanical stirrer, a heating system and a control device assisted by a thermocouple inserted into the reactor, a sampling valve for liquids, an inlet valve for gas introduction and an outlet sampling valve for gaseous products, was used in the catalytic batch experiments. The copper catalyst was introduced in the reactor, then this was evacuated and methanol was introduced through the sampling valve. The reactor was subsequently

pressurized with H₂ up to 80 atm and heated at 180 °C for 4 h. After the activation step, the reactor was cooled at room temperature and degassed. The reactor was evacuated and the methanol removed under vacuum, then the proper amount of MeONa, dissolved in the methanol/*n*-propanol mixture, was introduced through the gas sampling valve. The reactor was subsequently pressurized with the proper gas. The reaction was followed by collecting at different times portions of the reaction mixture, quickly cooled at 0 °C, through the sampling valve. At the end of each experiment, the reactor was rapidly cooled at room temperature, slowly degassed through a trap maintained at –30 °C, in order to condense the liquid products eventually present in the gas phase, and finally the liquid reaction mixture was analyzed by GC after the addition of a known amount of benzene as internal standard.

2.3. Analytical procedures

The analysis of the reaction products was performed by GC on a Perkin-Elmer Sigma 3B chromatograph equipped with a thermal conductivity detector, a CE Instruments DP 700 integrator and a 2 m Poropak PS packed column with a stationary phase based on ethylvinylbenzene/divinylbenzene resin. Helium was used as carrying gas with a 25 ml/min flowing rate. The following temperature program of the oven was adopted: 80 °C for 5 min, then the temperature was increased by a 8 °C/min heating until 210 °C was reached; this value was maintained constant for further 15 min. For the quantitative determination of the reaction mixtures, through the areas of the CG peaks of the individual components, mixtures of authentic samples of known composition were prepared, using benzene as internal standard. This procedure allowed one to determine the chromatographic response factor for each individual component.

3. Results and discussion

3.1. Catalytic Guerbet condensation of methanol with *n*-propanol to give isobutanol in the presence of catalytic systems based on Cu-Raney and sodium methoxide

The experiments were in general carried out by using a rather high methanol/*n*-propanol molar ratio

(12.5), similar to that obtained in the HAS process starting from syngas. Although in all the entries Cu-Raney was pre-activated at 180 °C under 80 atm of H₂ prior its use, hydrogen atmosphere was preliminarily adopted (30 atm) in order to be sure to maintain the metal dehydrogenating/hydrogenating component at the zero reduced state as well as to favour the formation of the saturated Guerbet alcohol. Moreover, an excess of soluble NaOMe with respect to the amount of *n*-propanol was employed in order to prevent the deactivation of the system by the water formed in the reaction.

As reported in Table 1, whereas MeONa alone was completely inactive in the condensation reaction to isobutanol (entry 1), its use in combination with Cu-Raney gave rise to the formation of an active catalytic system. In particular, all the catalytic experiments showed a nearly complete selectivity to the Guerbet alcohol, isobutanol being the main reaction product (>98%), only traces of autocondensation products (C₆ alcohols) being formed. When the temperature was increased from 180 to 220 °C, still maintaining constant the other reaction parameters, a significant improvement of activity was observed, the

conversion of PrOH to *i*BuOH going from 5 to about 69% (entries 2–5) after 6 h, the corresponding productivity having turnover number (TN, expressed as mol *i*BuOH/(mol Cu × h)) values of 0.3 and 4.6 h⁻¹, respectively.

Taking into account the rather high PrOH conversion, the effect of the progressive reduction of MeONa concentration was studied. When this was reduced to 1/2 and to 1/4 (entries 6 and 7, respectively) as compared with entry 4, the activity was found to significantly decrease (TN = 1.6 and 0.4, as compared with 4.0 h⁻¹), in spite of the use of an increased amount of Cu-Raney for balancing the effect. Therefore, it is evident that the concentration of the base is a crucial parameter, thus confirming previous results [15]. Indeed, the water formed in the reaction (Scheme 1) reacts with MeONa to give MeOH and NaOH, thus consuming the basic component of the catalyst. It is noteworthy that when the hydrogen atmosphere was progressively replaced by nitrogen a sharp increase of activity was observed (compare entries 8 and 9 with 2). These results may be interpreted assuming that hydrogen depresses the initial equilibrium of alcohols dehydrogenation to the corresponding aldehydes (which

Table 1

Synthesis of isobutanol (*i*BuOH) through condensation of methanol (MeOH) with *n*-propanol (PrOH) by the MeONa(B)/Cu-Raney catalytic system^a

Entry	Cu-Raney (mmol)	MeONa (mmol)	B/Cu (mol/mol)	PrOH/Cu (mol/mol)	T (°C)	P _{H₂} (atm)	P _{N₂} (atm)	P _{CO} (atm)	<i>i</i> BuOH	
									Yield (%) ^b	TN (h ⁻¹) ^c
1	–	160	–	–	180	30	–	–	0	–
2	2.5	160	64	40	180	30	–	–	5.0	0.3
3	2.5	160	64	40	200	30	–	–	41.1	2.7
4	2.5	160	64	40	210	30	–	–	59.5	4.0
5	2.5	160	64	40	220	30	–	–	68.8	4.6
6	5.0	80	16	20	210	30	–	–	46.9	1.6
7	10	40	4	10	210	30	–	–	21.6	0.4
8	2.5	160	64	40	180	10	20	–	22.1	1.5
9	2.5	160	64	40	180	–	30	–	23.8	1.6
10	2.5	160	64	40	180	20	–	10	6.6	0.4
11	2.5	160	64	40	180	–	20	10	9.1	0.6
12 ^d	2.5	160	64	54	180	–	30	–	22.6	2.0
13 ^e	2.5	160	64	76	180	–	30	–	21.5	2.7

^a Reaction conditions: MeOH + PrOH = 1350 mmol; MeOH: 1250 mmol, if not otherwise specified; MeOH/PrOH = 12.5 mol/mol, if not otherwise specified; time, 6 h; the selectivity to *i*BuOH was about 100% in all the experiments.

^b Expressed as: (mol *i*BuOH/mol PrOH) × 100.

^c Turnover number expressed as: mmol *i*BuOH/(mmol Cu-Raney × h).

^d MeOH: 1215 mmol; MeOH/PrOH = 9 mol/mol.

^e MeOH: 1160 mmol; MeOH/PrOH = 6 mol/mol.

represent the chain carriers of the process (Scheme 2)), this being the rate determining step, at least under the adopted conditions (180 °C). It is interesting to underline that CO atmosphere, in combination with hydrogen, is not an irreversible poison for the catalyst (see entries 2 and 10). Indeed, in the presence of a 2:1 H₂/CO atmosphere two opposite effects are probably involved, a negative one caused by the interaction of CO with the metal sites to give carbonyl species, thus inhibiting the hydrogenating/dehydrogenating character of the catalyst, and a positive one related to the reduction of H₂ partial pressure. On the other side, a detrimental effect was observed when CO was used to replace nitrogen (see entries 9 and 11), in this case only the former negative effect being present. In the absence of added CO, no carbon monoxide was ever found in the reaction gases discharged at the end of the process, thus excluding the possible occurrence of the retro-synthesis of methanol to syngas. Finally, the influence of the methanol/propanol molar ratio was

examined. On increasing the relative concentration of PrOH, although the conversion of PrOH to *i*BuOH appeared slightly lower (see entries 9, 12 and 13), the turnover number of the process was improved, TN passing from 1.6 in entry 9 to 2.0 and 2.7 h⁻¹ in entries 12 and 13, respectively. The selectivity of the process remained substantially complete.

3.2. Catalytic Guerbet condensation of methanol with *n*-propanol to give isobutanol in the presence of catalytic systems based on copper chromite and sodium methoxide

When Cu-Raney was replaced by copper chromite, under the same conditions, in terms of hydrogen atmosphere, reaction temperature, amount of basic component as well as of methanol/*n*-propanol feed and duration, a sharp increase of conversion and productivity was observed (entry 14, Table 2, as compared with entry 2, Table 1).

Table 2

Synthesis of isobutanol (*i*BuOH) through condensation of methanol (MeOH) with *n*-propanol (PrOH) by the MeONa(B)/copper chromite catalytic system^a

Entry	Cu-catalyst (mmol)	MeONa (mmol)	B/Cu (mol/mol)	PrOH/Cu (mol/mol)	T (°C)	P _{H₂} (atm)	P _{N₂} (atm)	<i>i</i> BuOH	
								Yield (%) ^b	TN (h ⁻¹) ^c
14	2.5	160	64	40	180	30	–	53.1	3.5
15	2.5	320	128	40	180	30	–	62.7	4.2
16	2.5	80	32	40	180	30	–	33.6	2.2
17	5.0	80	16	20	180	30	–	33.7	1.1
18	5.0	80	16	20	210	30	–	62.4	2.1
19	5.0	160	32	20	180	30	–	57.1	1.9
20	5.0	320	64	20	180	30	–	72.8	2.4
21	2.5	160	64	40	180	–	30	64.5	4.3
22	2.5	160	64	40	180	–	60	61.4	4.0
23	2.5	160	64	40	180	–	5	68.5	4.5
24	2.5	160	64	40	180	–	1	58.3	3.9
25	2.5	160	64	40	200	–	30	72.0	4.8
26 ^d	2.5	160	64	40	200	–	30	77.5	9.8
27	1.4	20	14.3	71	200	–	30	23.6	2.8
28	1.25	160	128	80	200	–	30	55.9	7.8
29	11.2	160	14.3	9	180	–	30	56.0	0.8
30	2.5	20	8	40	200	–	30	20.8	1.4
31	1.25	160	128	80	200	–	30	54.6	7.3
32	0.625	160	256	160	200	–	30	45.6	12.2
33	0.312	160	513	320	200	–	30	41.4	22.1

^a Reaction conditions: MeOH + PrOH = 1350 mmol; MeOH: 1250 mmol, if not otherwise specified; MeOH/PrOH = 12.5 mol/mol, if not otherwise specified; time: 6 h; in all the experiments the selectivity to *i*BuOH was about 100%.

^b Expressed as: (mol *i*BuOH/mol PrOH) × 100.

^c Turnover number expressed as: mmol *i*BuOH/(mmol copper chromite × h).

^d MeOH: 1160 mmol; MeOH/PrOH = 6 mol/mol.

Indeed, the conversion improved from 5 to 53.1% and TN from 0.3 to 3.5 h⁻¹. Moreover, the selectivity of the process remained nearly complete. As previously found for the catalyst based on Cu-Raney, also in the case of copper chromite the relative amount of MeONa largely affected the activity of the catalyst, an increase of that improving the PrOH conversion to *i*BuOH (compare entries 15 and 16 with entry 14, as well as entries 19 and 20 with entry 17, Table 2). On the contrary, the increase of the amount (doubled) of copper chromite with respect to MeONa, this being maintained constant, reduced (halved) the productivity of the catalyst (compare entries 16 and 17), thus suggesting that the catalyst amount employed in entry 16 (2.5 mmol) is more suitable. The enhancement of the reaction temperature (from 180 to 210 °C) caused again an increase of activity without reducing the selectivity of the process (see entries 17 and 18). When hydrogen atmosphere was replaced by nitrogen, an increase of activity and productivity was observed, although a less marked effect was found than that in the case of the catalyst based on Cu-Raney (compare entries 21 and 14 (Table 2), with respect to entries 9 and 2 (Table 1)). This occurrence suggests a less relevant influence of the first dehydrogenation step for this catalyst. The change of the pressure of nitrogen from 60 to 1 atm did not cause a remarkable variation of productivity, TN values being quite similar in all the range of pressure (see entries 21–24). The increase of temperature (from 180 to 200 °C) caused an improvement of activity also under nitrogen atmosphere, the conversion of PrOH to *i*BuOH reaching 72% (compare entries 21 and 25). Analogously to what previously found for the catalyst based on Cu-Raney, the increase of the relative amount of PrOH with respect to methanol caused (entry 26) a further increase of activity, the conversion to *i*BuOH reaching 77.5% and the productivity showing a TN value equal to 9.8 h⁻¹ (a value more than doubled with respect to the best result obtained with the previous catalytic system). When both the amount of copper chromite and MeONa were reduced with respect to the MeOH/PrOH mixture a remarkable decrease of activity was observed (entries 27 and 30). However, when the amount of MeONa was maintained constant and that of the copper component was progressively reduced the productivity significantly increased (compare entry 28 with entry 25, entry 29 with entry 21 and 31–33 with entry 25). In

particular, when the amount of copper catalyst was reduced to about one order of magnitude with respect to the first experiments (~0.3 mmol), a TN = 22.1 h⁻¹ was reached, the conversion to *i*BuOH being still quite high (41.4%).

Taking into account that all the data reported in the literature suggest that the Guerbet reaction proceeds through a mechanism involving the formation of aldehydes as intermediates, some experiments were performed by adding different amounts of *n*-propanal to the methanol/*n*-propanol mixture. The reaction conditions adopted were the same as those reported for entry 21 (Table 2) for what temperature, relative amounts of copper chromite and MeONa as well as pressure of nitrogen are concerned.

As reported in Table 3, when 30 mmol of PrOH were replaced by *n*-propanal, the conversion of this alcohol to *i*BuOH decreased from 64.5 to 59.9% (compare entries 34 and 21).

By increasing the amount of *n*-propanal replacing PrOH a further decrease of conversion to *i*BuOH was observed (entry 35), until the entire substitution of PrOH by *n*-propanal caused the complete disappearance of *i*BuOH in the reaction products (entry 36), *n*-propanal being always almost completely converted to self-condensation products. The key for the high selectivity in the Guerbet reaction to isobutanol is lightly due to the fact that on the catalyst surface the aldehyde intermediates, formed by dehydrogenation, are rapidly reacted to give the cross-condensation alcohol, the low concentration of the intermediates and the relatively high excess of methanol favoring

Table 3
Synthesis of isobutanol (*i*BuOH) through condensation of methanol (MeOH) with *n*-propanol (PrOH) by the MeONa/copper chromite catalytic system, in the presence of different amounts of *n*-propanal (EtCHO)^a

Entry	PrOH (mmol)	EtCHO (mmol)	<i>i</i> BuOH yield (%)	TN (h ⁻¹) ^b
21	100	0	64.5	4.3
34	70	30	59.9	2.8
35	30	70	51.3	1.0
36	0	100	0	–

^a Reaction conditions: copper chromite: 2.5 mmol; MeONa: 160 mmol; MeOH: 1250 mmol; T: 180 °C; P_{N₂}: 30 atm; time: 6 h; in all entries EtCHO was completely converted to self-condensation products.

^b Turnover number expressed as: mmol *i*BuOH/(mmol copper chromite × h).

the selectivity to *i*BuOH. These data are in agreement with previous results reported by Miller and Bennet [11], as represented in step ii) of Scheme 2. Indeed, the aldehyde added to the reaction mixture is not able to be adsorbed on the catalyst surface, thus evolving exclusively to self-condensation products.

4. Conclusions

On the basis of the obtained results some conclusive remarks may be drawn.

1. Heterogeneous catalysts based on copper derivatives, when combined with MeONa as basic component, are active in the Guerbet reaction, thus allowing to give isobutanol from methanol and *n*-propanol mixtures with nearly complete selectivity, at least in the presence of a large excess of methanol. On the contrary, MeONa alone is not able to give the Guerbet alcohol.
2. The increase of temperature in the 180–220 °C range favors the isobutanol formation, without reducing the selectivity of the process.
3. A large excess of MeONa with respect to the metal component is required in order to obtain high ProH conversion and productivity, due to the fact that the water formed in the reaction generates NaOH from MeONa, thus reducing its concentration.
4. The nature of gas environment strongly affects the activity of the catalyst. In particular, CO is well tolerated when combined with hydrogen and this occurrence is of significant interest in the perspective of using as feed the alcohol mixture deriving from HAS processes. Nitrogen is far better than hydrogen, this disfavoring the rate determining step, i.e. the dehydrogenation of alcohols to the corresponding aldehydes, which in turn are considered the chain carriers of the reaction.
5. At constant ProH/MeONa molar ratio the decrease of the amount of copper component favors the productivity of the process to *i*BuOH.
6. Catalysts based on copper chromite display an activity of about one order of magnitude higher than Cu-Raney under the same reaction conditions.
7. Experiments carried out in the presence of *n*-propanal in the feed allowed to conclude that reactive intermediate aldehydes, formed in situ on the catalyst surface and present in low con-

centration, are the key to maximize the formation of *i*BuOH, strongly reducing the contribution of self-condensation reactions.

8. The high selectivity of the Guerbet reaction, at least under the adopted conditions, is very promising to design an improved two-step isobutanol synthesis from syngas, although the catalyst activity is likely to be improved.

Work is in progress devoted to the study of the Guerbet reaction by the above catalytic system starting from feeds based on ethanol/*n*-propanol and methanol/ethanol/*n*-propanol mixtures. Moreover, heterogeneous catalysts based on transition metals of VIII group as well as on solid basic components will be studied, with the aim also to transfer the process from batch to continue experiments using flow reactors.

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