



# Selective synthesis of isobutanol by means of the Guerbet reaction Part 2. Reaction of methanol/ethanol and methanol/ethanol/*n*-propanol mixtures over copper based/MeONa catalytic systems

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## Abstract

The synthesis of isobutanol via the Guerbet condensation between methanol and ethanol was studied by using sodium methoxide (MeONa) as soluble basic component and copper-based catalysts as heterogeneous dehydrogenating/hydrogenating metal species. The effect of the nature of the catalyst and the relative amount of its individual components with respect to the reacting alcohols as well as of temperature on productivity and selectivity of the process was investigated. The collected data indicated that the copper chromite/MeONa was more active than Cu-Raney/MeONa system. The reaction was shown to proceed with the formation only of *n*-propanol and isobutanol. Ethanol conversion up to 61% with selectivity to isobutanol up to 98.4% was obtained. The same catalytic systems were also employed in the reaction of the methanol/ethanol/*n*-propanol ternary mixture. Again copper chromite/MeONa resulted more active than the Cu-Raney/MeONa system. Finally, experiments were carried out on methanol/*n*-propanol mixtures in the presence of the copper chromite/MeONa catalytic system by recycling both the recovered solid copper component and the liquid reaction mixture for evidencing eventual copper leaching by MeONa. On the basis of the obtained results it was concluded that in the Guerbet reaction copper chromite works as heterogeneous catalyst. © 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Copper chromite; Sodium methoxide; Guerbet isobutanol synthesis; Condensation of methanol with higher alcohols

## 1. Introduction

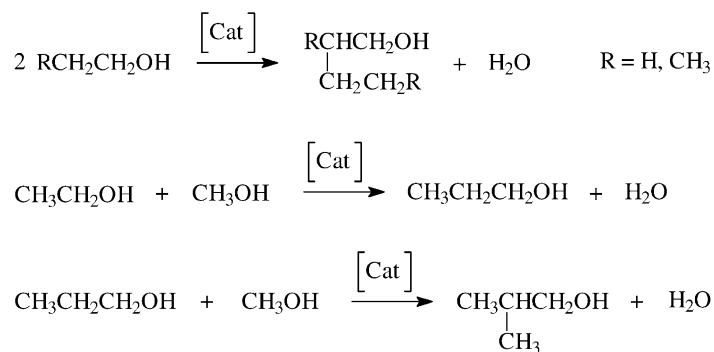
Recently, the catalytic synthesis of isobutanol (*i*-BuOH) has gained an increased research interest due to its potential application as a precursor of

gasoline additives. Indeed, it may be used for obtaining isobutene, which in turn may be converted either to methyl *tert*-butyl ether (MTBE) or to iso-octane [1]. At present, the direct synthesis of *i*-BuOH from syngas at high temperature and pressure over heterogeneous catalysts, named higher alcohols synthesis (HAS) process, is characterized by rather low selectivity and productivity [2]. An alternative route would be the two-step process [3,4] consisting of a

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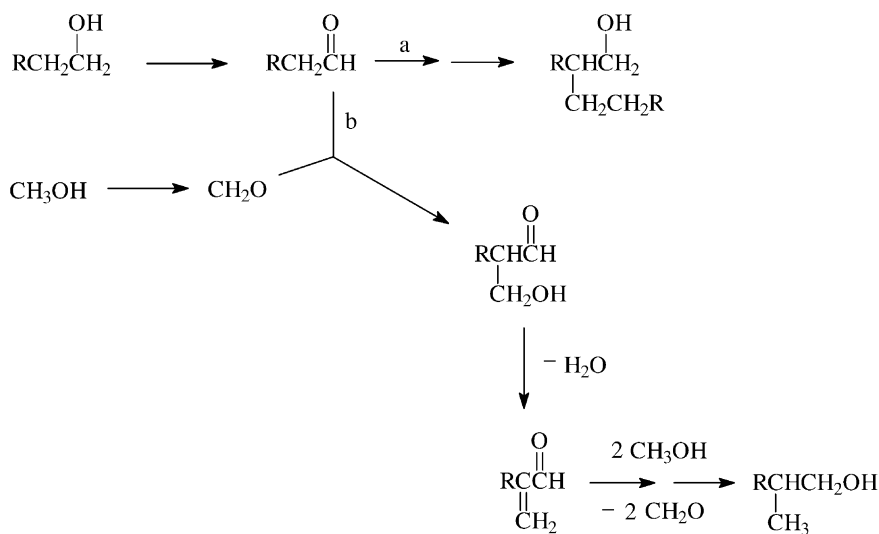
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Scheme 1.

first stage where methanol (MeOH) and higher alcohols are obtained from syngas at low temperature with modified MeOH catalysts and of a second step where the above alcohols mixture is converted to an *i*BuOH-rich product by using a high temperature MeOH catalyst. However, this last step showed several drawbacks, particularly in terms of selectivity to *i*BuOH and retro-conversion of MeOH to syngas. Taking into account that in the first step the reaction product was typically constituted by about 10/1/1/1 MeOH/ethanol (EtOH)/*n*-propanol (PrOH)/*i*BuOH mixture, this would be converted more selectively at

lower temperature to an *i*BuOH-rich product through the Guerbet reaction which is based on a cross condensation between alcohols, promoted by a bifunctional catalyst consisting of a basic component and a dehydrogenating/hydrogenating metal species (Scheme 1). In particular, this type of reaction provides [5] three subsequent steps involving (1) dehydrogenation of the alcohols to the corresponding aldehydes, (2) the aldol condensation of the resulting aldehydes and (3) the hydrogenation of the unsaturated condensation products to the higher alcohols. It is known [6–8] that at high temperature the condensation between MeOH

R = H, CH<sub>3</sub>

Scheme 2.

and a primary alcohol with a methyl or a methylene group in  $\beta$ -position to the hydroxy function, affords a carbon–carbon bond on the 2-position of the higher alcohol to give a 2-methylsubstituted Guerbet alcohol. Finally, it is noteworthy that *i*BuOH does not give further condensation reactions, due to its bulkiness and to the presence of only one hydrogen in  $\alpha$ -position to the methylol group. Recently, in a previous paper (Part 1) [9] we have investigated the synthesis of *i*BuOH from a MeOH/PrOH mixture as a model of the more complex product deriving from the first step of syngas reaction. It was found that in the presence of sodium methoxide (MeONa) as homogeneous basic component and copper chromite as heterogeneous dehydrogenating/hydrogenating metal derivative a nearly complete selectivity to *i*BuOH was achieved. Moreover, the conversion and productivity of PrOH to *i*BuOH increased with increasing both the temperature from 180 to 220 °C and the relative amount of MeONa with respect to copper. It is noteworthy that the replacement of H<sub>2</sub> atmosphere with N<sub>2</sub> caused a significant improvement of catalyst productivity, thus indirectly confirming that the dehydrogenation is the limiting step of the reaction. When the reaction was performed under CO/H<sub>2</sub> atmosphere the catalyst activity was substantially analogous to that found in the presence of H<sub>2</sub>. Finally, 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. In this context, it appeared interesting to extend the Guerbet reaction also to MeOH/EtOH and MeOH/EtOH/PrOH mixtures by using copper based/MeONa catalytic systems with the aim to verify the selectivity of the process and to improve the overall conversion to *i*BuOH (Scheme 2), thus better approaching the alcohols composition to that of the first stage of the above mentioned two-step process.

## 2. Experimental

### 2.1. Materials

MeOH (Prolabo), EtOH (Carlo Erba) and PrOH (Carlo Erba) were dried by distillation under dry argon after refluxing for 6 h on magnesium methoxide, according to the Lund and Bjerrum method [10].

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

Cu-Raney (Aldrich), commercialized as a slurry in water (50 wt.%), 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 MeOH at 180 °C for 5 h under 80 atm of H<sub>2</sub>.

Cu-1955P 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.

BO 134 catalyst, a copper chromite modified with zinc [11] having the following composition in wt.%: Cu (32.6), Cr (21.9), Zn (8.4), was activated following the same procedure as described for Cu-Raney.

### 2.2. Catalytic experiments for the condensation of methanol with higher alcohols

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 MeOH was introduced through the sampling valve. The reactor was subsequently pressurized with H<sub>2</sub> up to 80 atm and heated at 180 °C for 5 h. After the activation step, the reactor was cooled at room temperature and degassed. The reactor was evacuated and the MeOH removed under vacuum, then the proper amount of MeONa, dissolved either in the MeOH/EtOH or in the MeOH/EtOH/PrOH mixture, was introduced through the gas sampling valve. The reactor was subsequently pressurized with N<sub>2</sub>. 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 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.

Recycle experiments were performed adopting the following procedure: when the solid copper chromite

(Cu-1955P from Engelhard) was recycled, it was recovered from the direct experiment by filtration, carefully washed, dried under vacuum, weighed and finally recycled by adding the same amount of reagents and MeONa as those originally employed. When the liquid reaction mixture was recycled in order to verify the eventual metal leaching, the direct reaction was stopped after 6 h, then the liquid phase was carefully filtered under nitrogen in order to completely remove the solid component and the reaction was allowed to proceed for further 6 h.

### 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 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 GC 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. Guerbet condensation of methanol with ethanol in the presence of copper-based/sodium methoxide catalytic systems

As previously underlined by Ueda [8], when EtOH was allowed to react with MeOH over MgO at high temperature (ca. 360 °C) it was converted into PrOH and *i*BuOH, this last being formed by the subsequent Guerbet condensation of PrOH with MeOH. Therefore the same behaviour is expected to occur in the presence of copper-based/MeONa catalytic systems.

Preliminary blank experiments, carried out at 200 °C in the presence either of Cu-Raney alone or of sole MeONa, evidenced that the individual catalytic components are completely inactive, even in the initial dehydrogenation step, at least under the adopted conditions.

Therefore, the first experiment was carried out under nitrogen atmosphere on a MeOH/EtOH mixture containing an excess of MeOH (molar ratio = 12.5) at 180 °C in the presence of pre-activated Cu-Raney and a large excess of MeONa (base/Cu = 63 mol/mol) (entry 1, Table 1), conditions which in previous experiments had given the best performances for the MeOH/PrOH mixture [9]. Indeed, the main reaction product was *i*BuOH (79.6%) accompanied by PrOH (20.4%). It is noteworthy that neither *n*-butanol nor 2-methylpentan-1-ol were detected in the reaction products, thus confirming that the self-condensation of either EtOH or of the resulting PrOH did not occur, according to route a in Scheme 2. On the contrary, only the formation of higher alcohols resulting from MeOH/EtOH and MeOH/PrOH cross condensations (PrOH and *i*BuOH, respectively) occurred (route b, Scheme 2). Moreover, the absence of 2-methylbutan-1-ol in the reaction products allows one to exclude that a cross condensation between EtOH and PrOH may also occur. However, the productivity (*P*) of the catalyst was rather low, the conversion of EtOH being 11.2% after 6 h of reaction. If these results are compared with those previously obtained for the corresponding MeOH/PrOH mixture [9], EtOH results to be less reactive in the condensation with MeOH than PrOH, the latter reaching a 23.8% conversion after 6 h. This behaviour is better evidenced in Fig. 1, where the conversion of EtOH is plotted as a function of reaction time in comparison with that of PrOH previously mentioned.

This behaviour may be addressed to the easier dehydrogenation of PrOH with respect to EtOH [12,13]. However, when the temperature was increased up to 200 °C the other reaction conditions being retained (entry 2, Table 1) an improvement of activity was obtained, analogously to what reported for the MeOH/PrOH mixture with the same catalytic system [9]. Indeed, the conversion of EtOH after 6 h reached 22.3% and *P*, in terms of both PrOH and *i*BuOH formation, substantially doubled (1.45 h<sup>-1</sup> versus 0.73 h<sup>-1</sup>). On the other hand, it is ascertained that

Table 1

Synthesis of isobutanol (*i*BuOH) by condensation of methanol (MeOH) with ethanol (EtOH) in the presence of copper based/MeONa (B) catalytic systems<sup>a</sup>

Entry	Cu-catalyst <sup>b</sup>		B/Cu (mol/mol)	MeOH (mmol)	EtOH/Cu (mol/mol)	T (°C)	EtOH conversion <sup>c</sup> (%)	Selectivity (%) <sup>e</sup>		P <sup>d</sup> (h <sup>-1</sup> )
	Type	mmol						PrOH	<i>i</i> BuOH	
1	Cu-Raney	2.56	63	1250	40	180	11.2	20.4	79.6	0.73
2	Cu-Raney	2.56	63	1250	40	200	22.3	22.0	78.0	1.45
3	Cu-1955P	2.56	63	1250	40	180	32.0	18.0	82.0	2.08
4	Cu-1955P	2.56	63	1250	40	200	36.2	18.4	81.6	2.36
5	Cu-1955P	2.56	125	1250	40	180	33.6	13.0	87.0	2.19
6	Cu-1955P	2.56	125	1250	40	200	43.6	7.0	93.0	2.84
7	Cu-1955P	5.12	63	1250	20	180	41.0	9.8	90.2	1.33
8	Cu-1955P	5.12	63	1250	20	200	61.2	1.6	98.4	1.99
9 <sup>f</sup>	Cu-1955P	2.56	125	1157	75	200	31.5	15.8	84.2	2.05
10	BO 134	2.56	63	1250	40	180	17.4	16.5	83.5	1.13

<sup>a</sup> Reaction conditions: MeOH + EtOH = 1350 mmol; MeOH/EtOH = 12.5 if not otherwise specified; P<sub>N<sub>2</sub></sub>: 30 atm; time: 6 h.

<sup>b</sup> All the Cu-based catalysts were pre-activated (see Section 2); Cu-1955P and BO 134 are both copper chromite derivatives (for composition see Section 2).

<sup>c</sup> Overall conversion to both PrOH and *i*BuOH.

<sup>d</sup> Productivity expressed as: mol of (PrOH + *i*BuOH)/mol of Cu × h.

<sup>e</sup> Determined after 6 h of reaction.

<sup>f</sup> MeOH/EtOH = 6.0

Cu-Raney/MeONa resulted less active for the Guerbet reaction of MeOH with PrOH as compared with copper chromite/MeONa [9]; therefore we have also checked the catalytic behaviour of the latter system in the condensation of MeOH with EtOH. As a consequence, entries 1 and 2 were repeated just replacing

Cu-Raney with the pre-activated commercial copper chromite Cu-1955P (entries 3 and 4, Table 1), all other reactions conditions being retained. As expected, this catalyst displayed higher activity both at 180 and 200 °C, as compared with the Cu-Raney/MeONa system, EtOH conversion reaching 32.0 and 36.2%

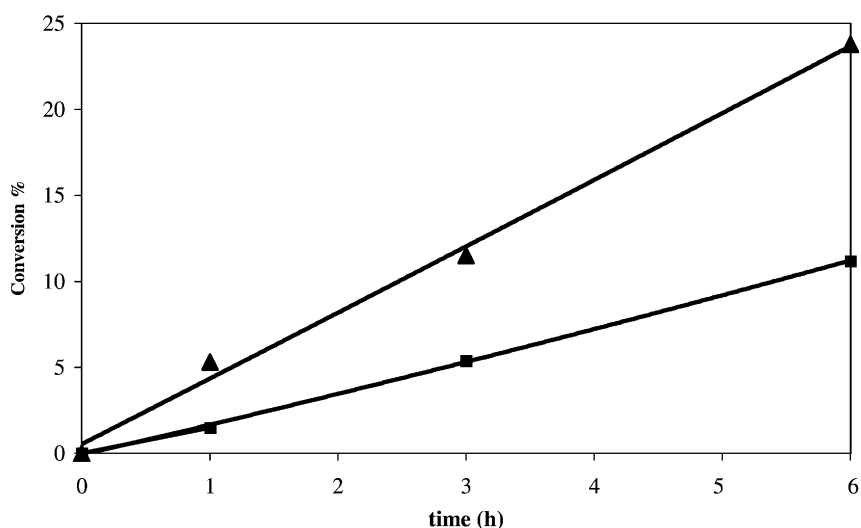


Fig. 1. Comparison between EtOH and PrOH reactivity with MeOH in the Guerbet condensation: (■) EtOH conversion (entry 1); (▲) PrOH conversion [9].

values, respectively, with  $P$ -values of 2.08 and  $2.36\text{ h}^{-1}$ , respectively. Under the adopted conditions the effect of the temperature increase on activity was found to be rather low (Fig. 2), differently from what observed for the Cu-Raney based system.

Moreover, the selectivity to  $i$ BuOH was slightly increased as compared with entries 1 and 2, values around 82% being reached.

When the relative amount of MeONa was doubled with respect to copper chromite at  $180^\circ\text{C}$  (entry 5, Table 1), no remarkable increase of productivity was observed (compare entry 5 with entry 3). It must be underlined that the effective activity of the catalyst in entry 5 is higher with respect to entry 3, not only due to the slight higher EtOH conversion but also for the improvement of selectivity to  $i$ BuOH. In fact, considering that  $i$ BuOH is formed in two steps (condensation of EtOH with MeOH and subsequently of the produced PrOH with MeOH), the catalytic system works one time in the formation of PrOH and twice in the production of  $i$ BuOH (Scheme 1).

A significant improvement of both productivity and selectivity to  $i$ BuOH (up to 93%) was observed in entry 6 carried out at  $200^\circ\text{C}$  (compare entry 6 with entry 4). The positive effect related to the increase of the base concentration may be explained taking into account that water is co-produced in the reaction (Scheme 1), a progressive hydrolysis of MeONa occurring with the reaction progress to give MeOH and inactive NaOH. As a consequence, the progressive

depletion of the basic component by hydrolysis does not allow to use MeONa in catalytic amount, but really as a reagent in stoichiometric amount.

When both MeONa and copper chromite were doubled with respect the amount of reacting alcohols (entries 7 and 8, Table 1) EtOH conversion increased (compare entries 7 and 8 with entries 5 and 6, respectively), reaching values  $>60\%$  after 6 h. At the same time an improvement of selectivity to  $i$ BuOH was also observed, an almost complete value being reached at  $200^\circ\text{C}$  (98.4%).

In order to check if the increase of EtOH concentration in the reacting alcohols mixture would favour its self-condensation, entry 6 was repeated using almost the double of the amount of EtOH with respect to MeOH, all other reaction parameters being retained (entry 9, Table 1). However, despite a negative effect on both productivity and selectivity to  $i$ BuOH, no formation of self-condensation products of EtOH was observed.

Finally, the commercial copper chromite was replaced by a not stoichiometric spinel (BO 134, see Section 2), considering that this catalyst had been used by us as hydrogenation system of crude oxo-aldehydes and displayed the best performances [11]. As shown in entry 10 of Table 1, this catalyst showed a higher activity as compared with the system based on Cu-Raney, but lower than that found for the catalyst based on Cu-1955P, without any gain of selectivity (compare entry 10 with entry 3).

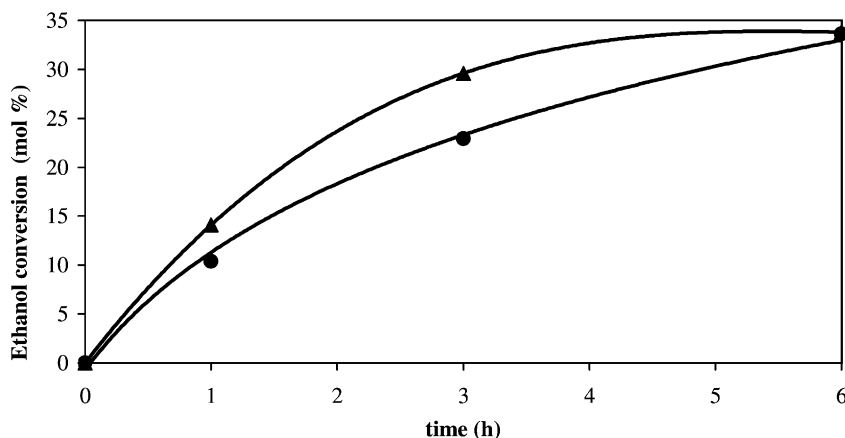


Fig. 2. Influence of reaction temperature on the Guerbet condensation of EtOH with MeOH carried out in the presence of copper chromite/MeONa catalytic system: (●)  $180^\circ\text{C}$ , entry 3; (▲)  $200^\circ\text{C}$ , entry 4.

In conclusion, EtOH in the Guerbet reaction with MeOH behaves as a source of PrOH to give finally *i*BuOH as the main product. This trend further confirms that the reactivity of PrOH is higher than that of EtOH, no progressive accumulation of the former being ever observed. In this context, it appeared interesting to investigate the Guerbet reaction when both EtOH and PrOH were allowed to react with MeOH in the presence of the copper-based/MeONa catalytic systems.

### 3.2. Guerbet condensation of methanol with ethanol and *n*-propanol in the presence of copper-based/sodium methoxide catalytic systems

All the catalytic experiments were performed by using pre-activated copper catalysts. In the first experiments Cu-Raney/MeONa catalytic system and a MeOH/EtOH/PrOH mixture with molar ratios 8/1/1 were used, the total amount of alcohols (1350 mmol) being equal to that used for the previous experiments on the MeOH/EtOH binary mixture with the same catalyst. When the reaction was carried out at 180 °C (entry 11, Table 2) under the same conditions as in entry 1 of Table 1, a similar EtOH conversion was obtained, the content of *i*BuOH in the higher alcohols of reaction mixture reaching 13.4 mol%, after 6 h.

Moreover, the concentration of PrOH resulted in slight excess (44.5%) with respect to that of EtOH (42.1%). However, this result cannot be interpreted in terms of lower reactivity of PrOH with respect to EtOH because the former in this case is contemporarily a reagent and an intermediate product (Scheme 1). When the same ternary mixture was allowed to react at 200 °C, although with a lower amount of Cu-Raney (entry 12, Table 2), an increase of both EtOH conversion and *i*BuOH concentration in the higher alcohols of reaction mixture (19.5 mol%) were ascertained.

When the commercial copper chromite was used in combination with MeONa as catalytic system (entries 13–21, Table 2) in all cases the percentage of *i*BuOH in the higher alcohols mixture significantly increased, thus confirming that this catalyst is more active than that based on Cu-Raney, analogously to what found for the binary MeOH/EtOH mixture. When entry 11 was repeated just replacing Cu-Raney with copper chromite (entry 13), EtOH conversion sharply increased up to 36.9%, the concentration of *i*BuOH in the higher alcohols erasing up to 31.0%. An analogous trend was observed when the reaction was carried out at 200 °C (compare entry 14 with entry 12). Moreover, from Fig. 3, where the composition of higher alcohols in the reaction mixture is plotted as a function of time (entry 14), it is possible to evidence

Table 2

Synthesis of isobutanol (*i*BuOH) by condensation of methanol (MeOH) with ethanol (EtOH) and *n*-propanol (PrOH) in the presence of copper based/MeONa (B) catalytic systems<sup>a</sup>

Entry	Cu-catalyst <sup>b</sup>		MeONa (mmol)	EtOH (mmol)	EtOH conversion (%)	T (°C)	Higher alcohols (mol%)		
	Type	mmol					EtOH	PrOH	<i>i</i> BuOH
11	Cu-Raney	6.75	160	135	15.6	180	42.1	44.5	13.4
12	Cu-Raney	2.56	160	135	18.9	200	41.5	39.0	19.5
13	Cu-1955P	6.75	160	135	36.9	180	31.5	37.6	31.0
14	Cu-1955P	2.56	160	135	38.4	200	30.7	38.7	30.4
15	Cu-1955P	2.56	160	135	34.1	180	32.8	38.6	28.5
16	Cu-1955P	6.75	160	135	39.7	200	30.2	38.3	31.5
17	Cu-1955P	2.56	320	135	37.3	180	31.4	31.9	36.8
18	Cu-1955P	6.75	320	135	52.2	180	23.9	23.7	52.4
19	Cu-1955P	6.75	320	135	71.2	200	14.4	15.4	70.3
20 <sup>c</sup>	Cu-1955P	6.75	320	180	49.4	180	33.7	17.3	49.0
21 <sup>d</sup>	Cu-1955P	6.75	320	90	51.0	180	14.3	27.9	57.9

<sup>a</sup> Reaction conditions: MeOH: 1080 mmol; MeOH + EtOH + PrOH = 1350 mmol, MeOH/EtOH = 8 and EtOH/PrOH = 1 mol/mol, if not otherwise specified;  $P_{N_2}$ : 30 atm; time: 6 h.

<sup>b</sup> All the Cu-based catalysts were pre-activated (see Section 2); Cu-1955P is commercial copper chromite.

<sup>c</sup> EtOH/PrOH = 2 mol/mol.

<sup>d</sup> EtOH/PrOH = 0.5 mol/mol.

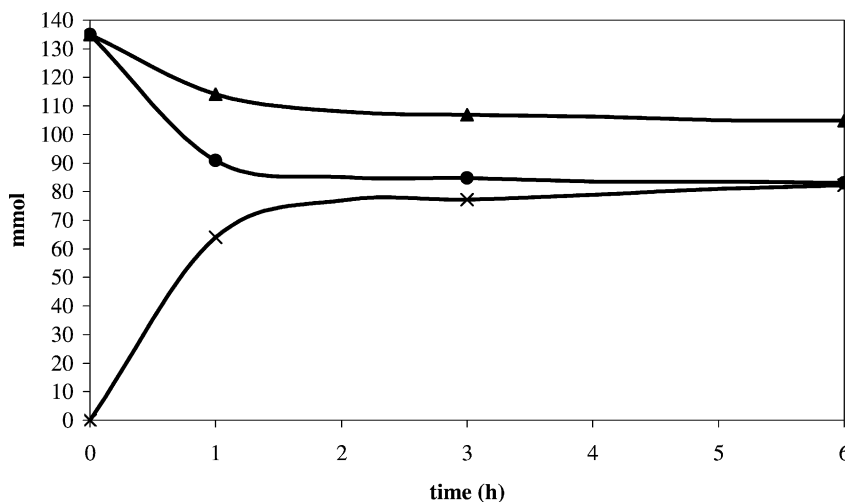


Fig. 3. Variation of the higher alcohols composition in the reaction mixture as a function of time (entry 14): (▲) PrOH, (●) EtOH and (×) *i*BuOH.

that under the adopted conditions the PrOH concentration is always higher than that of EtOH, which in turn is approached after 6 h by that of *i*BuOH.

Due to the better performance of copper chromite, also reducing its amount EtOH conversion of about 34% was obtained (compare entry 15 with entry 13).

When the entry 13 was replicated at 200 °C (entry 16) a further increase of catalytic activity was ascertained. When the concentration of the basic component was increased, a significant improvement of the content of *i*BuOH in the higher alcohols of the reaction mixture was observed (compare entry 17 with 15, entry 18 with 13 and entry 19 with 16). Particularly relevant were the performances in entry 19, where EtOH conversion up to 71.2% and *i*BuOH contents >70% were found. This result again confirms the crucial role played by the basic component concentration on the reaction progress (compare entry 19 with entry 16).

The effect of the variation of the relative concentration of the reagents was also studied (entries 20, 21, Table 2). When EtOH was doubled with respect to PrOH, only a slight decrease of the selectivity to *i*BuOH was observed. On the contrary, when PrOH was doubled, as expected, *i*BuOH concentration increased with respect to entry 18 where an equimolar amount of the two alcohols was employed thus suggesting that the *i*BuOH yield may be modulated

by combining the suitable catalytic system with the proper composition of the reagents mixture.

Finally, taking into account that under the adopted reaction conditions, particularly at 200 °C, the presence of a large excess of MeONa with respect to the copper catalyst could in principle favour the leaching of the metal into the solution with the formation of homogeneous active species, as evidenced for heterogeneous palladium precursors [14], some experiments were carried out in order to check if the metal species work in homogeneous and/or in heterogeneous phase. In order to better point out this behaviour a MeOH/PrOH mixture was chosen for the above experiments, taking into account that PrOH is more reactive than EtOH.

Considering that the MeOH/PrOH mixture over pre-activated copper chromite/MeONa was previously investigated by us [9], we adopted the reaction conditions which had displayed the best catalytic performances. In particular, a reference experiment was performed at 200 °C (entry 22, Table 3) under nitrogen (30 atm) with MeOH/PrOH, PrOH/Cu and MeONa/Cu molar ratios equal to 12.5, 320 and 513, respectively, the reaction being allowed to proceed for 12 h. Subsequently another experiment was carried out by using a double amount of copper chromite, the other quantities of reagents being retained (entry 23, Table 3). At the end of the reaction the copper catalyst



Table 3

Synthesis of isobutanol (*i*BuOH) from methanol (MeOH)/*n*-propanol (PrOH) mixtures in the presence of copper chromite (Cu-1955P)/sodium methoxide (MeONa)<sup>a</sup>

Entry	Cu-1955P (mmol)	PrOH conversion (%)				
		1 h	3 h	6 h	9 h	12 h
22	0.312	12.9	23.2	41.4	55.4	62.7
23	0.625	19.8	27.6	45.6	47.7	61.0
24 <sup>b</sup>	0.312	–	–	29.3	–	40.4
25 <sup>c</sup>	0.625	–	–	44.5	–	–
26 <sup>d</sup>	–	–	–	44.5	–	45.0

<sup>a</sup> Recycle experiments—reaction conditions: MeOH + PrOH = 1350 mmol; PrOH: 100 mmol; MeONa: 160 mmol; selectivity to *i*BuOH: 100%; time: 12 h.

<sup>b</sup> Recycle experiment carried out by using the Cu-1955P catalyst recovered in entry 23 and pre-activated (see Section 2).

<sup>c</sup> Experiment carried out under the same conditions as those of entry 23 and stopped after 6 h when the conversion to *i*BuOH was 44.5%.

<sup>d</sup> Experiment carried out for further 6 h by employing the reaction solution recovered from entry 25 after 6 h of reaction. The conversion to *i*BuOH of the reaction mixture at the beginning of the recycle was 44.5%.

was recovered, washed and dried, then it was again pre-activated and a portion of it recycled to repeat the experiment as in entry 23 (entry 24, Table 3). The obtained data indicated that after 12 h of reaction the activity of the recycled catalyst was still rather high, although lower than that observed for the fresh catalyst, the conversion to *i*BuOH being 40.4 and 62.7%, respectively. The minor activity of the recycled catalyst would be accounted to the higher “stress” caused by washing and pre-activation procedures. However, in order to check if homogeneous active metal species would be formed by a partial leaching of copper chromite in the presence of MeONa, the experiment as in entry 23 was repeated (entry 25, Table 3). In this case, after 6 h the reaction was stopped and the liquid mixture was separated from the solid catalyst under nitrogen, analyzed and then recycled for further 6 h (entry 26, Table 3). The analysis of the reaction products after the recycle experiment of the solution did not evidence any further advancement of the reaction, the conversion to *i*BuOH being substantially unchanged (44.5%). This result confirmed that copper chromite totally works in heterogeneous phase, the eventually leached copper species being inactive. Work is in progress in order to quantify the eventual copper leaching degree.

## 4. Conclusions

On the basis of the obtained results the following concluding remarks can be drawn:

- i*BuOH can be obtained with good yield by the Guerbet condensation of EtOH with MeOH carried out in the presence of a bifunctional catalytic system constituted by a copper-based component and MeONa. The catalysts based on copper chromite resulted significantly more active than those obtained by Cu-Raney. In addition to *i*BuOH, lower amount of PrOH was also found as unique by-product. A comparison with previous results clearly indicated that EtOH is less reactive than PrOH in the Guerbet condensation with MeOH.
- Due to the progressive hydrolysis of MeONa by the co-produced water, stoichiometric amounts of the basic component are required. This is an obvious drawback for this process and work is in progress for replacing the homogeneous base with an heterogeneous one, such as hydrotalcites which appear to be unaffected by water poisoning [15].
- When MeOH/EtOH/PrOH ternary mixtures with composition similar to that obtained in the HAS process were employed with the same catalytic systems *i*BuOH rich alcohols mixtures were achieved whose composition strongly depends on the reactions parameters. Indeed, the *i*BuOH yield can be modulated also by varying the relative amount of the reagents.
- Recycle experiments allowed to exclude copper leaching into solution thus confirming a complete heterogeneous reaction mechanism by this metal component.

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