

Selective synthesis of 2-ethyl-1-hexanol from *n*-butanol through the Guerbet reaction by using bifunctional catalysts based on copper or palladium precursors and sodium butoxide

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Abstract

The Guerbet self-condensation of *n*-butanol (BuOH) to 2-ethyl-1-hexanol (2EH) in the presence of different catalytic systems based on a metal hydrogenating/dehydrogenating component and a base was studied. In particular, homogeneous and heterogeneous palladium derivatives were used at 200 °C in combination with sodium butoxide (BuONa) as basic component. The effect of reaction parameters, such as BuONa concentration and amount of the metal component were investigated. Turnover numbers (TN) up to 80 mol of 2EH/(mol of Pd × h) were reached. In the case of heterogeneous palladium precursors an extensive leaching into solution was observed.

The catalytic system based on completely heterogeneous copper chromite in combination with BuONa was also studied. In this case the effect of reaction parameters, such as the base concentration, the addition of either an ancillary base (MgO) or a dehydrating agent (CaO, molecular sieves) as well as reaction temperature was investigated. TN values up to 22 were obtained working at 280 °C.

In all the experiments a complete selectivity to 2EH was ascertained, independently on the type of the adopted catalytic system and reaction conditions.

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1. Introduction

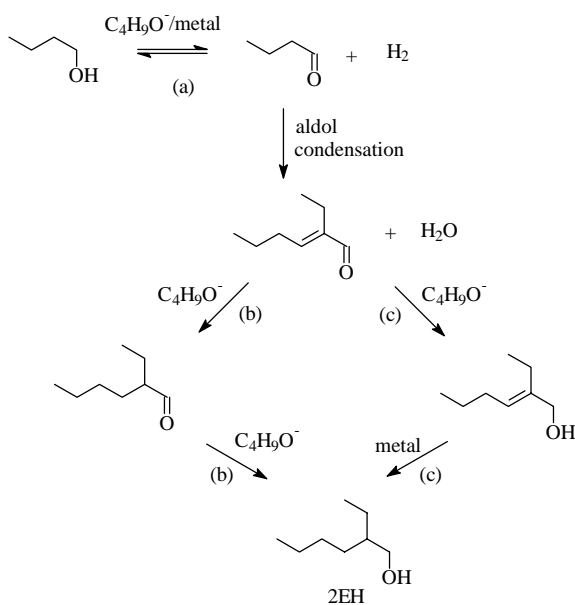
2-Ethyl-1-hexanol (2EH) is the most important compound belonging to the class of “plasticizers alcohols” (C₆–C₁₁ cut of higher alcohols). In fact, it is employed for the synthesis of bis(2-ethylhexyl)phthalate, the most widely applied plasticizer for poly(vinyl chloride) (PVC) [1]. In addition 2EH is used as a component of the catalyst system in the polymerization of acrylates for aqueous dispersions of copolymeric latexes [2]. 2EH is also utilized as precursor for the synthesis of the corresponding peroxydicarbonate, a free radical initiator employed in the homopolymerization of vinyl chloride. Moreover, it is also applied to the preparation of the corresponding trialkyl phosphite, employed as light stabilizer for plastics as well as for the synthesis of organotin derivatives as heat stabilizers of PVC [1].

Finally, 2EH is also used to make expanded polystyrene beads [3] and for preparing acrylates applied to pressure sensitive adhesives.

2EH is produced almost exclusively through a three-step process involving the hydroformylation of propene to butanal, its aldol condensation to 2-ethyl-2-hexenal and finally its hydrogenation to 2EH. An alternative route may consist in the preparation of butanal starting from ethylene via acetaldehyde. Both processes (the hydroformylation of propene to butanal as well as the oxidation of ethylene to acetaldehyde) require expensive homogeneous noble metal catalysts characterized by a rather high environmental impact. Therefore, it appeared of interest to develop a new process characterized by a single step, possibly involving heterogeneous metal catalysts. In this context, the synthesis of 2EH, through the Guerbet reaction, consisting into the self-condensation of *n*-butanol (BuOH), appeared a valid and attractive route. Indeed, it is well established that the Guerbet reaction may be split into subsequent three main steps such as: (1) dehydrogenation of alcohols to give the corresponding aldehydes, (2) the aldol condensation of the

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resulting aldehydes and (3) the hydrogenation of the unsaturated condensation products to give the higher Guerbet alcohols [4,5]. In order to realize this reaction a bifunctional catalyst, characterized by a dehydrogenating/hydrogenating metal species and a basic component, is required [6–8].

In particular, Burk evidenced the synergic interaction between the metal and the basic components when performed the self-condensation of BuOH to 2EH at low temperatures, in the presence of Rh/C and sodium butoxide (BuONa) [6,7]. Thus, as reported in Scheme 1, it was concluded that the initial dehydrogenation step (a) requires the catalysis of both the transition metal and the base, whereas the α,β -unsaturated aldehyde deriving from the aldol condensation may be reduced to the Guerbet alcohol through two pathways, one (b), promoted only by the base and the other (c), characterized by the successive assistance of both catalytic components.

Homogeneous catalysts at 120 °C based on phosphino-complexes of different transition metals (Rh, Ru, Ir, Pt, Pd, and Au) in the presence of sodium butoxide were also used in the Guerbet self-condensation of BuOH [9]. The reported results allowed to evidence that the catalysts based on Pd and Au derivatives, differently from those based on the other metal complexes, resulted inactive. This behaviour was attributed to the fact that the above complexes are not able to form stable hydrides but are reduced to low valent species. Very recently, we have also checked the activity of homogeneous Pd(0) and Pd(II) complexes or heterogeneous Pd/C catalysts, in combination with sodium methoxide (MeONa), for the Guerbet condensation of methanol (MeOH) with *n*-propanol (PrOH) to give isobutanol (ⁱBuOH), but using a higher reaction temperature (200 °C) [10]. These catalytic systems were found to display good activity, although a solid deposition and leaching effects were observed in the

two cases. Recycle experiments evidenced that the overall activity may be addressed to both homogeneous and heterogeneous species, probably involved in an equilibrium. In a previous paper the same reaction was carried out by using copper based-MeONa catalytic systems [11]. In particular, copper chromite resulted much more active than Cu-Raney and a large excess of MeONa with respect to the metal component was necessary in order to obtain high PrOH conversion to ⁱBuOH, due to the fact that the co-produced water generates inactive NaOH from MeONa, thus progressively reducing its concentration. Moreover, when the reaction was performed under N₂ atmosphere in the place of H₂, better catalytic performances were obtained, thus supporting the fact that the dehydrogenation of alcohols to the corresponding aldehydes is one rate limiting step of the reaction. In a more recent investigation [12], copper chromite was found to work essentially in heterogeneous phase, thus suggesting the Guerbet condensation as a more friendly environmental process with respect to the conventional ones up to now applied for the synthesis of 2EH. Therefore, this paper will deal with the selective synthesis of 2EH by self-condensation of BuOH in the presence of catalysts based on homogeneous and heterogeneous palladium systems as well as on copper chromite and BuONa.

2. Experimental

2.1. Materials

BuOH (Aldrich) was dried by distillation under dry argon after refluxing for 6 h on magnesium methoxide, according to the Lund and Bjerrum method [13].

Tetrahydrofuran (THF) (Baker) was dried by distillation under dry argon after refluxing on Na–K alloy.

Sodium hydride (NaH) (Aldrich) was used as received and stored under dry argon.

BuONa (Aldrich) has been prepared according to the literature [13] starting from NaH and anhydrous BuOH in THF solution. After the reaction was complete, the mixture was transferred in a Schlenk vessel, the solvent was removed under vacuum and the residual solid stored under dry argon.

Copper chromite, a commercial product from Engelhard (Cu-1955-P catalyst) having the following composition in % by weight: Cu (36.0), Cr (33.0), Mn (3.0), was activated prior to the use in a mechanically stirred Parr reactor in the presence of BuOH at 180 °C for 5 h under 8 MPa of H₂.

Palladium supported on activated charcoal (Pd10/C) is a commercial catalyst (Aldrich) containing 10 wt.% of metal.

Palladium supported on activated charcoal (Pd2/C) is a commercial catalyst (Johnson Matthey) containing 2 wt.% of metal.

Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] and [1,2-bis(diphenylphosphino)ethane] dichloro palladium(II) [Pd(dppe)Cl₂] (both from Aldrich) were used as received.

Magnesium oxide (MgO) has been prepared according to the literature [14] starting from commercial MgO (Aldrich). This was suspended in water under stirring for 24 h, then it was filtered, dried in the oven at 100 °C for 2 h and stored under dry argon. Finally, it was calcined at 600 °C for 2 h under vacuum and successively stored under dry argon. Its BET surface area value resulted to be 103 m²/g. Activated molecular sieves (Aldrich) of 3 Å were stored under dry argon.

Anhydrous calcium oxide (CaO) (Aldrich, 99.9%) was used as received and stored under dry argon.

2.2. Catalytic experiments for the self-condensation of *n*-butanol to 2-ethylhexan-1-ol

A 300 ml Parr reactor, equipped with a mechanical stirrer, a heating system and a control device assisted by a J thermocouple inserted into the reactor, a sampling valve for liquids, an inlet valve for gas introduction and an outlet sampling valve, was used in the catalytic batch experiments. The catalyst [preactivated copper chromite (1.25 mmol) or unreduced palladium derivative (0.05–0.31 mmol)] was introduced in the reactor, then this was evacuated and the proper amount of BuONa, dissolved in 545 mmol of BuOH, was added through the sampling valve. When either MgO was used as ancillary base or CaO or molecular sieves were employed as dehydrating component, they were introduced in the reactor successively to the copper catalyst, before the evacuation of the reactor. The reactor was subsequently pressurised with N₂ (3 MPa) and heated at the programmed temperature (usually in the 180–220 °C range). The reaction was followed by collecting at different times portions of the reaction mixture, quickly cooled at room temperature, through the sampling valve. At the end of each experiment, the reactor was rapidly cooled at room temperature and slowly degassed. Finally the liquid reaction mixture was analysed by GC.

When the recycle experiment of the liquid phase were carried out the reaction was stopped after 6 h, then the solid was separated from the liquid reaction mixture by careful filtration at room temperature. The liquid phase was then recycled in the reactor and the reaction was allowed to proceed for further 6 h. At the end the reaction mixture was analysed by GC. The turnover number (TN) was calculated at 6 h and expressed as—mol of 2EH/(mol of metal × h).

2.3. Analytical procedures

The analysis of the reaction products was performed in isotherm way at 190 °C for 15 min by GC on a Perkin-Elmer Autosystem XL chromatograph equipped with a thermal conductivity detector. The resulting data were processed, through a Perkin Elmer 600 series LINK, by the software TOTALCHROM™ WORKSTATION 6.2. A 2 m Poropak PS packed column with a stationary phase based on ethylvinylbenzene/divinylbenzene resin was used. Helium was employed as carrier gas with a 22 ml/min flowing rate.

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.

BET surface area value of MgO sample was obtained using a single point ThermoQuest Surface Area Analyzer Qsurf S1.

Quantitative determination of the Pd content in the recovered catalysts after the catalytic cycle was carried out by employing a X-ray fluorescence Phillips PW 1480 apparatus. The sample was ground and pressed to form a disk with 2 cm diameter. The leaching degree was determined by comparison the intensity data of the recovered catalyst with those of the original catalyst of known Pd content [15,16].

3. Results and discussion

3.1. Self-condensation of BuOH to 2EH by homogeneous and heterogeneous palladium-based/BuONa catalysts

Preliminary experiments were carried out by employing homogeneous palladium complexes as dehydrogenating/hydrogenating species and BuONa as basic component in the Guerbet self-condensation of BuOH. In particular Pd(II) and Pd(0) precursors were used under reaction conditions similar to those employed in the synthesis of ¹BuOH from MeOH and PrOH in the presence of MeONa as basic component [10]. Taking into account that BuOH was the alcoholic reagent, BuONa was used as basic component in the place MeONa, with the aim to avoid the concomitant formation of alcohols deriving from a cross-condensation between BuOH and MeOH generated by the hydrolysis of MeONa due to the co-produced water. Finally, an excess of base with respect to the metal component and N₂, as gaseous atmosphere, were used.

When Pd(dppe)Cl₂ was adopted, the amount of the base was varied still retaining that of the metal component (0.313 mmol) and of the substrate (545 mmol) with the aim of studying the effect of the concentration of the basic component on the activity of the system (entries 1 and 2, Table 1).

As shown in Table 1 the BuOH conversion to 2EH was very similar in the two cases within the first 6 h of reaction (ca. 23%); however, for prolonged times the conversion in entry 2 (where the amount of BuONa was doubled with respect to that of entry 1) progressively became higher.

The above behaviour is readily explained considering that in entry 1 after 6 h the amount of co-produced water is about 60 mmol, very close to that of BuONa initially used in the experiment (80 mmol); therefore, differently from entry 2, a large fraction of the base was subjected to hydrolysis to give inactive NaOH and BuOH. It is also to underline that the progressive hydrolysis of BuONa gives rise to BuOH.

Table 1

Self-condensation at 200 °C of *n*-butanol (BuOH) to 2-ethyl-1-hexanol (2EH) by homogeneous and heterogeneous palladium-based catalysts in the presence of BuONa as basic component

Entry	Palladium precursor		BuONa (mmol)	BuOH conversion (%)					TN (h ⁻¹)
	Type	(mmol)		1 h	3 h	6 h	9 h	12 h	
1	Pd(dppe)Cl ₂	0.313	80	5.8	12.7	23.0	28.5	29.7	33.4
2	Pd(dppe)Cl ₂	0.313	160	–	9.2	23.1	31.1	42.6	33.5
3	Pd(dppe)Cl ₂	0.056	18	–	–	6.3	7.7	9.4	51.1
4	Pd(PPh ₃) ₄	0.125	80	0.0	0.0	0.0	0.0	0.0	0.0
5	Pd10/C	0.125	80	2.2	7.4	17.4	22.0	25.5	63.2
6 ^a	Pd10/C	0.125	160	–	–	16.5	–	–	60.0
7	Pd2/C	0.125	160	–	–	22.0	–	43.3	79.9

^a The reaction was stopped at 6 h and the solid and the liquid reaction mixtures were used for recycle experiments.

Therefore, the conversion values are underestimated because in the calculations the formation of BuOH from the basic component has not been considered.

Moreover, it is noteworthy to mention that in both entries at the end of the reaction a black solid was found on the reactor walls, probably consisting of Pd(0).

Considering that in a previous paper the homogeneous PdBr₂(PPh₃)₂ complex, when used in combination with BuONa, was found to be inactive in the self-condensation of BuOH [9], we have performed an other experiment (entry 3, Table 1) by using the same amount of the metal component (0.056 mmol) and the same BuONa/Pd molar ratio as employed in the cited reference. The obtained results clearly indicate that the above catalytic system is active. However, due to the drastic reduction of the concentrations of metal and basic components with respect to those adopted in entries 1 and 2, the conversion to 2EH was strongly reduced, although the turnover number (TN) of the system after 6 h was found to be higher than that of the preceding experiments (51.1 versus 33.4 h⁻¹). Therefore, the inactivity of the palladium catalyst previously observed [9] could be due to the much lower reaction temperature used by the authors (120 °C) with respect to that (200 °C) adopted by us.

However, when the Pd(PPh₃)₄/BuONa catalyst was employed (entry 4, Table 1) no activity at all was ascertained, thus suggesting that also the oxidation state of the metal precursor may play a significant role in determining the catalytic performances.

Subsequently, heterogeneous palladium systems were checked in the Guerbet reaction when combined with BuONa. No pre-reduction with H₂ was carried out for all heterogeneous palladium systems, due to the detrimental effect previously observed in the MeOH/PrOH condensation [10]. In particular, the effect on the catalytic activity by the loading of the metal particles on the support was investigated and leaching problems were quantified.

When Pd10/C catalyst, containing 10 wt.% of metal on the activated charcoal as support, was used (entry 5, Table 1) a significant activity was observed. In fact, although the BuOH conversion was lower with respect to that observed with Pd(dppe)Cl₂ (entry 1) due to the lower amount of metal

used (ca. 1/3), the productivity of the catalyst after 6 h was higher (TN = 63.2 versus 33.4 h⁻¹).

When the experiment of entry 5 was repeated by doubling the amount of the base (BuONa/Pd = 160 mol/mol, still retaining constant the other reaction parameters, (entry 6, Table 1) after 6 h the BuOH conversion was substantially unchanged because, analogously to that found in the case of homogeneous palladium-based catalysts (entries 1 and 2), the effect of the increased relative amount of the base is evinced at longer reaction times.

When a catalyst with a lower metal loading was used, such as Pd2/C (containing 2 wt.% of metal on the activated charcoal), under the same conditions of entry 6 (entry 7, Table 1) an appreciable increase of activity was observed, the productivity improving from 60.0 to 79.9 h⁻¹. These data indicate, as expected, that the decrease of the percentage of the metal on the support plays a positive effect on catalyst activity because an excessive loading of the support prevents the single metal sites to operate at the maximum performances. It is noteworthy to mention that in all the experiments a complete selectivity to 2EH was achieved.

Finally, taking into account that for both homogeneous and heterogeneous palladium precursors the presence of a strong basic component such as MeONa caused [10] in the Guerbet condensation of MeOH with PrOH to ¹BuOH the formation of soluble and insoluble species in equilibrium each other both contributing to the overall catalytic performances, it appeared interesting to check if a metal leaching occurred also in the self-condensation of BuOH, catalyzed by the Pd/C//BuONa system. Therefore, entry 6 was stopped after 6 h and the solid catalyst was removed by filtration and the liquid phase was recycled and reacted for further 6 h. The conversion of BuOH was found to increase from 16.5 to 32.5%, thus clearly indicating that the liquid mixture is still active, due to soluble palladium species leached from the pristine heterogeneous catalyst.

In order to determine the amount of leaching the Atomic Absorption Spectrometry was firstly employed on the liquid reaction mixture recovered from the catalytic experiment after filtration from the residual solid. However, this technique, due to the interference of sodium deriving from BuONa, did not give reliable results. Therefore, the palla-

dium leaching extent was estimated by determining the content of the metal with the X-rays fluorescence spectroscopy (XRF) [15,16] on both the pristine and the recovered solid from catalytic experiment (entry 6) after 6 h of reaction. The XRF analysis indicated that about 50% of the original palladium catalyst was released into solution. This result is analogous to that recently reported by Köhler [17,18] for Pd/C in the Heck arylation of olefins. However, it is to underline that an appreciable amount of the palladium which at 200 °C works in homogeneous phase after cooling deposits on the reactor walls, the residual part remaining in the recycled solution.

This high leaching extent clearly reduces the interest for industrial application perspectives of heterogeneous palladium-based systems, thus inducing us to check copper chromite based catalysts whose complete heterogeneity was recently proved by us [12].

3.2. Self-condensation of BuOH to 2EH by copper chromite/BuONa catalysts

The self-condensation of BuOH to 2EH with the copper chromite/BuONa system has been carried out by using reaction conditions which in the Guerbet synthesis of ¹BuOH from MeOH and PrOH had given the best performances [11,12]. Therefore, in all cases, pre-activated catalyst, a large excess of base with respect to the metal component and N₂, as gaseous atmosphere, were adopted. In addition, considering that in the previous experiments the productivity to ¹BuOH increased by decreasing the amount of the copper catalyst with respect to that of PrOH, still maintaining constant the base/copper molar ratio, a limited amount of copper chromite was used (1.25 mmol). When the Guerbet reaction was carried out at 200 °C on BuOH by increasing the relative amount of the basic component with respect to the copper chromite (in the 40–160 mol/mol range), still maintaining constant the BuOH/Cu molar ratio (entries 8–10, Table 2) the conversion of BuOH to 2EH after 12 h was found to improve from 16.5 to 57.9%, thus confirming the key role of the excess of the alkoxide.

At the same time, the productivity, calculated after 6 h, increased from 3.2 to 15.1 mol of 2EH/(mol of metal × h), thus evidencing a certain activity of the catalyst, although lower as compared with palladium catalyst performances. It is also worth noting that the selectivity to 2EH was complete, analogously to that found for palladium systems, no by-products being formed. Moreover, the reactivity of BuOH was found to be quite similar to that of PrOH with MeOH to give ¹BuOH under analogous conditions [11]. If the BuOH conversion to 2EH after 12 h of reaction is expressed as a function of the amount of the basic component a linear trend is substantially obtained.

This is easily explained taking into account that, for instance, when the conversion in entry 10 reaches about 60%, all the employed base is completely consumed (160 mmol of water are formed). The same occurs in entries 8 and 9 where a rapid calculation allows us to verify that at 16.5 and 29.8% conversions about 40 and 80 mmol of water are co-produced, respectively, thus completely hydrolysing the amount of BuONa used in the two cases.

With the aim to evaluate the effect on the conversion of BuOH to 2EH by the presence of an ancillary heterogeneous base, entry 8 was repeated with a further addition of 20 and 40 mmol of MgO (entries 11 and 12, respectively, Table 2). The comparison of the obtained data with respect to those of entry 8 indicate that the presence of MgO initially causes an improvement of conversion with increasing its amount, whereas at longer reaction times the conversion in the two experiments approaches an asymptotic value slightly higher than that of entry 8.

With the aim to remove the co-produced water in order to prevent the hydrolysis of BuONa, entry 8 was also repeated in the presence of 100 mmol of CaO as dehydrating agent (entry 13, Table 2). Indeed, the presence of CaO in combination with BuONa significantly improved the BuOH conversion to 2EH (24.2% after 12 h). Taking into account that copper chromite/CaO system in absence of BuONa is not able to activate BuOH to 2EH (entry 14, Table 2), this is a strong indication that the improvement of activity in entry 13 is not due to the basic properties of CaO, but only to its

Table 2
Synthesis of 2-ethyl-1-hexanol (2EH) through self-condensation of *n*-butanol (BuOH) by the copper chromite/BuONa (B) catalytic system

Entry	BuONa (mmol)	Ancillary base (MgO) (mmol)	Dehydrating component (CaO) (mmol)	B/Cu (mmol)	T (°C)	BuOH conversion (%)			TN (h ⁻¹)
						1 h	6 h	12 h	
8	40	–	–	32	200	n.d.	8.8	16.5	3.2
9	80	–	–	64	200	14.3	25.2	29.8	9.1
10	160	–	–	128	200	20.0	41.5	57.9	15.1
11	40	20	–	32	200	n.d.	13.8	18.0	5.0
12	40	40	–	32	200	12.5	17.5	19.1	6.3
13	40	–	100	32	200	12.3	19.5	24.2	7.1
14	–	–	100	0.0	200	n.d.	0.0	0.0	0.0
15	80	–	Mol. sieves	64	200	14.5	21.4	24.7	7.8
16	80	–	–	64	180	n.d.	22.7	25.9	8.2
17	80	–	–	64	220	23.7	28.1	29.2	10.2
18	160	–	–	128	280	20.6	61.1	–	22.2

dehydrating characteristics. On the contrary, when activated molecular sieves were used (5 g) as dehydrating agents (entry 15, Table 2) no appreciable effect was obtained on the activity of the copper chromite/BuONa system (compare entry 15 with entry 9).

The reaction temperature effect was also investigated by repeating entry 9 at different temperatures (180 and 220 °C, entries 16 and 17, respectively, Table 2).

The obtained data confirm a positive but limited effect at short reaction times by the temperature enhancement, at longer reaction time prevailing the inhibition effect due to the hydrolysis of BuONa.

In order to further improve the catalytic performances, entry 10 was repeated at 280 °C (entry 18, Table 2). The results indicate that a large enhancement of temperature significantly accelerates the reaction, allowing to reach after 6 h a conversion higher than 60%.

4. Conclusions

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

- (1) Homogeneous and heterogeneous palladium based catalytic systems, when combined with BuONa as basic component, show a good activity (TN up to 80) in the self-condensation of BuOH to 2EH without the formation of any by-product. The catalytic performances are largely affected by the concentration of the base, its progressive hydrolysis, due to the co-produced water, deactivating the system.
- (2) Catalytic systems based on BuONa and heterogeneous palladium components show a significant metal leaching, the resulting homogeneous species being highly active. These catalyst characteristics prevent any possible industrial application in the Guerbet reaction for obtaining 2EH from BuOH.
- (3) Also the catalytic activity of the heterogeneous copper chromite/BuONa system results appreciable but once again limited by the hydrolysis of the basic component. A certain improvement of the catalytic performances can be reached by adding either an ancillary base (MgO) or a dehydrating agent such as CaO. A remarkable positive effect on BuOH conversion may be obtained by increasing the reaction to 280 °C.

However, the obtained results are not yet of industrial application due to the limited productivity and the progressive hydrolysis of the homogeneous BuONa. Work is in progress in order to overcome these drawbacks.

References

- [1] D.F. Cadogan, C.J. Howick, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 19, fourth ed., Wiley/Interscience, New York, 1991, p. 258.
- [2] C.J. Chang (to Rhom and Haas co.), 1986, Eur. Pat. Appl. 190892; Chem. Abstr. 105, 1986, 192220c.
- [3] K.K. Sekisui Kaseihin Kogyo, K.K. Eslen Kako, Jpn. Pat. 58,122,935 (1983); Chem. Abstr. 99 (1983) 176979j.
- [4] S. Veibel, J.I. Nielsen, Tetrahedron 23 (1967) 1723.
- [5] R.E. Miller, G.E. Bennett, Ind. Eng. Chem. 53 (1961) 33.
- [6] P.L. Burk, R.L. Pruett, K.S. Campo, J. Mol. Catal. 33 (1985) 1.
- [7] P.L. Burk, R.L. Pruett, K.S. Campo, J. Mol. Catal. 33 (1985) 15.
- [8] J. Sabadie, G. Descotes, Bull. Chim. Soc. Fr. Part II (1983) 253.
- [9] G. Gregorio, G.F. Pregaglia, R. Ugo, J. Organometal. Chem. 37 (1972) 385.
- [10] C. Carlini, M. Di Girolamo, A. Macinai, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chem. 204-205 (2003) 721.
- [11] C. Carlini, M. Di Girolamo, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chem. 184 (2002) 273.
- [12] C. Carlini, M. Di Girolamo, A. Macinai, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A Chem. 200 (2003) 137.
- [13] A.I. Vogel, in: Textbook of Practical Organic Chemistry, fifth ed., Longman Sci. & Tech., 1989.
- [14] W. Ueda, T. Ohshida, T. Kubawara, Y. Morikawa, Catal. Lett. 12 (1992) 97.
- [15] L. Leoni, G. Braca, G. Sbrana, E. Giannetti, Anal. Chim. Acta 80 (1975) 176.
- [16] N. Sado, (to Fuji Electric Co.) Jpn. Pat. 74858 (2000); Chem. Abstr. 132 (2001) 216246.
- [17] R.G. Heidenreich, J.G.E. Krauter, J. Pietsch, K. Köhler, J. Mol. Catal. A: Chem. 182-183 (2002) 499.
- [18] K. Köhler, R.G. Heidenreich, J.G.E. Krauter, J. Pietsch, Chem. Eur. J. 8 (2002) 622.