Guerbet condensation of methanol with *n*-propanol to isobutyl alcohol over heterogeneous bifunctional catalysts based on Mg–Al mixed oxides partially substituted by different metal components

Carlo Carlini[a,*], Mario Marchionna[b], Marilena Noviello[a,c], Anna Maria Raspolli Galletti[a],
Glauco Sbrana[a], Francesco Basile[d], Angelo Vaccari[d]

[a] *Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy*
[b] *EniTecnologie S.p.A., Via Maritano 26, 20097 San Donato Milanese, MI, Italy*
[c] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*
[d] *Dipartimento di Chimica Industriale e dei Materiali, Alma Mater Studiorum, University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy*

Abstract

The synthesis of isobutyl alcohol (*i*BuOH) from methanol (MeOH) and *n*-propanol (PrOH) through the Guerbet condensation has been studied in batch experiments using bifunctional heterogeneous systems based on a dehydrogenating/hydrogenating metal (Pd, Rh, Ni or Cu) and a basic Mg–Al mixed oxide derived from hydrotalcite-type (HT) precursors. Only copper-based systems showed appreciable performances. In particular, the Cu/Mg/Al mixed oxides catalysts obtained by the co-precipitation method offered the best results in terms of activity and selectivity, thus allowing to reduce pollution problems connected with the up to now adopted copper chromite. These co-precipitated systems were also tested in some preliminary experiments carried out in gas–solid phase in a flow reactor, thus confirming promising application perspectives.
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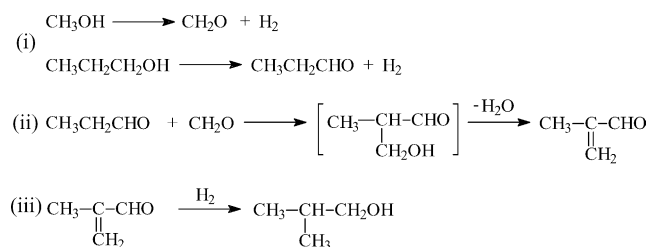
1. Introduction

Isobutyl alcohol (*i*BuOH) has gained an increasing interest in the last decade, owing to its potential employment as precursor for the preparation of either gasoline additives, such as methyl-*tert*-butyl-ether and isooctane, or plasticizers. Recently, we have proposed [1–4] the selective synthesis of *i*BuOH starting from methanol (MeOH) and *n*-propanol (PrOH) through the Guerbet reaction, a condensation between alcohols promoted by bifunctional catalysts based on a basic component and a metal species with dehydrogenating/hydrogenating properties. In particular, the above mentioned reaction is characterized by the following three steps:

(1) dehydrogenation of alcohols to the corresponding aldehydes, (2) aldol condensation of the resulting aldehydes and (3) hydrogenation of the unsaturated condensation products to give the higher alcohols [5,6], as reported in Scheme 1, where the reaction pathway is referred to the MeOH/PrOH condensation.

The relevant selectivity of the reaction to *i*BuOH is probably due to its steric hindrance and to the presence of only one hydrogen on the carbon atom in α-position to the methylol group [1].

In particular, when MeOH/PrOH mixtures were reacted in the presence of copper chromite/MeONa, an almost complete selectivity to *i*BuOH was observed [1]. The productivity was also found to increase by increasing the reaction temperature from 180 to 220 °C as well as the relative amount of MeONa with respect to the copper component. When N$_2$ was adopted

* Corresponding author. Tel.: +39 050 2219222; fax: +39 050 2219260.
  E-mail address: carlini@dcci.unipi.it (C. Carlini).

(i) $CH_3OH \longrightarrow CH_2O + H_2$

$CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CHO + H_2$

(ii) $CH_3CH_2CHO + CH_2O \longrightarrow \left[\underset{\underset{CH_2OH}{|}}{CH_3-CH-CHO} \right] \overset{-H_2O}{\longrightarrow} \underset{\underset{CH_2}{\|}}{CH_3-C-CHO}$

(iii) $\underset{\underset{CH_2}{\|}}{CH_3-C-CHO} \overset{H_2}{\longrightarrow} \underset{\underset{CH_3}{|}}{CH_3-CH-CH_2OH}$

Scheme 1.

in the place of H_2 as reaction atmosphere, better catalytic performances were obtained, thus indirectly confirming that the dehydrogenation of the alcohols to the corresponding aldehydes is the rate-limiting step of the reaction. Moreover, recycle tests allowed to conclude that copper chromite essentially works in heterogeneous phase, unlike that observed for Pd-, Rh- or Ru-based catalysts where the metal leaching was favoured by the presence of the methoxide anion [3,4].

However, the use of MeONa as homogeneous basic component represented for all the tested catalytic systems the main drawback for two reasons: (i) the progressive hydrolysis of the base to MeOH and inactive NaOH by the water co-produced in the condensation step [1,2,5,6] and (ii) corrosion problems as well as difficult separation of reaction products from the basic homogeneous catalytic component.

In this context, more recently, the use of completely heterogeneous two-component catalysts was proposed [7]. In particular, Mg–Al mixed oxides with a variable Mg/Al atomic ratio, obtained from the corresponding HT precursors by controlled calcination, were used as basic components in combination with pre-activated copper chromite. In all cases, an almost complete selectivity to ^{i}BuOH was found to occur. Moreover, the activity of these systems was not affected by the co-produced water, no evidence of inhibition during the course of the reaction being observed. Finally, the activity was found to be affected by the Mg/Al atomic ratio in the HT precursor, in correspondence to the variation of the relative amount of medium–strong and strong basic sites. In fact, in agreement with literature suggestions [8,9], the heterogeneous catalyst with the lowest Mg/Al atomic ratio and the highest basic strength showed [7] the maximum of productivity to ^{i}BuOH, thus opening interesting application perspectives. In this context, it appeared very appealing to investigate the catalytic activity of bifunctional heterogeneous catalysts, characterized by both dehydrogenating/hydrogenating and basic sites present in the same matrix, with the aim to simplify the catalytic system and exploit potential synergistic effects in the Guerbet condensation. Indeed, it is well known that the properties of hydrotalcite, a layered mineral having the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, may be easily tailored by partial substitution of cations and/or anions in its structure to afford a new class of materials named HT precursors compounds having the general formula $[(M_{1-x}^{2+}M_x^{3+}(OH)_2)^{x+}(A_{x/m}^{m-}) \cdot nH_2O]$, where M^{2+}

and M^{3+} are cations and A^{m-} is an interlayer anion [10–14]. When HT precursors are calcined at temperatures lower than ca. 650 °C, the resulting mixed oxides display (i) high surface area, (ii) basic properties and (iii) memory effect, since they may recover the original HT structure when contacted with water solutions containing various anions [12–14]. Therefore, in this paper, several bifunctional heterogeneous M/Mg/Al mixed oxides (M = Pd, Ni, Rh and Cu), containing both basic and dehydrogenating/hydrogenating sites, will be checked as catalysts in the Guerbet condensation of MeOH with PrOH for the synthesis of ^{i}BuOH in batch processes. Moreover, the most promising catalysts will be tested in gas–solid flow experiments which allow the facile separation of the catalyst from the reaction mixture and the continuous removal of the co-produced water. In this way, contrarily to what occurs in batch processes, the water accumulation in the reaction products is prevented, thus reducing any possible catalyst deactivation. Finally, these last experiments may help to have a preliminary insight on the life and stability of the catalytic system, although a subsequent deeper examination of the above parameters is required for the evaluation of potential industrial applications of this reaction.

2. Experimental

2.1. Materials

MeOH (Prolabo) 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 [15].

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

Copper acetate $(Cu(OAc)_2 \cdot 4H_2O$, Aldrich) and bis(dibenzylideneacetone)palladium(0) $(Pd(dba)_2$, Aldrich) were used as received.

Pd/C (10 wt.%, Aldrich) was activated prior to the use in a mechanically stirred Parr reactor in the presence of methanol at 180 °C for 5 h under 8 MPa of H_2.

M/Mg/Al (M = Pd, Rh, Ni, Cu) and Mg/Al HT precursors were prepared by co-precipitation of the corresponding nitrates with Na_2CO_3 maintaining the pH equal to 10.0 ± 0.1 by dropwise addition of a 1-M aqueous solution of NaOH. The precipitates were washed with water, dried overnight at 100 °C, calcined at 500 °C for 5 h and finally stored under argon [12,14,16–18]. The main characteristics of both Mg/Al (catalysts C1, C2) and M/Mg/Al (catalysts C6–C11) mixed oxides are reported in Table 1.

For the sake of comparison, Pd-based catalysts (C3–C5) were obtained also by impregnation of C2 with different amounts of $Pd(dba)_2$ in benzene solution (Table 1).

Analogously, a Cu-based bifunctional heterogeneous catalyst (C12) was also prepared by impregnation of C1 with a benzene solution of copper acetate (Table 1).

Table 1
Main characteristics of the heterogeneous catalysts based on Mg/Al and M/Mg/Al mixed oxides[a]

Catalyst	M/Mg/Al		Weight composition (%)			Surface area (m^2/g)
	M	Atomic ratio[a]	M_xO_y	MgO	Al_2O_3	
C1	–	71.0/29.0	0.0	65.9	34.1	232
C2	–	66.0/34.0	0.0	60.5	39.5	214
C3[b]	Pd	0.8/65.5/33.7	2.2	59.2	38.6	n.d.
C4[b]	Pd	0.4/65.7/33.9	1.1	59.8	39.1	n.d.
C5[b]	Pd	0.2/65.8/34.0	0.5	60.1	39.4	n.d.
C6	Pd	5.0/66.0/29.0	13.0	56.0	31.0	114
C7	Rh	1.0/71.0/28.0	7.0	62.0	31.0	80
C8	Ni	10.0/61.0/29.0	15.8	52.6	31.6	113
C9	Cu	2.2/68.8/29.0	4.0	62.6	33.4	139
C10	Cu	7.6/62.7/29.7	12.9	54.4	32.7	126
C11	Cu	11.1/60.1/28.8	18.5	50.7	30.8	140
C12[c]	Cu	7.6/62.7/29.7	12.9	54.4	32.7	n.d.

[a] Prepared by co-precipitation of the corresponding nitrates and subsequent calcination at 500 °C, if not otherwise specified.

[b] Prepared by impregnation of C2 with different amount of Pd(dba)$_2$ in benzene solution.

[c] Prepared by impregnation of C1 with Cu(OAc)$_2$·4H$_2$O in benzene solution.

All the catalytic systems prepared by the impregnation method were dried by solvent evaporation overnight under vacuum at 100 °C, calcined at 500 °C for 5 h and finally stored under argon.

2.2. Catalytic experiments for the condensation of MeOH with PrOH in a batch reactor

A 300-ml Parr reactor, equipped with a mechanical stirrer, a heating system, a temperature control device, 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 heterogeneous catalyst was introduced into the reactor which was closed and subsequently evacuated. MeOH was then introduced by suction through the liquid sampling valve and the reactor was pressurized with H$_2$ up to 8 MPa and heated at 180 °C for 5 h for the metal component pre-reduction. The reactor was evacuated, MeOH was removed under vacuum, and subsequently, the alcohols mixture was introduced by suction through the liquid sampling valve. Finally, the reactor was pressurized at 3 MPa with the proper gas and the reaction was carried out at the chosen temperature (200–220 °C). The reaction was followed by collecting at different times, through the sampling valve, portions of the reaction mixture quickly cooled to 0 °C. At the end of each experiment, the reactor was rapidly cooled at room temperature and degassed through a trap maintained at 30 °C, in order to condense any vapour present in the gas phase. Finally, the liquid reaction mixture was analysed by gas chromatography (GC) after the addition of a known amount of benzene as internal standard.

2.3. Catalytic experiments for the Guerbet condensation in a continue flow reactor

The experiments in a continuous flow reactor were carried out in an Autoclave Engineering Bench Top Reaction System (BTRS), equipped with a 15-cm length stainless steel cylin-

der whose inlet diameter is 0.6 cm. The adopted catalyst, a Cu/Mg/Al sample (C11) having a 600–850 μm particle size, was firstly calcined at 500 °C and then pre-reduced, using a 60-ml/min stream of H$_2$/Ar (10/90, v/v), with a constant heating rate of 1 °C/min starting from room temperature up to 300 °C. In the experiments, a catalytic bed of 2.7 g was employed. After the pre-reduction of the catalyst, the experiments were carried out by feeding a liquid MeOH/PrOH mixture characterized by a 6.25 molar ratio. The liquid reactants were introduced by means of a HPLC pump with a flow rate of 0.1 ml/min. Under the adopted reaction conditions (room pressure and temperature over 200 °C), the reactants were vaporized before reaching the reactor. Therefore, the contact time adopted was 20 g h mol^{-1}. After an established time, the outlet gaseous stream was condensed and the collected liquid reaction mixture was analyzed by GC.

2.4. Analytical procedures

The analysis of the reaction products was performed by GC using a Perkin-Elmer Sigma 3B chromatograph, equipped with a thermal conductivity detector, a CE Instruments DP 700 integrator and a 2-m length Poropak PS packed column (0.32 cm internal diameter) with a stationary phase based on ethylvinylbenzene/divinylbenzene resin. Helium was used as carrier gas with a 25-ml/min flow rate. The following temperature program was adopted for the oven: 80 °C for 5 min, then the temperature was increased by a 8 °C/min heating until 210 °C was reached, maintaining this value constant for further 15 min. For the quantitative determination of the reaction mixtures, the chromatographic response factor for each individual component was determined using mixtures of pure compounds of known composition, with benzene as internal standard.

In all the batch experiments, an almost total selectivity to ^{i}BuOH was observed. Indeed, only traces (<0.5 mol%) of methyl and propyl formate were detected by GC/MS analysis carried out employing a HP5973 Mass Selective

Detector and a HP6890 Series GC System, equipped with a HP5-MS crosslinked 5% phenylmethylsiloxane column ($30\,m \times 0.25\,mm \times 0.25\,\mu m$).

In the case of flow experiments, a wide range of by-products were detected by GC/MS and quantified by GC analysis.

2.5. Catalysts characterization

The adsorption and temperature programmed desorption (TPD) of CO_2, as probe-molecule for determining the basic properties of the M/Mg/Al and Mg/Al mixed oxides, was carried out on a Pulse Chemisorb 2705 Micromeritics instrument. Each sample (nearly 0.5 g) was pre-treated under He at $500\,°C$ for 2 h to eliminate water and gas impurities eventually present. After cooling the sample, the adsorption of CO_2 at $21\,°C$ was carried out until surface saturation was reached; the presence of physically adsorbed CO_2 was avoided by performing the adsorption under a He flow. The temperature was then increased linearly from room temperature up to $500\,°C$ and CO_2 evolution was monitored by mass spectrometry. The basic strength distribution of the sites was evaluated from the capability of the material to retain the probe molecule during desorption. The TPD profiles were analyzed by a deconvolution program (Galactic Peaksolve) in order to determine the signal number and position. The quality of the elaboration obtained by the Levenberg–Marquadt algorithm was evaluated on the basis of the correlation coefficient ($R^2 > 0.97$).

BET surface area values were obtained using a single point ThermoQuest Surface Area Analizer Qsurf S1.

3. Results and discussion

3.1. Guerbet condensation of MeOH with PrOH in batch processes

As mentioned in Section 1, completely heterogeneous systems based on the combination of copper chromite and a basic Mg/Al mixed oxides component, particularly when this was

characterized by a very low amount of Mg content (Mg/Al molar ratio <2, catalyst C2), were found to display [7] an activity similar to that observed with the homogeneous MeONa base [1]. The best performances obtained in the presence of C2 as basic component were attributed to the highest concentration of strong basic sites. Therefore, with the aim to check if other metal components would be active when combined with heterogeneous basic Mg/Al mixed oxides, the catalyst obtained as a mechanical mixture of Pd/C and C2 (Pd/C//C2 catalyst) was preliminarily checked in the Guerbet condensation of MeOH with PrOH (Table 2). Moreover, the absence in liquid phase of methoxide basic species would prevent any metal leaching from the catalytic system.

In all cases, a feed with a MeOH/PrOH molar ratio equal to 12.5 and usually $200\,°C$ as reaction temperature were used, as those optimized in previous papers for the Guerbet condensation [3,4,7]. When the reaction was performed under nitrogen atmosphere and Pd/C was pre-activated, either in MeOH at $180\,°C$ for 5 h (entry 1) or in the presence of MeONa (subsequently eliminated by washing with MeOH) (entry 2), no activity at all was observed. Analogous results were obtained when a N_2/H_2 mixed atmosphere was used (entry 3). Also when the Pd/C was not pre-activated (entries 4 and 5) and the reaction temperature was increased up to $220\,°C$ (entry 5), only a very low catalytic activity was observed. When Rh/C was used in the place of Pd/C under the same conditions as those adopted in entry 4, no appreciable activity was ascertained. Considering that under these last conditions, both Pd/C and Rh/C//MeONa systems displayed a rather high activity to give $^{i}BuOH$ [3,4], these results clearly indicate that the mechanical combination of the basic component C2 with these dehydrogenating/hydrogenating supported metal species is not able, differently from the copper chromite/C2 system, to operate as a real bifunctional catalyst. Moreover, these data represent an indirect confirmation of the determinant role played on the catalytic activity by the homogeneous Pd and Rh species released in the liquid phase when MeONa was used [3,4]. Therefore, catalytic systems, prepared by impregnation of C2 with different amounts of Pd(dba)₂ (C3–C5), were checked in the Guerbet reaction with the aim

Table 2
Guerbet condensation of MeOH with PrOH in batch processes to yield $^{i}BuOH$ in the presence of the Pd/C//C2 catalysts containing different relative amounts of basic and dehydrogenating/hydrogenating sites[a]

Entry	C2, MgO (mmol)	Pd (mmol)	P_{N_2} (PMa)	P_{H_2} (PMa)	$^{i}BuOH$ yield (mol%)[b]		
					1 h	6 h	12 h
1	60	0.85	3	–	0.0	0.0	0.0
2[c]	20	0.13	3	–	0.0	0.0	0.0
3	60	0.85	1	2	0.0	0.0	0.0
4[d]	60	0.13	3	–	0.0	1.0	5.0
5[d,e]	60	0.85	3	–	0.0	0.0	7.0

[a] Reaction conditions: MeOH, 1250 mmol; PrOH, 100 mmol; $T = 200\,°C$, if not otherwise specified; Pd/C was pre-activated in MeOH with 8 MPa of H_2 at $180\,°C$ for 5 h, if not otherwise specified.

[b] Calculated as (mol of $^{i}BuOH$/initial mol of PrOH) × 100.

[c] Pd/C was pre-reduced in the presence of MeONa which was subsequently removed by washing with MeOH.

[d] Pd/C was not submitted to pre-activation.

[e] At $220\,°C$.

Table 3

Guerbet condensation of MeOH with PrOH in batch processes to yield ^{i}BuOH in the presence of heterogeneous catalysts (C3–C5) obtained by impregnation of C2 with different relative amounts of Pd(dba)$_2$ [a]

Entry	Catalyst	Basic component, MgO (mmol)	Dehydrogenating/hydrogenating component, Pd (mmol)	^{i}BuOH yield (mol%)[b]		
				1 h	6 h	12 h
6	C3	20	0.25	0.5	1.4	3.0
7	C4	45	0.25	0.0	0.3	0.8
8	C5	60	0.25	0.0	1.6	1.6
9	C4	20	0.12	0.0	0.2	0.5
10[c]	C4	20	0.12	0.5	1.5	2.8
11	C3	20 + 20 C2	0.25	0.0	0.3	1.0
12	C3	20 + 160 MeONa	0.25	15.4	40.0	50.1

[a] Reaction conditions: MeOH, 1250 mmol; PrOH, 100 mmol; $T = 200\,^\circ$C; $P_{N_2} = 3$ MPa; catalysts C3–C5 were pre-activated in MeOH with 8 MPa of H$_2$ at 180 $^\circ$C for 5 h.

[b] Calculated as (mol of ^{i}BuOH/initial mol of PrOH) × 100.

[c] Catalyst C4 was submitted to a second calcination at 500 $^\circ$C for 5 h.

to increase the catalytic performances. In fact, owing to a higher dispersion of the metal sites, the closer vicinity of basic and dehydrogenating/hydrogenating sites would favour synergistic effects on the activity.

However, when the pre-activated catalyst C3, containing Pd/Mg/Al atomic ratios equal to 0.8/65.5/33.7, was used under nitrogen atmosphere again a very low activity (3% of ^{i}BuOH yield after 12 h) was observed (entry 6; Table 3).

No significant improvement of activity was obtained by progressively reducing the loading of the metal on C2 up to 0.2% (catalysts C4 and C5, entries 7 and 8, respectively; Table 3). This in contrast to that reported by Chen et al. [19] for the synthesis of methyl isobutyl ketone from acetone with analogous catalysts where the above loading value was reported to be the optimum. In fact, higher loading values are probably responsible of the formation of Pd aggregates on the catalyst surface, thus covering and deactivating the basic sites. When the amount of catalyst was halved as compared to entry 8, only traces of ^{i}BuOH were obtained (entry 9; Table 3). Moreover, when catalyst C4 was submitted to a second calcination at 500 $^\circ$C, a slight improvement of activity was observed but still very unsatisfactory (entry 10; Table 3). However, it must be underlined that the preparation of the catalyst by metal impregnation, although would guarantee to maintain unchanged the structure of the basic component C2, may cause the adsorption of the metal species mainly on the

catalyst surface. This occurrence could be responsible of basic sites inhibition due to their coverage. Therefore, entry 10 was repeated by adding to C3 an equivalent amount of C2 in terms of MgO (entry 11; Table 3). However, also in this case, modest performances were observed. The only way to activate the system was the addition of MeONa to C3 (entry 12; Table 3), which caused a sharp increase of activity as expected [4].

With the aim to detect if the lack of activity of the above catalytic systems was due to their preparation procedure (impregnation method), new catalysts were prepared by calcination at 500 $^\circ$C of the corresponding HT precursors obtained by co-precipitation of nitrates of Mg, Al and the metal chosen (Pd, Rh, Ni and Cu). In this way, the metal would be homogeneously dispersed on the surface and inside the structure of the basic matrix and the closer vicinity of basic and dehydrogenating/hydrogenating sites, would favour synergetic effects on activity. In this context, catalysts based on Pd, Rh and Ni (C6, C7 and C8, respectively) were firstly checked in the Guerbet condensation of MeOH with PrOH to give ^{i}BuOH (Table 4).

The obtained results indicate that also these catalytic systems (entries 13–15; Table 4) did not reveal superior performances, only Rh-based C7 catalyst showing a slight higher activity (12.6 mol% ^{i}BuOH yield after 12 h). These data also seem to suggest that the co-precipitation method has to be preferred in the preparation of these heterogeneous catalysts,

Table 4

Guerbet condensation in batch processes of MeOH with PrOH to give ^{i}BuOH using M/Mg/Al mixed oxides obtained from the corresponding HT precursors by co-precipitation and subsequent calcination (catalysts C3–C5)[a]

Entry	Catalyst	Basic component, MgO (mmol)	Dehydrogenating/hydrogenating component, metal (mmol)	^{i}BuOH yield (mol%)[b]		
				1 h	6 h	12 h
13	C6	25	Pd (1.9)	0.0	0.8	4.0
14	C7	18	Rh (0.25)	0.0	1.1	12.6
15	C8	25	Ni (4.1)	0.0	0.0	0.0

[a] Reaction conditions: MeOH, 1250 mmol; PrOH, 100 mmol; $P_{N_2} = 3$ MPa; $T = 200\,^\circ$C.

[b] Calculated as (mol of ^{i}BuOH/initial mol of PrOH) × 100.

Table 5

Guerbet condensation in batch processes of MeOH with PrOH to give ^{i}BuOH using Cu/Mg/Al mixed oxides obtained from the corresponding HT precursors by co-precipitation and subsequent calcination at 500 °C (catalysts C9–C11)[a]

Entry	Catalyst	Basic component, MgO (mmol)	Dehydrogenating/hydrogenating component, Cu (mmol)	T (°C)	^{i}BuOH yield (mol%)[b]		
					1 h	6 h	12 h
16	C9	88	3.6	200	7.3	18.5	27.5
17	C9	88	3.6	210	12.1	21.5	40.6
18	C9	41	1.7	200	4.2	11.1	18.5
19	C10	41	5.0	200	1.4	14.8	26.0
20	C10	21	2.5	200	2.6	10.9	14.9
21	C10	56	6.7	200	1.9	10.9	27.7
22	C11	40	7.4	200	4.3	13.6	22.0
23	C11	60	11.1	200	3.8	21.9	35.2
24	C11	60	11.1	210	7.0	27.8	37.5
25[c]	C12	21	2.5	200	1.9	6.6	10.1

[a] Reaction conditions: MeOH, 1250 mmol; PrOH, 100 mmol; $P_{N_2} = 3$ MPa; C9–C11 were pre-activated in MeOH under 8 MPa of H_2 at 180 °C for 5 h.

[b] Calculated as (mol of ^{i}BuOH/initial mol of PrOH) × 100.

[c] Catalyst C12 was prepared by impregnation of C1 with $Cu(OAc)_2 \cdot 4H_2O$ in benzene solution and displays the same composition as catalyst C10.

although the type of metal cation, which modifies the HT precursor, appears very crucial.

In this context, Cu/Mg/Al mixed oxides with variable compositions and obtained by the co-precipitation method were checked in the Guerbet condensation of MeOH with PrOH to give ^{i}BuOH. In all cases, the catalysts were pre-activated under H_2 atmosphere at 180 °C according to previous experiments [1,2,7].

When catalyst C9 containing the lowest amount of copper was employed (entry 16; Table 5) by using reaction conditions and similar amounts of basic and metal components as for the copper chromite/C1 catalyst in a previous paper [7], a comparable activity was observed, the yield to ^{i}BuOH progressively increasing from 7.3 to 27.5 mol% after 1 and 12 h of reaction, clearly showing that the copper-based bifunctional catalysts obtained directly by co-precipitation could be efficiently employed in the Guerbet condensation between MeOH and PrOH.

When the reaction temperature was increased to 210 °C (entry 17; Table 5), still maintaining constant the other reaction parameters, a further increase of activity was achieved (40.6% yield of ^{i}BuOH after 12 h). When entry 16 was repeated just halving the amount of catalyst with respect to the reactants (entry 18; Table 5), a lower PrOH conversion to ^{i}BuOH was obtained. Considering that both components (metal and basic sites) were contemporary halved, it is not possible to address the activity reduction to one individual species of the two types. In order to clarify this point, cat-

alyst C10, having a higher content of copper with respect to C9 was used, and entry 18 was repeated employing the same amount of the basic component (entry 19; Table 5). In this experiment, a remarkable improvement of activity was observed, the yield to ^{i}BuOH being about 40% higher after 12 h. Considering that in this case the amount of copper was almost three-fold as compared to that of entry 18, this result seems to indicate that the metal amount may play an important role. When the amount of C10 was halved with respect to entry 19 (entry 20; Table 5) also the ^{i}BuOH yield halved, the catalyst productivity remaining substantially the same. On the contrary, when the amount of C10 was increased with respect to entry 19 (entry 21; Table 5), no significant improvement of ^{i}BuOH yield was found. When catalyst C11, containing the highest amount of copper, was employed by using an amount of the basic component equal to 40 mmol (entry 22; Table 5), analogous to that adopted in entries 18 and 19, intermediate catalytic performances were substantially found with respect to those obtained in the cited experiments. However, when the amount of catalyst was increased to reach a value of basic component similar to that employed in entry 21 (entry 23; Table 5), a significant improvement of ^{i}BuOH yield was observed. Again the enhancement of reaction temperature to 210 °C (entry 24; Table 5) caused a further increase of activity (37.5 mol% of ^{i}BuOH yield). When catalyst C12, obtained by impregnation of C1 and having the same composition as catalyst C10, was used under the same conditions as in entry 20 (entry 25; Table 5), a signifi-

Table 6

Distribution of the basic sites evaluated by CO_2 adsorption in the TPD experiments

Basic catalyst (Cu/Mg/Al at. ratio %)	Overall amount of desorbed CO_2 (μmol/g)	Weak basic sites (μmol/g)	Medium basic sites (μmol/g)	Medium–strong basic sites (μmol/g)	Strong basic sites (μmol/g)
C1 (0/71/29)[a]	249	17	59	135	38
C2 (0/66/34)[a]	284	39	10	117	118
C10 (7.6/62.7/29.7)	110	8	54	41	7
C11 (11.1/60.1/28.8)	112	7	66	34	5

[a] Data reported in Ref. [7].

Table 7
^{i}BuOH yield obtained in the Guerbet condensation of MeOH with PrOH with a continuous reactor in the presence of the C11 catalyst[a]

Entry	Temperature (°C)	PrOH Conversion (mol%)	^{i}BuOH yield (mol%)[b]	Selectivity (%)
26	250	22.0	19.7	86.4
27	280	100.0	79.3	79.3

[a] Reaction conditions: C11, 2.7 g; MeOH/PrOH, 6.25 mol/mol; contact time, 20 g h mol^{-1}.
[b] Calculated with respect to PrOH.

cant reduction of activity was achieved, 10.1 mol% of ^{i}BuOH yield after 12 h being obtained versus 14.9 mol%. This result confirms that the co-precipitation method is by far the best one for preparing the M/Mg/Al mixed oxides bifunctional catalysts.

Finally, it must be underlined that in all the experiments, the selectivity to ^{i}BuOH was almost complete, no side-products deriving from PrOH self-condensation or by Cannizzaro reaction being formed.

With the aim to have a deeper insight on the relations between activity and concentration as well as strength of the basic sites in the copper-based co-precipitated systems, the catalysts C10 and C11, with lower Mg/Al atomic ratios, were characterized as previously reported for catalysts C1 and C2 [7] by TPD analysis. The data are reported in Table 6 and compared with those achieved in Ref. [7] for catalysts C1 and C2.

The TPD characterization of the catalysts clearly shows that the partial substitution of Mg cations with copper remarkably decreases not only the total amount of basic sites but also the percentage of medium–strong and strong basic sites. However, catalysts C10 and C11 have the same concentration of overall basic sites and the slightly higher concentration of medium–strong and strong basic sites in C10 may be compensated by the lower content of copper dehydrogenating/hydrogenating sites, the performances of the two catalysts being quite similar.

In conclusion, the systems obtained by the co-precipitation method, which display performances comparable with those obtained by blending copper chromite with C1, appear very promising. In fact, C9–C11 catalysts are also preferred because they allow to eliminate chromium, a non-environmental-friendly metal, and at the same time, they are more simple consisting of only one component.

In this context, this Cu-based catalyst (C11) was checked in preliminary experiments where the Guerbet condensation of MeOH with PrOH was carried out in flow processes.

3.2. Guerbet condensation of MeOH with PrOH in flow processes

The catalytic experiments were carried out in gas–solid phase with a contact time equal to 20 g h mol^{-1}, a value very similar to that previously reported for analogous processes [20].

The first experiments were performed at 200 °C by using a molar ratio MeOH/PrOH equal to 6.25 at room pressure

and by analysing the reaction products every 10 min. Under these conditions, as shown by GC/MS analysis on the product obtained after 1 h of reaction, ^{i}BuOH was formed only in traces, unreacted reagents being substantially recovered. On increasing the reaction temperature from 200 to 250 °C (entry 26) and then to 280 °C (entry 27), a progressive improvement of the yield to ^{i}BuOH was observed (Table 7).

In both cases, after 1 h of reaction, a steady state was reached, the yield to ^{i}BuOH being about 20 and 80% for reaction temperatures of 250 and 280 °C, respectively. The selectivity, although not complete, was always around 80% (Table 7). Several by-products were identified such as propanal, 2-methyl-propanal, 2-methyl-pentanal, methyl 2-methyl-propanoate and some ketones, such as butan-2-one, 3-methyl-butan-2-one and pentan-3-one. A tentative to explain how some of the above by-products may be formed is reported in Scheme 2.

These results, to the best of our knowledge, have shown values of selectivity and yield to ^{i}BuOH much higher than those previously reported in similar experiments where a reaction temperature of 300 °C was adopted [20,21]. Indeed, the catalytic systems used in these last experiments exclusively consisted of heterogeneous basic components without any hydrogenating/dehydrogenating metal species, which, as already shown, plays a fundamental role in the Guerbet reaction [5].

It must be underlined that the results obtained in flow reactor are quite promising although several aspects have to be further investigated, such as the influence of the contact time,
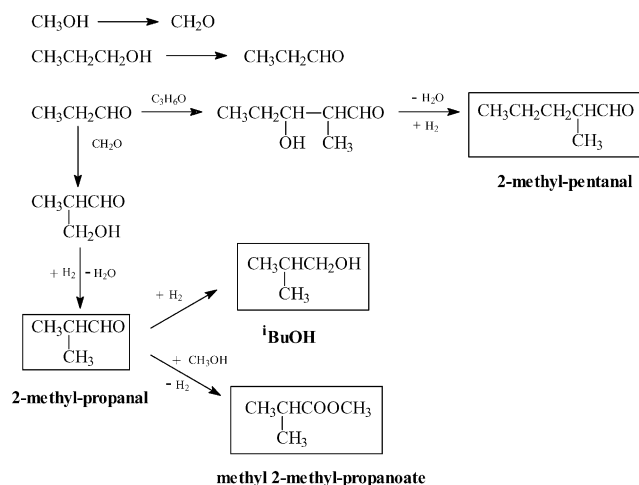
Scheme 2.

the effect of the nature of different catalytic systems and the adoption of a liquid feed.

4. Conclusions

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

1. When the Guerbet condensation of MeOH with PrOH was performed in the presence of completely heterogeneous catalytic systems, based on mechanical mixtures of basic Mg/Al mixed oxides and different metals (such as Pd, Rh and Ni supported on carbon), no activity was substantially observed, differently from what was previously found when the same basic components were employed in combination with copper chromite.
2. No significant improvement of the catalytic performances was ascertained when these mechanical combinations were replaced by bifunctional heterogeneous systems obtained from the corresponding metal species and basic components by impregnation or co-precipitation.
3. On the contrary, when bifunctional systems based on Cu/Mg/Al mixed oxides were obtained by both impregnation or co-precipitation methods, appreciable activity and selectivity were observed, particularly when co-precipitated systems were adopted. These results allowed to overcome the use of copper chromite, thus performing more environmental friendly catalytic processes.
4. These promising results were also confirmed in preliminary experiments carried out in a continuous flow reactor adopting a gas–solid phase, in order to open new application perspectives for this type of reaction.

Acknowledgments

References

[1] C. Carlini, M. Di Girolamo, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chem. 184 (2002) 273.
[2] 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.
[3] 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.
[4] C. Carlini, A. Macinai, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chem. 206 (2003) 409.
[5] S. Veibel, J.I. Nielsen, Tetrahedron 23 (1967) 1723.
[6] R.E. Miller, G.E. Bennett, Ind. Eng. Chem. 53 (1961) 33.
[7] C. Carlini, C. Flego, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, F. Basile, A. Vaccari, J. Mol. Catal. A: Chem. 220 (2004) 215.
[8] A. Corma, V. Fornés, R.M. Martin-Aranda, F. Rey, J. Catal. 134 (1992) 58.
[9] D. Tichit, M.M. Lhouty, A. Guida, B.H. Chiche, F. Figueras, A. Auroux, D. Bartalini, E. Garrone, J. Catal. 151 (1995) 50.
[10] S. Miyata, T. Kumura, Chem. Lett. (1973) 843.
[11] S. Miyata, Clays Clay Miner. 23 (1975) 369.
[12] F. Cavani, F. Trifirò, A. Vaccari, Catal. Today 11 (1991) 173.
[13] F. Trifirò, A. Vaccari, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, vol. 7, Pergamon, Oxford, 1996, p. 251.
[14] A. Vaccari, Catal. Today 41 (1998) 53.
[15] A.I. Vogel, Textbook of Practical Organic Chemistry, fifth ed., Longman, London, 1989.
[16] F. Basile, G. Fornasari, E. Poluzzi, A. Vaccari, Appl. Clay Sci. 13 (1998) 329.
[17] B. Montanari, A. Vaccari, M. Gazzano, P. Käβner, H. Papp, J. Pasel, R. Dziembaj, W. Makowski, T. Lojewski, Appl. Catal. B: Environ. 13 (1997) 205.
[18] F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifirò, A. Vaccari, Chem. Commun. (1996) 2435.
[19] Y.Z. Chen, C.M. Hwang, C.W. Liaw, Appl. Catal. A: Gen. 169 (1998) 207.
[20] J.I. Di Cosimo, C.R. Apesteguìa, M.J.L. Ginés, E. Iglesia, J. Catal. 190 (2000) 261.
[21] W. Ueda, T. Kuwabara, T. Ohshida, Y. Morikawa, J. Chem. Soc. Chem. Commun. (1990) 1558.