



Selective synthesis of isobutanol by means of the Guerbet reaction Part 3: Methanol/*n*-propanol condensation by using bifunctional catalytic systems based on nickel, rhodium and ruthenium species with basic components

Carlo Carlini^{a,*}, Alessandro Macinai^a, Mario Marchionna^b, Marilena Noviello^{b,c},
Anna Maria Raspolli Galletti^a, Glauco Sbrana^a

^a Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

^b Snamprogetti S.p.A., Via Maritano 26, San Donato Milanese (MI), Italy

^c Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy

Abstract

The synthesis of isobutanol (*i*BuOH) from methanol/*n*-propanol (MeOH/PrOH) mixtures has been studied by the Guerbet reaction in the presence of either supported or homogeneous nickel-based/sodium methoxide (MeONa) catalytic systems. The catalysts performances were studied as a function of reaction parameters, such as pre-activation or not of the nickel component, temperature, MeONa/Ni molar ratio, gaseous atmosphere (H₂ or N₂) and the relative amount of the metal in the reacting alcohols mixture. In particular, PrOH conversions to *i*BuOH up to 75% were obtained when Ni/kieselguhr//MeONa system was employed. This system appeared more active than Ni/alumina//MeONa. Also homogeneous complexes of nickel such as nickel acetate tetrahydrate and nickel dichloro bis triisopropylphosphine, when combined with MeONa, displayed significant catalytic activity with turnover numbers (TN) up to about 66 mol of *i*BuOH/mol of Ni × *h*. In all cases the selectivity of the process to *i*BuOH was substantially complete. Also supported ruthenium and rhodium-based/MeONa catalytic systems were investigated. The results obtained indicated that all the investigated catalysts, when combined with MeONa, resulted active in the synthesis of *i*BuOH. The catalytic performances were improved when the metal component was employed without any pre-activation step, very low amount of metal component being sufficient to assure high productivity (turnover values up to about 150 mol of *i*BuOH/mol of Ru × *h*).

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1. Introduction

The selective synthesis of isobutanol (*i*BuOH) has recently gained an increasing interest because this alcohol is a potential precursor of gasoline additives

in the sense that it may be easily transformed into isobutene, and hence either into methyl butyl ether (MTBE) or into isooctane. *i*BuOH may be directly synthesized from syngas through the higher alcohols synthesis (HAS) process carried out at high temperature and pressure over heterogeneous catalysts. However, this process is characterized by rather low selectivity and productivity [1]. An alternative route would be represented by a two-step process [2,3] where in the

* Corresponding author. Tel.: +39-050-918-222;

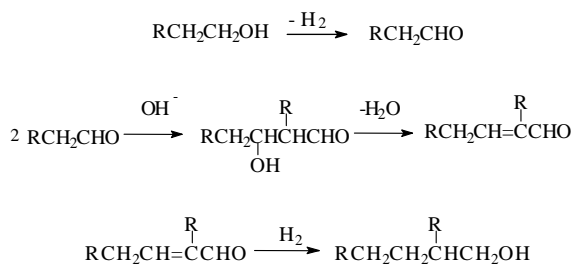
fax: +39-050-918-260.

E-mail address: carlini@dccl.unipi.it (C. Carlini).

first stage methanol and higher alcohols are obtained from syngas at low temperature by adopting methanol modified catalysts and in the second step they are converted to an isobutanol-rich product by using a high temperature methanol catalyst. However, this last step shows several drawbacks, particularly in terms of selectivity to isobutanol and retro-conversion of methanol to syngas. In this context, taking into account that from the first step of the above mentioned process a methanol (MeOH)/ethanol (EtOH)/*n*-propanol (PrOH) mixture with a large excess of methanol was generally obtained [2], it appeared attractive to transform this mixture in an *i*BuOH rich product through the Guerbet reaction, a condensation reaction between alcohols, promoted by a bifunctional catalytic system based on a basic component and a metal species with dehydrogenating/hydrogenating properties. In particular, it is well established that the Guerbet reaction is characterized by three main steps such as: (1) dehydrogenation of alcohols to give the corresponding aldehydes, (2) the aldol condensation of the resulting aldehydes and (3) the hydrogenation of the unsaturated condensation products to give the higher Guerbet alcohols [4,5] (Scheme 1).

It is also known [6,7] that at high temperatures (>160 °C) the Guerbet condensation between MeOH and primary alcohols having in α -position to the methylol function either a methylene or a methyl group, gives rise to a 2-methyl-substituted higher alcohol. Finally, it has to be underlined that *i*BuOH does not afford subsequent condensation products, likely due to its bulkiness and to the presence of only one hydrogen on the carbon atom in the α -position to the methylol group.

Recently, the Guerbet reaction of MeOH with either PrOH or EtOH as well as with EtOH/PrOH mixtures has been investigated by us adopting



Scheme 1.

copper-based/sodium methoxide (MeONa) catalytic systems [8,9]. In particular, when MeOH/PrOH mixtures were reacted in the presence of copper chromite/MeONa an almost complete selectivity to *i*BuOH was observed, the yield increasing with a temperature enhancement from 180 to 220 °C. In all cases the activity of the catalysts based on copper chromite resulted higher than those obtained from Cu-Raney. The yield was found also to improve with increasing the relative amount of MeONa with respect to the copper component. Moreover, the reactivity of PrOH was higher than that of EtOH. When the reaction was carried out under nitrogen atmosphere better catalytic performances were obtained than under hydrogen atmosphere, thus indirectly confirming that the dehydrogenation of the alcohols to the corresponding aldehydes is the rate limiting step of the reaction, at least under these adopted reaction conditions. In addition, recycle experiments of both the solid copper component and the liquid reaction mixture allowed to conclude that copper chromite essentially works in heterogeneous phase. When MeOH/EtOH/PrOH mixtures were employed in the presence of the copper chromite/MeONa catalytic system [9], no cross condensation between EtOH and PrOH occurred, due to the high C1/C2–C3 alcohols molar ratio. Indeed, MeOH reacted with EtOH to give rise to PrOH which in turn afforded *i*BuOH, by reacting with MeOH. As a consequence, the application of the Guerbet reaction to alcohols mixtures, as those obtained from either the HAS process or the first stage of the above mentioned two-step process, appeared rather promising from an industrial point of view.

With the aim to improve the catalytic performances, in terms of both activity and selectivity to *i*BuOH, as well as to clarify mechanistic aspects of the Guerbet reaction, the use of transition metal catalytic components appeared very appealing. In this context, a brief description of what known in the literature on this topic appeared therefore convenient.

Miller showed that Pd/C and Ni-Raney, characterized by dehydrogenating/hydrogenating properties, have a positive effect on the Guerbet reaction [5]. Sabadie investigated the condensation of MeOH with undecan-1-ol concluding that Pd/C and Ni-Raney, the former better than the latter, displayed higher activity as compared with Ru/C, and PdCl₂ [10]. Burk studied the condensation of MeOH with C3–C5 secondary

alcohols in the presence of Rh/C and of a basic component, thus ascertaining that the presence of the metal favored the dehydrogenation of the alcohols to the corresponding aldehydes and allowed to perform the Guerbet reaction at lower temperatures [11]. Finally, a wide literature based on industrial patents is also available. In particular, several heterogeneous metal components have been proposed such as ferric nitrate [12], ferric sulfate, zinc chloride and acetate [13,14], and more complex systems based on Ni(0) [15] and insoluble lead salts [16]. However, the most part of these patents are related to the condensation of higher alcohols, in particular decan-1-ol, for applications in the field of synthetic detergents. Very recently, both heterogeneous and homogeneous palladium-based/MeONa catalysts were employed by us for the selective synthesis at 200 °C of *i*BuOH from MeOH and PrOH [17]. In particular, the Pd/C//MeONa system displayed an activity higher than that found with Cu-based/MeONa catalysts. However, differently from these last catalysts, they showed a significant metal leaching. Recycle experiments allowed to evidence that both homogeneous or colloidal and heterogeneous palladium species contribute to the overall activity. When homogeneous palladium complexes, such as tetrakis(triphenylphosphine)palladium(0), [1,2-bis-(diphenylphosphino)ethane]dichloro palladium(II), bis(dibenzylideneacetone)palladium(0), were used in combination with MeONa, similar results were obtained, thus suggesting that an equilibrium exists between heterogeneous and homogeneous palladium species during the catalytic reaction.

From literature examination it may be concluded that substantially no data exist about the use of Ni, Rh and Ru derivatives in combination with basic components for the synthesis, through the Guerbet condensation, of *i*BuOH from MeOH and C2–C3 primary alcohols and therefore this topic will be the subject of the present work.

2. Experimental

2.1. Materials

Methanol (Prolabo), ethanol (Carlo Erba) and *n*-propanol (Carlo Erba) were dried by distillation under dry argon after refluxing for 6 h on magne-

sium methoxide, according to the Lund and Bjerrum method [18].

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

Magnesium oxide (MgO) (Riedel–de Haen) has been treated according to the literature [7]. In particular, it was suspended in water and the mixture refluxed for 6 h, then filtered and dried at 110 °C. The obtained solid was then calcined at 600 °C and stored under dry argon.

Nickel supported on kieselguhr (Ni/k) is a commercial catalyst (G 49 from Girdler) containing 5 wt.% of metal.

Nickel supported on alumina (Ni/Al₂O₃) is a commercial catalyst (3288 from Engelhard) containing 60 wt.% of metal.

Ruthenium supported on alumina (Ru/Al₂O₃) is a commercial catalyst (ESCAT 44 from Engelhard) containing 5 wt.% of metal.

Ruthenium on charcoal (Ru5/C) is a commercial catalyst (Aldrich) containing 5 wt.% of metal.

Rhodium on alumina (Rh/Al₂O₃) is a commercial catalyst (Engelhard) containing 3 wt.% of metal.

Rhodium on charcoal (Rh/C) is a commercial catalyst (Aldrich) containing 5 wt.% of metal.

Nickel acetate tetrahydrate (Ni(OAc)₂, Aldrich) was used as received.

Nickel dichloro bis triisopropylphosphine [NiCl₂(P^{*i*}Pr₃)₂] was prepared according to the literature [19] and stored under dry argon.

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

A 300 ml Parr reactor, equipped with a mechanical stirrer, a heating system and a control device assisted by a thermocouple inserted into the reactor, a sampling valve for liquids, an inlet valve for gas introduction and an outlet sampling valve for liquid products, was used in the catalytic batch experiments. When the heterogeneous catalyst was pre-activated, it was introduced in the reactor, then this was evacuated and methanol was introduced through the sampling valve. The reactor was subsequently pressurized with H₂ up to 80 atm and heated at 180 °C for 4 h. After the activation step, the reactor was cooled at room temperature and degassed. The reactor was evacuated and the methanol removed under vacuum, then the proper amount of the basic

component, dissolved in the proper alcohols mixture, was introduced through the gas sampling valve. The reactor was subsequently pressurized with either H₂ or N₂. When the heterogeneous or homogeneous catalyst were employed without any pre-activation, they were introduced in the reactor which was closed and evacuated. Subsequently, the basic component, dissolved in the alcohols mixture, was introduced through the gas sampling valve. Finally, the reactor was pressurized with N₂. In both cases the reaction was followed by collecting at different times portions of the reaction mixture, quickly cooled at 0 °C, through the sampling valve. At the end of each experiment, the reactor was rapidly cooled at room temperature, slowly degassed through a trap maintained at –30 °C, in order to condense the liquid products eventually present in the gas phase, and finally the liquid reaction mixture was analyzed by GC chromatography after the addition of a known amount of benzene as internal standard.

2.3. Analytical procedures

The analysis of the reaction products was performed by GC on a Perkin-Elmer Sigma 3B chromatograph equipped with a thermal conductivity detector, a CE Instruments DP 700 integrator and a 2 m Poropak PS packed column with a stationary phase based on ethylvinylbenzene/divinylbenzene resin. Helium was used as carrying gas with a 25 ml/min flowing rate. The following temperature program of the oven was adopted: 80 °C for 5 min, then the temperature was increased by a 8 °C/min heating until 210 °C was reached; this value was maintained constant for further 15 min. For the quantitative determination of the reaction mixtures, through the areas of the 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. In all the experiments a substantially complete 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% phenyl methyl siloxane column (30 m × 0.25 mm × 0.25 μm).

3. Results and discussion

3.1. Guerbet condensation of methanol with *n*-propanol to give isobutanol in the presence of nickel catalysts in combination with MeONa as basic component

Taking into account that the MeOH/PrOH mixture was previously found to be more reactive as compared with the MeOH/EtOH mixture in the Guerbet reaction [9], the experiments were carried out on the former mixture by using nickel catalysts and adopting reaction temperatures in the 180–200 °C range, which gave the best performances for the copper-based/sodium methoxide (MeONa) catalytic systems [8,9]. A MeOH/PrOH molar ratio equal to 12.5 was chosen, as previously adopted [8,9], to approach that usually present after the first stage of the HAS process. Moreover, a large excess of MeOH is required for preventing self-condensation by PrOH. Considering that no data were available on nickel-based catalysts about the effect of pre-activation with H₂ and the influence of this gas during the Guerbet reaction, preliminary experiments were carried out under H₂ (30 atm) and by using a pre-activated commercial 5 wt.% supported nickel on kieselguhr (Ni/k) (entries 1–3, Table 1). In these experiments was also studied the effect of different basic components in combination with Ni/k. When the heterogeneous basic MgO was used (entry 1) an extremely low activity was obtained, even adopting a rather high temperature (200 °C), the conversion of PrOH to *i*BuOH being only 0.8 mol% after 6 h.

An analogous experiment (entry 2), performed by replacing MgO with a double amount of soluble KOH, the other reaction conditions being still retained, did not appreciably improve the catalyst activity, the conversion to *i*BuOH being 1.3 mol%. However, when MeONa was used with the same amount as that adopted in entry 2 (entry 3), a remarkable increase of activity was obtained (conversion to *i*BuOH = 20 mol%). Taking into account that MeONa without any metal with dehydrogenating/hydrogenating properties is completely inactive under these conditions [8] and that the reaction does not proceed in the presence of Ni/k alone, the activity of the bifunctional catalyst has to be addressed to the synergism of both catalytic components. This is in agreement with that

Table 1

Synthesis of isobutanol (*i*BuOH) through the condensation of methanol (MeOH) with *n*-propanol (PrOH) by nickel-based supported catalysts and different basic components (B)^a

Entry	Ni-catalyst ^b		Basic component		B/Ni	Time (h)	<i>T</i> (°C)	<i>P</i> _{H₂} (atm)	<i>P</i> _{N₂} (atm)	<i>i</i> BuOH	
	Type	mmol	Type	mmol						Yield ^c (%)	TN ^d (h ⁻¹)
1 ^e	Ni/k	2.56	MgO	80	31	6	200	30	–	0.8	0.05
2 ^e	Ni/k	2.56	KOH	160	63	6	200	30	–	1.3	0.08
3 ^e	Ni/k	2.56	MeONa	160	63	6	180	30	–	20.0	1.30
4 ^e	Ni/k	0.97	MeONa	160	165	12	200	–	30	55.3	9.50
5 ^e	Ni/k	0.20	MeONa	160	800	6	200	–	30	49.5	41.2
6 ^f	Ni/k	0.20	MeONa	160	800	6	200	–	30	48.0	40.0
7 ^e	Ni/Al ₂ O ₃	0.45	MeONa	160	355	12	200	–	30	48.8	18.1
8 ^e	Ni/Al ₂ O ₃	0.20	MeONa	160	800	12	200	–	30	25.5	21.1
9 ^f	Ni/Al ₂ O ₃	0.20	MeONa	160	800	6	200	–	30	41.0	34.2
10 ^f	Ni(OAc) ₂	0.125	MeONa	160	1280	6	200	–	30	31.3	41.7
11 ^f	NiCl ₂ (P ^{<i>i</i>} Pr ₃) ₂	0.098	MeONa	160	1633	6	200	–	30	38.6	65.6

^a Reaction conditions—MeOH: 1250 mmol; MeOH/PrOH = 12.5 mol/mol.

^b Ni/k represents a commercial catalyst (G49 from Girdler) containing 5 wt.% of nickel on kieselguhr, whereas Ni/Al₂O₃ represents a commercial catalyst (3288 from Engelhard) containing 60 wt.% of nickel on alumina.

^c Calculated with respect to PrOH.

^d Turnover number calculated after 6 h of reaction and expressed as: mol *i*BuOH/(mol Ni × *h*).

^e Pre-activated nickel catalysts were used (see Section 2).

^f No pre-activation of the metal catalyst was performed.

depicted in Scheme 1 and previously ascertained in the case of rhodium-based catalysts for the Guerbet self-condensation of *n*-butanol [11]. If we compare the turnover number (TN) of this reaction [1.30 mol *i*BuOH/(mol of Ni × *h*)] with those previously obtained under the same conditions in the presence of copper-based/MeONa catalysts [8], we may conclude that the Ni/k//MeONa system is more active than Cu-Raney/MeONa (TN = 0.3 h⁻¹) and less active than copper chromite/MeONa (TN = 3.5 h⁻¹). The above data confirmed the key role of MeONa and the parallelism with the previous results obtained with copper-based/MeONa catalysts [8]. Taking into account that for these latter systems the catalytic activity was significantly enhanced not only by increasing the reaction temperature from 180 to 200 °C and by reducing the relative amount of the metal but mainly by replacing H₂ with N₂ [8], these reaction conditions were adopted in entry 4 (Table 1).

Indeed, also for the pre-activated Ni/k//MeONa system an analogous behavior was found: a significant improvement of the conversion to *i*BuOH after 6 h was obtained, a value of 55.3 mol% being reached with a TN equal to 9.5 h⁻¹. This result confirmed that the presence of H₂ negatively affects also nickel-based

catalysts, again supporting that the alcohols dehydrogenation step plays a key role in the overall Guerbet reaction mechanism. A further reduction of the relative amount of Ni/k, the other reaction parameters being retained (entry 5, Table 1), allowed to verify that an even higher enhancement of TN was reached after 6 h (41.2 h⁻¹). When entry 5 was repeated without any pre-activation with H₂ of the Ni/k component (entry 6, Table 1), differently from what previously observed for the Pd/C//MeONa system [17], no appreciable improvement of activity was observed, TN values being substantially the same (40 h⁻¹). These results indicate that the pre-activation of the Ni/k component plays a minor role in the Guerbet reaction for this particular system. A more detailed analysis of these two experiments as a function of reaction time (Fig. 1) confirmed the above statement, the time evolution of the Ni/k//MeONa catalytic activity being very similar in the two cases, although a shorter induction period would be present in the reaction catalyzed by the pre-activated system.

When a 60 wt.% of nickel supported on alumina (Ni/Al₂O₃) pre-activated catalyst was used under N₂ in combination with MeONa by employing 0.45 mmol of nickel (entry 7, Table 1), the other reaction

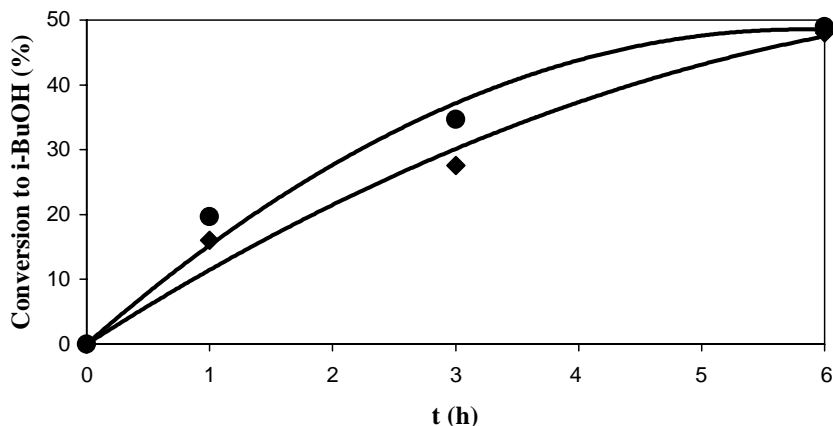


Fig. 1. Time evolution of the PrOH conversion to *i*BuOH in the MeOH/PrOH Guerbet reaction catalyzed by the Ni/k//MeONa system in the presence (●) (entry 5), or in the absence (◆) (entry 6), of pre-activation by H₂ of the Ni/k component.

parameters being the same as those in entry 5, a conversion of 48.8 mol% to *i*BuOH was reached with a TN equal to 18.1 h⁻¹. A further reduction of the amount of nickel to 0.20 mmol (entry 8, Table 1), under the same conditions as in entry 7, caused a decrease of yield to *i*BuOH (25.5 mol%) but an improvement of TN (21.1 h⁻¹). The above data clearly indicate that under the same conditions the pre-activated Ni/Al₂O₃//MeONa catalyst is less active than the corresponding Ni/k//MeONa system (compare entries 8 and 5). Moreover, the pre-activated Ni/Al₂O₃//MeONa system has substantially the same activity as that displayed by the pre-activated copper chromite/MeONa system, but adopting for this last an

even lower amount of metal catalyst [8]. When entry 8 was repeated by using the Ni/Al₂O₃//MeONa catalytic system without any pre-activation of the metal component (entry 9, Table 1), differently from what observed for the Ni/k//MeONa system, a remarkable improvement of activity was observed, a TN value of 34.2 h⁻¹ being reached (compare entries 8 and 9). This occurrence may be better showed in Fig. 2, where the conversion to *i*BuOH is plotted as function of reaction time in the two cases.

The different behavior, in terms of pre-activation or not, of Ni/k as compared with Ni/Al₂O₃ when combined with MeONa in the Guerbet reaction at present is quite obscure and could be addressed to a different

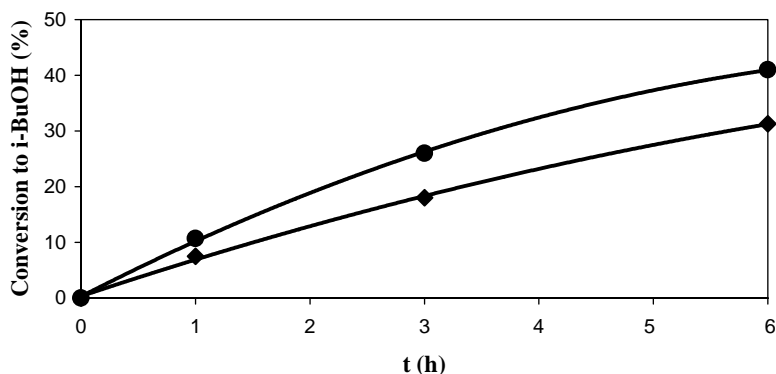


Fig. 2. Time evolution of the PrOH conversion to *i*BuOH in the MeOH/PrOH Guerbet reaction catalyzed by the Ni/Al₂O₃//MeONa system in the presence (◆) (entry 8), or in the absence (●) (entry 9), of pre-activation by H₂ of the Ni/Al₂O₃ component.

interaction of the metal (and also of the methoxide) with the two solid supports also considering the remarkable nickel loading difference in the two cases.

It is noteworthy to mention that in all the above experiments *i*BuOH was substantially the only reaction product, the selectivity of the process being almost complete, only traces (<0.5 mol%) of methyl and propyl formate being detected. Moreover, although the results reported in Table 1 are referred to 6 h reaction time, the experiments related to entries 4, 7 and 8 were prolonged up to 12 h. In these last experiments the conversion to *i*BuOH was found to further increase with time up to about 75% (entry 4), as shown in Fig. 3, thus indicating that a high yield to *i*BuOH may be obtained from PrOH.

Taking into account that homogeneous palladium complexes were found to be significantly active in the Guerbet reaction [17], as mentioned in the introduction, analogous experiments were carried out by using soluble Ni(OAc)₂ and NiCl₂(P^{*i*}Pr₃)₂ in combination with MeONa at 200 °C (entries 10 and 11, Table 1, respectively). Indeed, both the two nickel complexes displayed a significant catalytic activity towards the formation of *i*BuOH, high TN values being found, particularly in the case of the NiCl₂(P^{*i*}Pr₃)₂/MeONa system (65.6 h⁻¹). However, as previously reported for the palladium complexes/MeONa systems [17], when the reaction was stopped a dark precipitate was observed, thus suggesting that also in the nickel-based

systems an equilibrium between homogeneous (or colloidal) and heterogeneous species probably exists, at least under the adopted reaction conditions.

With the aim to improve the yield to *i*BuOH, Rh and Ru-based catalysts were also employed in combination with MeONa, this basic component having showed the best performances.

3.2. Guerbet condensation of methanol with *n*-propanol to give isobutanol in the presence of supported rhodium and ruthenium in combination with MeONa as basic component

Preliminarily two experiments were carried out at 180 °C on the MeOH/PrOH mixture using pre-activated Ru/Al₂O₃ and Rh/Al₂O₃, containing 5 and 3 wt.% of metal, respectively, combined with MeONa as basic component (entries 12 and 13 of Table 2, respectively).

When Ru/Al₂O₃ was employed under the same conditions as in entry 3 (Table 1), where the Ni/k//MeONa and H₂ atmosphere were used, the conversion to *i*BuOH after 6 h was found to be lower (5.2 mol%), TN values being about one fourth with respect to that obtained for the above mentioned catalyst. A low activity was also achieved when the pre-activated Rh/Al₂O₃//MeONa system was used notwithstanding a lower metal amount and N₂ atmosphere were adopted in order to enhance catalyst performances

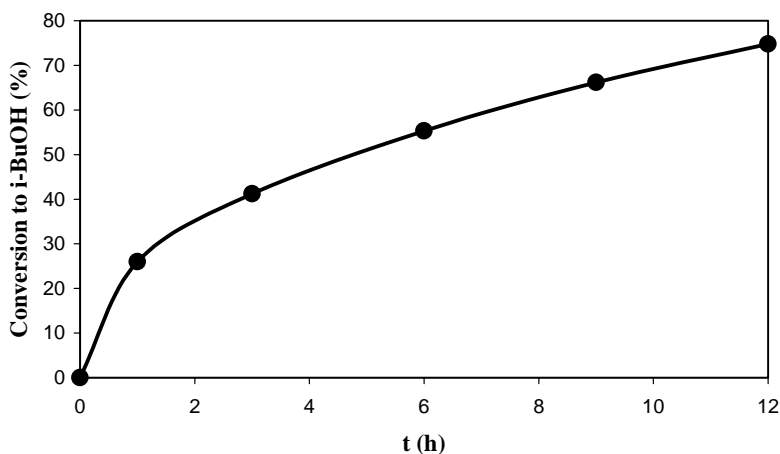


Fig. 3. Time evolution of the PrOH conversion to *i*BuOH in the MeOH/PrOH Guerbet reaction catalyzed by the Ni/k//MeONa system (entry 4).

Table 2

Synthesis of isobutanol (*i*BuOH) through the condensation of methanol (MeOH) with *n*-propanol (PrOH) by ruthenium and rhodium-based supported catalysts in combination with MeONa (B) as basic component^a

Entry	Metal catalyst		MeONa (mmol)	B/metal (mol/mol)	Time (h)	<i>T</i> (°C)	<i>P</i> _{H₂} (atm)	<i>P</i> _{N₂} (atm)	<i>i</i> BuOH		TN ^c (h ⁻¹)
	Type	mmol							Yield (%) ^b		
									6 h	12 h	
12	Ru/Al ₂ O ₃ ^d	2.56	160	63	6	180	30	–	5.2	–	0.3
13	Rh/Al ₂ O ₃ ^e	0.64	160	250	6	180	–	30	9.0	–	2.3
14	Ru5/C ^f	0.25	160	640	12	200	–	30	15.6	17.2	10.4
15	Ru5/C ^{f,g}	0.25	160	640	6	200	–	30	48.5	73.3	32.3
16	Ru5/C ^{f,g}	0.125	160	1280	12	200	–	30	47.5	–	63.4
17	Ru5/C ^{f,g}	0.050	160	1280	12	200	–	30	36.3	74.2	121.0
18	Rh/C ^h	0.25	160	640	12	200	–	30	41.0	74.0	27.3
19	Rh/C ^h	0.25	90	360	12	200	–	30	22.0	41.5	14.7
20	Rh/C ^{g,h}	0.25	160	640	12	200	–	30	58.8	78.3	39.2

^a Reaction conditions—MeOH: 1250 mmol; PrOH: 100 mmol; MeOH/PrOH = 12.5 mol/mol; pre-activated metal supported catalysts were used (see Section 2), if not otherwise specified.

^b Calculated with respect to PrOH.

^c Turnover number calculated after 6 h of reaction and expressed as: mol *i*BuOH/(mol Ni × h).

^d 5 wt.% of Ru on alumina (Engelhard).

^e 3 wt.% of Rh on alumina (Engelhard).

^f 5 wt.% of Ru on charcoal (Aldrich).

^g No pre-activation of the metal catalyst was performed.

^h 5 wt.% of Rh on charcoal (Aldrich).

(entry 13, Table 2). As a consequence all subsequent catalytic experiments were carried out at 200 °C and under N₂ atmosphere. Thus, when a low amount of Ru/C (Ru 5 wt.%) was employed (entry 14, Table 2) an appreciable activity (TN = 10.4 h⁻¹ after 6 h) was obtained. This result may be addressed to the synergistic effect of the increase of reaction temperature from 180 to 200 °C and also of the minor amount of metal used, as previously observed for copper/MeONa catalysts [8]. However, the yield to *i*BuOH after 6 h (15.6 mol%) resulted still lower than that obtained in the presence of Ni/k//MeONa and no appreciable increase was obtained with further 6 h of reaction (conversion to *i*BuOH = 17.2 mol%). This result seems to suggest that the catalyst is progressively deactivated. When Ru/C was used without any pre-activation in combination with MeONa under the same conditions as in entry 14 (entry 15, Table 2), a sharp improvement of activity was observed (yield to *i*BuOH = 48.5 mol% after 6 h) and a high TN value was reached (32.3 h⁻¹). When entry 15 was repeated halving the metal amount, still retaining all the other reaction parameters (entry 16, Table 2), a comparable conversion to *i*BuOH was ascertained and conse-

quently an about double productivity was reached (TN = 63.4 h⁻¹ after 6 h). In order to evaluate the minimum amount of metal component necessary to maintain an appreciable conversion extent to *i*BuOH, entry 16 was repeated (entry 17, Table 2) by adopting only 0.05 mmol of ruthenium. Indeed, under these conditions a still significant conversion was achieved (36.3 mol% with a TN value equal to 121 h⁻¹ after 6 h), although lower than that occurred in entry 16, thus indicating that there is a metal threshold value below which is not suitable to work for practical catalytic applications. Therefore, it may be concluded that for this catalytic system the pre-activation procedure causes a remarkable detrimental effect on activity and rather low amounts of metal component may be adopted. When the pre-activated Rh/C//MeONa system was used under the same conditions as in entry 14 (entry 18, Table 2) a significant improvement of activity was observed as compared with the analogous Ru/C//MeONa system, the conversion to *i*BuOH reaching 41 mol% and TN a value of 27.3 h⁻¹ after 6 h. Moreover, when the reaction was allowed to proceed for further 6 h a conversion to *i*BuOH very close to 75 mol% was obtained. When the amount of

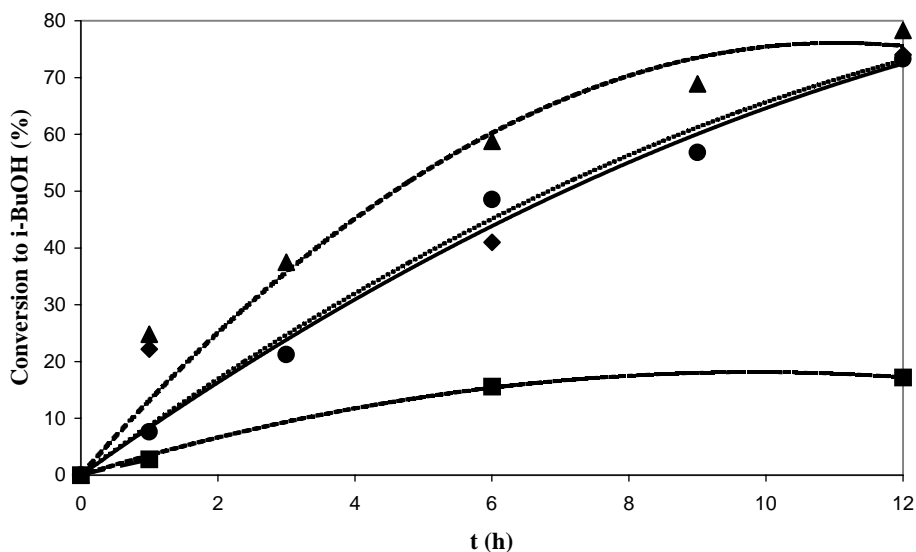


Fig. 4. Time evolution of the PrOH conversion to *i*BuOH in the MeOH/PrOH Guerbet reaction in the presence of: pre-activated Ru5C/MeONa system (■) (entry 14), non pre-activated Ru5C/MeONa system (●) (entry 15), pre-activated Rh/C/MeONa system (◆) (entry 18) and non pre-activated Rh/C/MeONa system (▲) (entry 20).

MeONa was decreased, the other reaction parameters being retained (entry 19, Table 2) an appreciable reduction of activity was ascertained, thus confirming that also for this metal component the decrease of the relative amount of base caused a detrimental effect on the activity, due to the co-production of water which hydrolyses MeONa to MeOH and inactive NaOH. Analogous results were also obtained in the case of Cu-based/MeONa catalysts [8,9]. However, when entry 18 was repeated, just by using a not-pre-activated Rh/C sample in combination with MeONa (entry 20, Table 2), a remarkable improvement of activity was ascertained, an *i*BuOH yield of 58.8 mol% after 6 h and a corresponding TN equal to 39.2 h⁻¹ being achieved. These data clearly confirm that the pre-activation caused a detrimental effect on activity also in the case of Rh-based catalysts.

The comparison, in terms of catalytic performances, between Ru/C and Rh/C in combination with MeONa, either in the presence or in the absence of pre-activation is better depicted in Fig. 4.

As previously observed for the nickel-based catalysts also in all the experiments carried out in the presence of either ruthenium or rhodium-based catalytic

systems an almost complete selectivity to *i*BuOH was ascertained.

Work is in progress in order to evaluate eventual metal leaching occurrence for the above heterogeneous catalysts, analogously to what recently found for palladium-based catalytic systems when employed under similar conditions [17].

4. Conclusions

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

1. All the investigated heterogeneous metal-based systems, when combined with MeONa, resulted active in the Guerbet condensation of MeOH with PrOH to give *i*BuOH with almost complete selectivity.
2. Also the tested homogeneous nickel(II) complexes in combination with MeONa displayed a significant catalytic activity.
3. The pre-activation step caused a clear detrimental effect on ruthenium and rhodium-based catalytic systems, whereas this treatment did not determined

a relevant effect on activity for nickel-based catalysts.

4. The catalytic performances may be optimized in dependence of the nature of the catalyst, the relative amounts of its individual components with respect to the reacting alcohols as well as of temperature and gaseous environment.

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