



# Synthesis of isobutanol by the Guerbet condensation of methanol with *n*-propanol in the presence of heterogeneous and homogeneous palladium-based catalytic systems

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

The catalytic synthesis of isobutanol (*i*BuOH), via the Guerbet condensation of methanol with *n*-propanol is described. In particular, bifunctional catalysts based on either heterogeneous or homogeneous dehydrogenating/hydrogenating palladium species and on sodium methoxide (MeONa) as basic component were investigated. When heterogeneous Pd/C and MeONa was used as catalytic system a high activity was obtained with turnover numbers up to about 110 mol of *i*BuOH/(mol of Pd h). The increase of the MeONa/Pd molar ratio increased the activity of the catalyst. However, differently from Cu-based/MeONa catalysts, a significant metal leaching was observed; recycle experiments indicated that both heterogeneous and homogeneous palladium species are involved in the catalysis. When homogeneous palladium complexes, such as tetrakis(triphenylphosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>], diphenylphosphinoethane(dichloro)palladium(II) [Pd(dppe)Cl<sub>2</sub>] and bis(dibenzylideneacetone)palladium(0) [Pd(dba)<sub>2</sub>], were used in combination with MeONa a remarkable activity was also obtained, independently of the oxidation state of the palladium precursor. During the reaction deposition of a solid was observed and recycle experiments carried out both on the recovered solid and on the liquid phase suggested that also in this case the activity has to be addressed to both heterogeneous and homogeneous (or colloidal) palladium species.

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## 1. Introduction

In the recent years, a growing interest has been devoted to the synthesis of isobutanol (*i*BuOH) which

represents a potential gasoline additive and a precursor for obtaining isobutene, which in turn can be converted to attractive components for clean burning gasolines, either methyl *tert*-butyl ether (MTBE) or isooctane (via isobutene dimerization and successive hydrogenation), whenever MTBE will be no more desired in gasoline, as for example in California [1].

A largely explored approach to obtain *i*BuOH is the direct synthesis from CO and H<sub>2</sub> (higher alcohols

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synthesis (HAS)), but this process is performed under drastic conditions (100–300 atm and 350–500 °C) and does not allow to achieve high selectivity and productivity [2].

An alternative approach was the two-step process [3], where, in the first stage, methanol and a mixture of higher alcohols are obtained from syngas at low temperature with modified methanol catalysts and, in the second stage, the mixture is converted to an isobutanol-rich product with high temperature methanol catalysts. With this approach an increased formation of isobutanol was observed although the high temperature of the second stage causes selectivity problems and undesired retro-conversion of methanol to syngas.

In this context, with the aim to design a synthetic process able to give isobutanol with even better performance, preserving the advantages of the two-step processes but reducing the drawbacks of the second stage, we have decided to investigate the conversion to isobutanol of the alcohol mixture from the first stage through a lower temperature route as the Guerbet reaction [4–7]. Indeed, part of the excess methanol and most of ethanol and *n*-propanol from the first stage reaction could be reacted together to afford an enriched isobutanol mixture. Actually, in the Guerbet reaction primary alcohols are condensed in the presence of a system containing both hydrogenating/dehydrogenating catalysts and basic species [4,5]. This multi-step reaction involves the preliminary dehydrogenation of the alcohol to the corresponding aldehyde, followed by its base-catalysed aldolic condensation and by successive hydrogenation to the saturated higher alcohol according to Scheme 1, as proposed by Veibel and Nielsen [4].

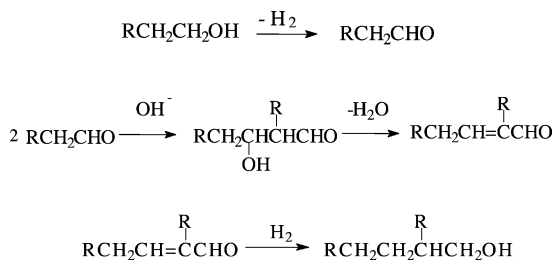
In a study on *n*-butanol condensation, Burk et al. [8] observed that at least the first step in the Guerbet

reaction required the hydrogenating/dehydrogenating metal component; indeed, they found that using only a basic component the reaction proceeded starting from the intermediate aldehyde. However, the metal is involved also in the hydrogenation of the unsaturated intermediate alcohol.

Although heterogeneous metal components with hydrogenating/dehydrogenating properties were mainly employed for the Guerbet reaction, Gregorio et al. studied the behaviour of soluble complexes of VIII group transition metals in the presence of sodium butoxide in boiling *n*-butanol; they found that in nearly all cases the starting homogeneous complexes underwent a quick metal separation because of the reducing properties of the strong basic component [9]. In particular, they found that palladium complexes were completely inactive in the self-condensation of *n*-butanol, although it must be pointed out that the adopted reaction temperature (about 120 °C) is rather low for this type of reaction. On the other hand, rhodium precursors showed a significant catalytic activity, due to an easy hydrogen abstraction from alcohols by Rh<sup>III</sup>, Rh<sup>I</sup> and Rh<sup>0</sup> complexes which form stable metal hydrides.

Subsequently, the behaviour of Rh-based systems for *n*-butanol condensation in the presence of sodium alkoxide was also studied by Burk et al. [8,10], adopting both homogeneous and heterogeneous rhodium precursors. Homogeneous complexes, such as [Rh(COE)<sub>2</sub>Cl]<sub>2</sub> (COE = cyclooctene) quickly decomposed to Rh<sup>0</sup>, which was considered to be responsible for the ascertained catalytic activity. When an ancillary ligand, such as a phosphine or a phosphite, was added stabilisation of the homogeneous component was observed with consequent lowering of the Guerbet activity. Only when the heterogeneous Rh<sup>0</sup> component became appreciable some catalytic activity was ascertained, thus allowing the authors to conclude that if a purely homogeneous pathway to Guerbet alcohols existed, its activity was significantly lower than the heterogeneous counterpart.

Very recently, we have reinvestigated the Guerbet reaction for the selective synthesis of *i*BuOH from the methanol/*n*-propanol (PrOH) model mixture in the presence of heterogeneous copper catalysts combined with sodium methoxide as basic component [11]. In the present paper, we have extended the investigation to palladium-based homogeneous and heterogeneous



Scheme 1.

precursors as hydrogenating/dehydrogenating components in the presence of sodium methoxide as base.

## 2. Experimental

### 2.1. Materials

Methanol (Prolabo) and *n*-propanol (Carlo Erba) were dried by distillation under dry argon after refluxing for 6 h on magnesium methoxide, according to Lund and Bjerrum method [12].

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

Pd/C (10 wt.%, Aldrich) was purchased as a dry sample. When pre-activated prior to the use, it was mechanically stirred in a Parr reactor in the presence of methanol at 180 °C for 5 h under 80 atm of H<sub>2</sub>.

Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [1,2-bis(diphenylphosphino)ethane]dichloro palladium(II) [Pd(dppe)Cl<sub>2</sub>] (both commercially purchased from Aldrich) were used as received.

Bis(dibenzylideneacetone)palladium(0) [Pd(dba)<sub>2</sub>] was prepared according to Moseley and Maitlis [13].

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

A 300 ml Parr reactor, equipped with a mechanical stirrer, a heating system and a control device assisted by a thermocouple inserted into the reactor, a sampling valve for liquids, an inlet valve for gas introduction and an outlet sampling valve for gaseous products, was used in the catalytic batch experiments. When a homogeneous metal precursor was employed, this was completely dissolved in the alcohols mixture and introduced by suction in the reactor. When a heterogeneous metal component was used, it was introduced in the reactor which was subsequently evacuated. In the case of pre-activation of the heterogeneous metal precursor, methanol was introduced through the sampling valve. The reactor was subsequently pressurised with H<sub>2</sub> up to 80 atm and heated at 180 °C for 5 h. After the activation step, the reactor was cooled at room temperature and degassed, then the proper amount of MeONa, dissolved in the alcohols mixture, was introduced through the gas sampling valve. When the heterogeneous metal precursor was not pre-activated,

the alcohols mixture was directly added to the reactor through the sampling valve.

In all cases, the reactor was subsequently pressurised with 30 atm of N<sub>2</sub>. The reaction was followed by collecting at different time 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 and finally the liquid reaction mixture was analysed by gas chromatography (GC) after the addition of a known amount of benzene as internal standard.

The recycle experiments were carried out as follows: when both heterogeneous and homogeneous palladium components were used in combination with MeONa, the reaction was stopped after 6 h, then the solid (in the case of the use of homogeneous precursors a black solid was deposited during the reaction) was separated from the liquid reaction mixture by careful filtration or centrifugation. 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 as previously reported. On the other hand, the collected solid component was washed with methanol under nitrogen, then dried under vacuum, weighed and recycled by adding the same amount of fresh reagents and MeONa as those originally employed. The reaction was then allowed to proceed for further 12 h and at intervals the reaction mixture was analysed by GC.

### 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 an ethylvinylbenzene/divinylbenzene resin. Helium was used as carrier 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, mixtures of authentic samples of known composition were prepared, using benzene as internal standard.

In all the experiments, a substantially complete selectivity to isobutanol was observed. Indeed, only traces (<0.5%) 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

All the experiments were carried out in a batch reactor, using a MeOH/PrOH molar ratio (12.5) quite similar to that obtained in the synthesis of methanol and higher alcohols in the presence of modified low temperature metal catalysts [3,14–17].

MeONa was employed as the basic component: it is soluble in the reaction mixture and generally was used in a large excess as compared with the amount of PrOH, in order to minimise the deactivation of the system by the water co-produced in the reaction.

#### 3.1. Synthesis of isobutanol by Guerbet condensation of methanol with *n*-propanol in the presence of heterogeneous Pd/C and sodium methoxide

First of all the catalytic behaviour of the Pd/C component in the absence of MeONa was checked (Blank run) and no activity at all was ascertained, thus confirming that a basic component is essential for the Guerbet reaction. Therefore, the catalytic system was based on the Pd/C and MeONa system, usually the metal component being preliminarily pre-activated under H<sub>2</sub>.

With a progressive decrease of the amount of palladium with respect to that of the basic component a corresponding improvement of activity was observed (Runs 1–4, Table 1), the turnover number (TN) reaching values up to about 110 mol of *i*BuOH/(mol Pd h) (Run 4). Moreover, all the catalytic experiments showed an almost complete selectivity to the Guerbet alcohol, therefore, the *i*BuOH yield was considered equal to PrOH conversion.

On the contrary, a progressive lowering of the base concentration caused a drastic reduction of activity (compare Runs 3, 5 and 6, Table 1), analogously to what previously observed with Cu-based/MeONa cat-

Table 1

Guerbet condensation from methanol (MeOH)/*n*-propanol (PrOH) mixtures in the presence of Pd/C and sodium methoxide (MeONa)<sup>a</sup>

| Run            | Pd/C (mmol) | MeONa (mmol) | <i>i</i> BuOH yield (%) |      |      | TN <sup>b</sup> (h <sup>-1</sup> ) |
|----------------|-------------|--------------|-------------------------|------|------|------------------------------------|
|                |             |              | 1 h                     | 6 h  | 12 h |                                    |
| Blank          | 0.125       | 0            | 0                       | 0    | 0    | 0                                  |
| 1              | 2.500       | 160          | 11.7                    | 41.6 | 48.8 | 2.8                                |
| 2              | 0.250       | 160          | 16.2                    | 52.5 | 65.3 | 35.0                               |
| 3              | 0.125       | 160          | 26.0                    | 56.6 | 72.8 | 75.5                               |
| 4              | 0.063       | 160          | 17.1                    | 41.5 | 59.7 | 109.8                              |
| 5              | 0.125       | 80           | 16.5                    | 34.0 | 66.8 | 55.3                               |
| 6              | 0.125       | 40           | 8.8                     | 18.8 | 19.1 | 25.1                               |
| 7 <sup>c</sup> | 0.125       | 160          | 42.7                    | 60.6 | 93.2 | 80.8                               |

<sup>a</sup> Reaction conditions: heterogeneous catalysts were used after pre-activation with H<sub>2</sub> carried out in MeOH at 180 °C for 5 h, if not otherwise specified; *T* = 200 °C; *P*<sub>N<sub>2</sub></sub> = 30 atm; MeOH: 1250 mmol; PrOH: 100 mmol.

<sup>b</sup> Turnover number expressed as: mol *i*BuOH/(mol Pd h) and calculated after 6 h reaction.

<sup>c</sup> The metal precursor was not submitted to pre-activation with H<sub>2</sub>.

alysts [11]. This behaviour is better pointed out in Fig. 1 and must be addressed to the progressive depletion of MeONa concentration due to its transformation into the inactive NaOH and MeOH by the co-produced water.

The different trend observed in the run with 160 mmol of MeONa with respect to that with 80 mmol of MeONa is likely due to the higher conversion of PrOH after 6 h and thus to an increased influence of water inhibition in the following 6 h.

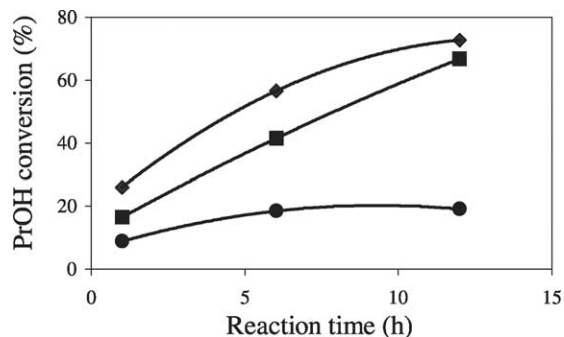


Fig. 1. Influence of MeONa concentration on PrOH conversion in catalytic experiments carried out with the same amount of Pd/C (0.125 mmol); amount of MeONa: 160 mmol (◆) Run 3, 80 mmol (■) Run 5 and 40 mmol (●) Run 6.

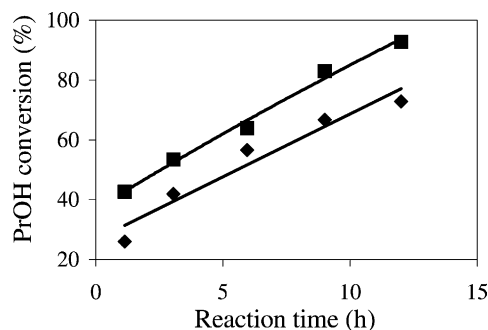


Fig. 2. Influence of the  $H_2$  pre-treatment on PrOH conversion by using Pd/C and MeONa as catalytic system under the same reaction conditions: palladium catalyst pre-treated (◆) Run 3, or not (■) Run 7 with  $H_2$ .

It is worthy noting that without the pre-reduction of Pd/C with  $H_2$ , an increase of the activity was observed (compare Run 7 with Run 3, Table 1). Indeed, the pre-treatment with hydrogen, which was found to be necessary with copper-based systems [11], exerted a detrimental effect, as recently also reported for highly metal loaded Pd/C catalysts in debenzilation reactions [18]. This effect is better evidenced in Fig. 2. Taking into account this result, pre-activation of the solid metal precursors was omitted in the subsequent experiments.

In order to verify if the ascertained high activity could be exclusively related to the catalyst working in heterogeneous phase, especially in the presence of a strong excess of an aggressive agent as the alkoxide, metal leaching was evaluated for the Pd/C//MeONa system, carefully removing the solid catalyst after 6 h of reaction and going on for further 6 h only with the liquid reaction mixture (Run 8, Table 2). The data clearly indicated that a further significant advancement of the reaction (from 60.6 to 86.7% of PrOH conversion) occurred after removal of the solid component, thus suggesting that palladium homogeneous or colloidal species may contribute to the catalytic activity, contrarily to what observed for Cu-based heterogeneous catalysts in the presence of MeONa [19]. It has to be pointed out that, on the basis of our results, we are not able to distinguish between palladium complexes or colloidal particles in solution.

Moreover, the recycle of the recovered solid catalyst after reaction was also considered (Run 9, Table 2). The obtained data indicated that also the

Table 2

Synthesis of isobutanol ( $i$ BuOH) from MeOH/PrOH mixtures in the presence of Pd/C and MeONa: recycle experiments<sup>a</sup>

| Run            | Metal catalyst                      | PrOH conversion (%) |      |
|----------------|-------------------------------------|---------------------|------|
|                |                                     | 6 h                 | 12 h |
| 8 <sup>b</sup> | Leached Pd species                  | 26.1 <sup>c</sup>   | –    |
| 9 <sup>d</sup> | Solid catalyst recovered from Run 7 | 38.8                | 66.2 |

<sup>a</sup> Reaction conditions:  $T = 200^\circ C$ ;  $P_{N_2} = 30$  atm; MeONa: 160 mmol; MeOH: 1250 mmol; PrOH: 100 mmol; no pre-activation of the Pd/C by  $H_2$  was adopted.

<sup>b</sup> Run 8 was repeated under the same conditions as Run 7, after 6 h the reaction was stopped (PrOH conversion: 60.6%) and the solid catalyst was removed; then the reaction was continued for further 6 h only by using the recovered liquid reaction mixture.

<sup>c</sup> Represents the further PrOH conversion (from initial 60.6 to 86.7%).

<sup>d</sup> Run 9 was carried out with the solid catalyst recovered from Run 7 by adding the fresh reagents and the basic component.

heterogeneous recovered component still exerted a significant catalytic activity. Therefore, from these preliminary data, it appears that both homogeneous (or colloidal) and heterogeneous palladium species should contribute to the overall activity. A very similar leaching effect was observed very recently also in a study about the Heck reaction carried out in the presence of Pd/C catalyst [20]. Also, in that case it was difficult to establish whether the reaction took place on the solid Pd surface or in the liquid phase, due to palladium species leached from Pd/C, this last acting as a metal reservoir.

Indeed, in our experiments the determination of palladium concentration in solution (before and after recycle) resulted difficult to be evaluated, due to the very low amount of leached metal and to the presence of a large excess of sodium methoxide which makes not practicable an ordinary analytical procedure such as electrothermal atomization spectroscopy.

The above evidenced leaching effect prompted us to extend the investigation also to homogeneous palladium precursors in the presence of MeONa.

### 3.2. Synthesis of isobutanol by Guerbet condensation of methanol with *n*-propanol in the presence of homogeneous palladium complexes and sodium methoxide

In this context, the catalytic activity of Pd( $PPh_3$ )<sub>4</sub>, Pd(dba)<sub>2</sub> and Pd(dppe)Cl<sub>2</sub> was checked

Table 3

MeOH/PrOH Guerbet condensation in the presence of MeONa and soluble palladium precursors<sup>a</sup>

| Run | Palladium precursor                |       | PrOH conversion (%) |      |      |      |      | TN <sup>b</sup><br>(h <sup>-1</sup> ) |
|-----|------------------------------------|-------|---------------------|------|------|------|------|---------------------------------------|
|     | Type                               | mmol  | 1 h                 | 3 h  | 6 h  | 9 h  | 12 h |                                       |
| 10  | Pd(PPh <sub>3</sub> ) <sub>4</sub> | 0.125 | 18.8                | 27.0 | 36.3 | –    | –    | 48.4                                  |
| 11  | Pd(dba) <sub>2</sub>               | 0.125 | 17.2                | 35.4 | 44.5 | 67.1 | 74.6 | 59.3                                  |
| 12  | Pd(dppe)Cl <sub>2</sub>            | 0.125 | 22.0                | 35.0 | 53.5 | –    | –    | 71.3                                  |
| 13  | Pd(dppe)Cl <sub>2</sub>            | 0.312 | 43.2                | 64.7 | 84.2 | –    | –    | 44.9                                  |

<sup>a</sup> Reaction conditions:  $T = 200\text{ }^{\circ}\text{C}$ ;  $P_{\text{N}_2} = 30\text{ atm}$ ; MeONa: 160 mmol; MeOH: 1250 mmol; PrOH: 100 mmol; no pre-activation of the homogeneous palladium complexes by H<sub>2</sub> was adopted.

<sup>b</sup> Turnover number expressed as: mol <sup>t</sup>BuOH/(mol Pd h) and calculated after 6 h reaction.

in combination with MeONa as basic component (Table 3).

It is noteworthy to mention that in all cases (Runs 10–13), independently of the oxidation state of the homogeneous palladium precursor, a remarkable activity was observed, TN values up to about 70 h<sup>-1</sup> being reached. However, for all the experiments, at the end of the catalytic reaction the deposition of a black solid compound was observed, whose characterisation together with that of the liquid phase is still in progress. Therefore, it was decided that also for these homogeneous precursors recycle experiments should be performed (Table 4). In order to verify the catalytic activity of the liquid phase, Runs 10 and 13 were duplicated with the variation that after 6 h

the deposited solid component was carefully removed and the reaction was allowed to start again for further 6 h (Runs 14 and 15, respectively) only in the presence of the liquid reaction mixture (in the case of Run 15 fresh PrOH was also added due to the high conversion reached before the solid removal). The obtained results pointed out a further appreciable catalytic activity which should be addressed to palladium species in the homogeneous or colloidal phase.

Also, the solid catalysts recovered after Runs 10 and 13 were stopped and subsequently employed for a second catalytic cycle with fresh reagents and fresh methoxide. The obtained data (Runs 16 and 17, respectively, Table 4) clearly indicated that also the

Table 4

Synthesis of <sup>t</sup>BuOH from MeOH/PrOH mixtures in the presence of palladium homogeneous complexes and MeONa: recycle experiments<sup>a</sup>

| Run             | Metal catalyst   | Converted PrOH (mmol) |                  |                   |      |      |
|-----------------|--|-----------------------|------------------|-------------------|------|------|
|                 |  | 1 h                   | 3 h              | 6 h               | 9 h  | 12 h |
| 14 <sup>b</sup> | Catalyst precursor [Pd(PPh <sub>3</sub> ) <sub>4</sub> ] | –                     | 4.8 <sup>c</sup> | 14.1 <sup>d</sup> | –    | –    |
| 15 <sup>e</sup> | Catalyst precursor [Pd(dppe)Cl <sub>2</sub> ]            | –                     | 6.7 <sup>f</sup> | 30.7 <sup>g</sup> | –    | –    |
| 16 <sup>h</sup> | Solid catalyst recovered from Run 10                     | 4.9                   | 13.4             | 21.8              | 28.8 | 44.8 |
| 17 <sup>i</sup> | Solid catalyst recovered from Run 13                     | 0.5                   | 9.6              | 21.3              | 25.9 | 26.1 |

<sup>a</sup> Reaction conditions:  $T=200\text{ }^{\circ}\text{C}$ ;  $P_{\text{N}_2} = 30\text{ atm}$ ; MeONa: 160 mmol; MeOH: 1250 mmol; PrOH: 100 mmol; no pre-activation of either the homogeneous palladium complexes or the recovered solid by H<sub>2</sub> was adopted.

<sup>b</sup> Run 14 was repeated under the same conditions as Run 10; after 6 h the reaction (mmol of converted PrOH = 36.3) was stopped and the solid catalyst was removed, then the reaction was continued for further 6 h only by using the liquid reaction mixture.

<sup>c</sup> Represents the further mmol of converted PrOH (from initial 36.3 to 41.1).

<sup>d</sup> Represents the further mmol of converted PrOH (from initial 36.3 to 50.4).

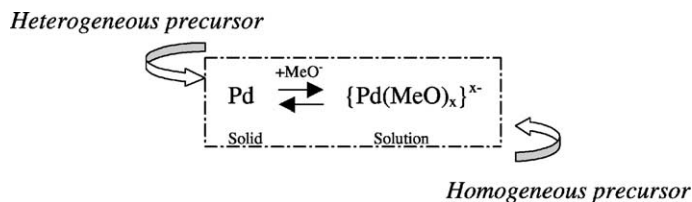
<sup>e</sup> Run 14 was repeated under the same conditions as Run 13; after 6 h the reaction was stopped (mmol of converted PrOH = 84.2) and the solid catalyst was removed, then the reaction was continued for further 6 h, after addition of further 50 mmol of PrOH, only by using the liquid reaction mixture.

<sup>f</sup> Represents the further mmol of converted PrOH (from initial 84.2 to 90.9).

<sup>g</sup> Represents the further mmol of converted PrOH (from initial 84.2 to 115.9).

<sup>h</sup> Run 16 was carried out with the solid catalyst recovered from Run 10 by adding the fresh reagents and basic component.

<sup>i</sup> Run 17 was carried out with the solid catalyst recovered from Run 13 by adding the fresh reagents and basic component.



Scheme 2.

heterogeneous recovered component still exerted a significant catalytic activity.

Therefore, analogously to what was observed in the case of Pd/C system, also starting from homogeneous precursors in different oxidation state, homogeneous (or colloidal) and heterogeneous palladium species are formed, both contributing to the overall activity. Indeed, an equilibrium between solid and homogeneous Pd species might be proposed, according to the following general pathway (Scheme 2).

The present work strictly resembles the recently published paper on the Heck reaction [20] and a very careful analytical work should be performed in order to establish in a more quantitative way the extent of the contribution of palladium in solution and in the solid state, also considering the dynamic equilibrium between each other.

Work is also in progress in order to spectroscopically identify the nature of the palladium species in solution and in the solid state in order to better rationalise the reaction mechanism. From a merely speculative point of view, analogously to what proposed by Maitlis for diene telomerization with alcohols [21], an oxidative addition of the alcoholic substrate to a palladium(0) species may be supposed to give rise to an alcoholate palladium(II) hydride.

As recently reported by Nishimura and Onue [22], the formed alcoholate intermediate could evolve by  $\beta$ -hydrogen elimination giving the corresponding aldehyde which in turn generates the Guerbet alcohol by base-catalysed condensation and successive hydrogenation of the unsaturated intermediate, probably caused by heterogeneous palladium species (Scheme 1).

#### 4. Concluding remarks

On the basis of the reported results the following remarks can be drawn:

- (a) Pd/C appeared to be an effective catalyst for Guerbet condensation of MeOH with PrOH to give *i*BuOH with complete selectivity. The presence of sodium methoxide as basic component resulted necessary for the catalytic activity. Differently from Cu-based systems, recycle experiments pointed out metal leaching in solution and an appreciable activity of the homogeneous liquid phase.
- (b) Homogeneous precursors (such as Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(dba)<sub>2</sub> and Pd(dppe)Cl<sub>2</sub>) showed a good catalytic activity although solid deposition during the reaction was always observed. Also, in this case recycle experiments evidenced that the overall catalytic activity may be addressed both to homogeneous and heterogeneous species, probably both involved in an equilibrium.
- (c) The above preliminary results have never been reported in the literature. Work is in progress to better evaluate the extent of the contribution of palladium in solution and in the solid state as well as to clarify the nature of the involved catalytic species in order to gain a deeper insight on the reaction mechanism.

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