



Cu/SiO₂: a step forward in the heterogenization of the 2,6-dimethyl-phenol polymerization catalytic system

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Received 19 September 2002; received in revised form 19 February 2003; accepted 7 March 2003

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

Abstract

The activity of supported copper catalysts in the oxidative coupling of 2,6-dimethyl-phenol (DMP) has been studied with the aim of lowering as much as possible the metal leaching during the reaction. To achieve this goal both the influence of the catalyst support and of the solvent/amine couple have been investigated. The second one turned out to be decisive and the use of toluene/dibutylamine (DBA) allowed to reduce the leaching to <3%.

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Keywords: Heterogeneous copper catalyst; 2,6-Dimethyl-phenol polymerization; Polyphenylene-ether production; Oxidative coupling; Homogeneous/heterogeneous catalysis relationship

1. Introduction

Poly-2,6-dimethyl-1,4-phenylene-ether (PPE) is an important engineering plastic produced worldwide on a 300,000 tonnes per year scale. It is utilised in blends with polystyrene to give resins with outstanding properties like optimal heat and flame resistance, very good electrical properties, low specific gravity and resistance to hot water, acids and alkalis. These resins are used in housings and enclosures for printers, copy machines and personal computers, chassis for CD&DVD-ROM drives, deflection yokes, water line valves, joints, tanks, large interior panels in automobiles and many others [1].

PPE can be obtained through oxidative coupling polymerization of its monomer 2,6-dimethyl-phenol

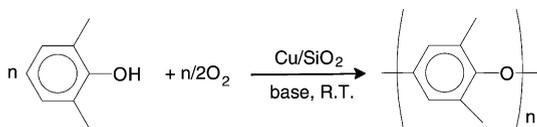
(DMP) in the presence of oxygen (Scheme 1). The reaction is industrially carried out at 25–50 °C by flowing O₂ through a vigorously stirred DMP solution containing a catalyst typically composed of a copper halide salt and one or more aliphatic amines. Attempts to heterogenize the catalytic system mainly rely on the use of supported copper complexes [2,3] and have been till now unsuccessful, although the interest from the environmental point of view is evident.

Improvements proposed by the recent patent literature involve mainly process technologies like separation and recovery of metal catalysts [4], recovery or recycling of solvents [5,6], oxygen pressure control [7].

The first example of a heterogeneous catalytic system involves the use of prerduced supported Cu on silica in methanol–pyridine solution and under 1 atm of oxygen [8].

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Scheme 1.

A severe leaching of the metallic phase takes place under these conditions. However, the catalyst was found to be reusable and the rate of the second cycle was higher than that of the first one. Characterization of the catalyst before the first run showed that two kinds of metallic particles are present on the surface: two-dimensional particles with a partial positive charge due to the interaction with the support and well formed three-dimensional crystallites [9]. The formation of the last ones has to be ascribed to the catalyst preparation method, as had been shown by previous work [10]. Characterization by TEM and FTIR of the adsorbed CO on the catalyst after the first run, showed that after the leaching only one kind of metallic particles survived on the catalyst surface, namely the two-dimensional ones. This feature, together with the increase in reaction rate during the second run, led to the identification of two-dimensional particles as the more active ones in the polymerization reaction in methanol/pyridine.

These preliminary results prompted us to further investigate this catalytic system. Here we report the results obtained by focussing on copper leaching.

2. Experimental

2.1. Catalysts preparation

Copper catalysts, all with a metal loading of 8–9% by weight, were prepared by the chemisorption-hydrolysis (CH) method as already reported [10] by adding the support to a solution containing $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and slowly diluting the slurry with water. The solids were separated by filtration, washed with water, dried overnight at 120 °C and calcined in air at 350 °C for 4 h. The sample obtained by incipient wetness method (Cu/SiO₂, IW) was prepared by adding an aqueous solution of Cu(NO₃)₂ of suitable concentration and volume to the support.

SiO₂ (BET = 320 m²/g, PV = 1.75 ml/g), SiO₂-TiO₂ (0.3% TiO₂, BET = 330 m²/g, PV =

1.90 ml/g), SiO₂-Al₂O₃ 0.6 (0.6% Al₂O₃, BET = 500 m²/g, PV = 1.45 ml/g) and SiO₂-Al₂O₃ 13 (13% Al₂O₃, BET = 475 m²/g, PV = 0.79 ml/g) were supplied from Grace Davison (Worms, Germany). Copper content before and after the catalytic reaction was determined by atomic adsorption spectroscopy.

2.2. Catalytic tests

The catalysts (0.4 g, ~0.5 mmol of Cu) were calcined in air at 270 °C for 20 min, treated under vacuum at 270 °C for 20 min and then reduced under H₂ at the same temperature in a glass reactor. After cooling at room temperature, 0.4 g of DMP (3.3 mmol) in 10 ml solvent and 2 ml amine were added under N₂; then O₂ (1 atm) was introduced.

The oxygen uptake was measured continuously through a gas burette and the initial rate was calculated as the derivative for $t = 0$ of the curves of oxygen uptake versus time. These values were used to monitor the catalytic activity of the different catalytic systems. Phenol conversion was monitored by GLC using a methylsilicone capillary column.

When the oxygen uptake stopped, the reaction mixture was filtered off. For reactions carried out in methanol, the catalyst was separated from the polymer by extraction in Soxhlet with toluene for 3 h, the extract was concentrated and methanol added to precipitate the polymer. PPE from the reaction mixture was precipitated by adding hydrochloric acid. The two portions were added and the total weight was used to calculate the yield. When reactions were carried out in toluene, after filtration the reaction mixture was concentrated and the polymer precipitated by adding methanol.

For the recycle tests, the catalyst was extracted in both cases. The amount of substrate used was measured in order to keep the same catalyst/substrate ratio by weight.

The product was analyzed by elemental analysis, IR and ¹³C NMR spectroscopy and molecular weight distribution was carried out by gel permeation chromatography.

2.3. Heterogeneity tests

One reaction carried out with Cu/SiO₂ in toluene/dibutylamine (DBA) was stopped at about 30%

Table 1

Initial oxygen absorption rates and Cu leaching for the four catalysts studied in the polymerization of 2,6-dimethyl-phenol ($P = 1$ bar O_2 ; $T = 25$ °C)

| Entry | Catalyst | Cu (% by weight) | V_{in} (ml O_2 /s mmol $_{Cu}$) | Δ_{Cu} (% by weight) |
|-------|----------------------|------------------|--------------------------------------|-----------------------------|
| 1 | Cu/Si | 8.6 | 0.088 | 55 |
| 2 | Cu/Si recycled | 3.9 | 0.143 | 44 |
| 3 | Cu/SiTi 0.3 | 8.2 | 0.068 | 39 |
| 4 | Cu/SiTi 0.3 recycled | 5.0 | 0.200 | 39 |
| 5 | Cu/SiAl 0.6 | 8.4 | 0.139 | 41 |
| 6 | Cu/SiAl 0.6 recycled | 4.9 | 0.212 | n.d. |
| 7 | Cu/SiAl 13 | 8.7 | 0.105 | 48 |
| 8 | Cu/SiAl 13 recycled | 4.5 | 0 | 0 |

conversion and filtered under O_2 . The filtrate was then allowed to react further for 6 h (time required by the heterogeneous system to go to completion).

3. Results and discussion

In order to reduce the amount of copper leaching into solution during the coupling reaction, we adopted two different strategies.

On one hand we looked for a support suitable to stabilize the metallic phase under the reaction conditions while on the other one we investigated the influence of varying the solvent and the amine.

3.1. Effect of the support

In order to investigate the chance to stabilize the metallic phase through interaction with the support, we compared under the same experimental conditions the performance of Cu on silica gel (Cu/Si) with that of three copper-based catalysts prepared by the same technique but using three different commercial supports. The copper loading for all the catalysts was around 8% by weight.

Two silicas modified with a low amount of a second oxide, namely a silica–titania with 0.3% by weight of titania (SiTi 0.3) and a silica modified with 0.6% by weight of alumina (SiAl 0.6) were chosen as the interaction of copper with a Lewis acid center could stabilize the metallic phase. A silica–alumina cogel containing 13% by weight of alumina (SiAl 13) was also taken into account as the Cu/SiAl 13 catalyst has been recently characterized by several techniques and has been found to be completely different from Cu/Si

and Cu/SiTi, particularly in the morphology of the metallic phase [11]. Thus, FTIR of adsorbed CO reveals, on the surface of the reduced sample, only one kind of particles, with very strong interactions with the support at a wavenumber (2156 cm^{-1}), higher than those ascribed to both two-dimensional (2130 cm^{-1}) and three-dimensional ones (2100 cm^{-1}). The higher activity of plate-like two-dimensional particles with a partial positive charge previously observed, suggested us that particles with even higher charge could be more active and more stable in DMP polymerization reaction.

Results obtained with these catalysts are summed up in Table 1, oxygen uptake versus time is reported in Fig. 1.

All the catalysts were found to be active in the first run with a huge metal loss. Only Cu/SiAl 13 was found not to be reusable.

Results reported in Table 1 clearly show that the modification of the support, at least among those taken into account in the present paper, does not lead to a significant improvement as far as copper leaching is concerned.

3.2. Solvent/amine effect

Copper leaching from our catalysts under the reaction conditions considered in the previous paragraph can be readily accounted for on the basis of metallic copper reactivity. Thus, it is known that metallic copper reacts with molecules containing acidic hydrogen atoms in the presence of molecular oxygen and an amine. In particular, a suspension of copper powder is stable up to 60 °C in methanol under an oxygen atmosphere, but it uptakes 0.7 mol of O_2 /mol of

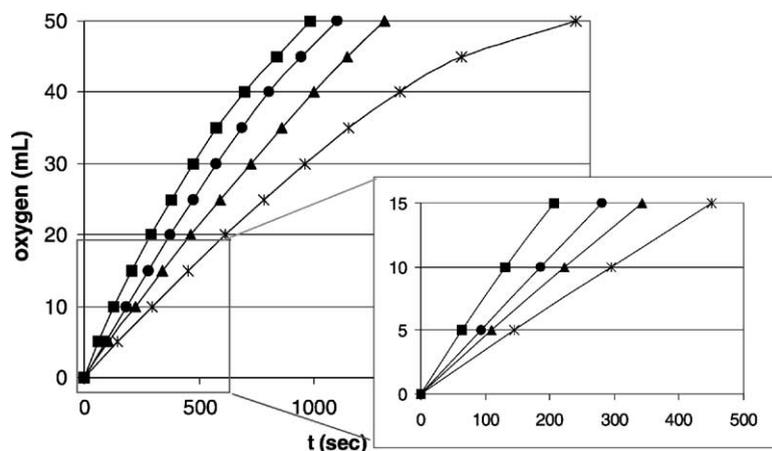


Fig. 1. Oxygen uptake vs. time for the four different copper catalysts considered: (■) Cu/SiAl 0.6; (●) Cu/SiAl 13; (▲) Cu/Si; (X) Cu/SiTi 0.3.

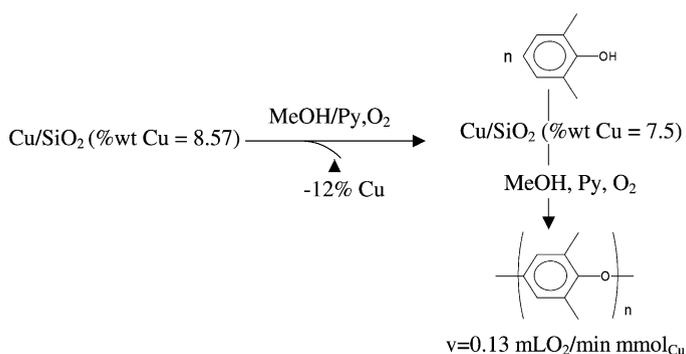
copper at room temperature when pyridine is added, with formation of $\text{Cu}(\text{OCH}_3)_2$ [12].

Therefore, a contribution of this reaction to the copper leaching has to be considered. This has been shown to be true by allowing the catalyst to react under oxygen with a methanol/pyridine solution in the absence of phenol (Scheme 2). The solution uptook a small amount of oxygen and the catalyst lost 12% by weight of the copper present. The same sample was recovered, reactivated and used in a catalytic run: the reaction rate was comparable with that of the catalyst recycled (Table 1, entry 2), showing that “surface cleaning” with uncovering of the more active particles

is an effect of the methanol/pyridine couple. A relevant contribution to the metal loss can then be related to the secondary complexation and oxidation reactions involving the substrate.

The reactivity of a molecule with the copper/pyridine/oxygen system depends on the acidity of its protons. Thus, alkenes and halogenated hydrocarbons, lacking mobile hydrogen atoms, failed to react while those containing very weak acids, like ethanol and diphenylacetylene produced very slow oxygen consumption.

This prompted us to substitute methanol with toluene, an hydrocarbon which is also a very good



Scheme 2.

Table 2

Effect of varying the solvent/amine couple on reaction rate, copper leaching and yield in the polymerization of DMP

| Catalyst | Solvent | Amine | O ₂ uptake (ml) | V _{in} (ml O ₂ /s mmol _{Cu}) | Δ _{Cu} (%) | Yield (%) |
|--------------------|----------|------------|----------------------------|--|---------------------|-----------|
| Cu/SiTi | Methanol | Morpholine | 65 | 0.052 | 39 | 46 |
| | Methanol | Pyridine | 55 | 0.068 | 39 | 55 |
| | Methanol | DBA | 65 | 0.051 | 13 | 51 |
| | Toluene | DBA | 35 | 0.0061 | 3.7 | 70 |
| Cu/Si | Methanol | Morpholine | 65 | 0.051 | 48 | 42 |
| | Methanol | Pyridine | 70 | 0.088 | 56 | 50 |
| | Methanol | DBA | 70 | 0.077 | 22 | 65 |
| | Toluene | Morpholine | 55 | 0.0044 | 11.3 | 76 |
| | Toluene | Pyridine | 50 | 0.0098 | 7 | 74 |
| | Toluene | DBA | 35 | 0.0036 | <3 | 80 |
| Cu/Si, IW | Methanol | Pyridine | 60 | 0.041 | 44 | 50 |
| | Toluene | DBA | – | 0.000 | – | – |
| Cu/Si ^a | Toluene | DBA | – | 0.000 | – | – |

^a Catalyst used in methanol/pyridine.

solvent for the polymer, and to look for other amines. It is known that in industrial processes dibutylamine, alone or together with butyl-dimethylamine (BDMA) and *N,N'*-di-*tert*-butyl-ethylenediamine (DBED), is widely used.

Most significant results obtained are summed up in Table 2 and Fig. 2.

It is apparent from these data that moving from methanol to toluene had the most significant effect on lowering the copper leaching according with the above mentioned hypothesis, even though the reaction rates were much lower. However, direct comparison of the reaction rates does not account for the relevant oxygen uptake due to complexation and oxidation secondary reactions occurring in methanol/amine

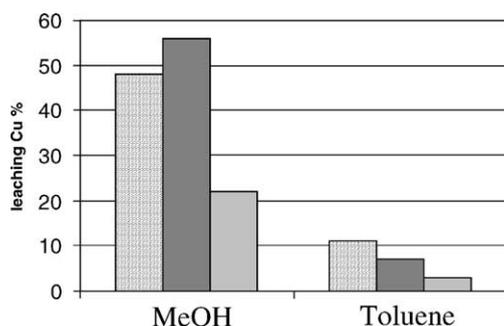


Fig. 2. Copper leaching from Cu/SiO₂ under different solvent/amine conditions: (▨) morpholine; (■) pyridine; (■) DBA.

systems. Among the three amines considered, pyridine gave the higher loss, according to its high coordinating ability, whereas DBA, more basic but with a very low coordinating power gave the best results, allowing to lower the metal leaching to less than 3%.

Under these conditions, the oxygen uptake roughly corresponds to that required by the reaction stoichiometry, showing that in methanol/amine systems both the oxygen consumption and the metal leaching are due mainly to secondary oxidation reactions.

In order to verify whether, or how much, the leached metal contributes to the polymerisation reaction, several experiments were carried out by filtering the solid material under O₂ at about 30% conversion and allowing the filtrate to react further (see Section 2). Under these conditions the amount of polymer recovered from the solution corresponded to less than one-third of the usual amount, showing that no PPE formation took place after removing the solid catalyst.

It is also worth noting that in homogeneous catalysed reactions small and basic amines favour C–O coupling reactions with respect to C–C coupling ones [13]. When using Cu/SiO₂ in toluene the yield in polymer keeps almost unchanged by varying the amine. This suggests that the mechanism in this case is significantly different from the homogeneous one and that the amine acts only as a base and does not enter in the coordination sphere of the active metal site.

One more point strongly supporting the heterogeneous mechanism is that the catalytic system works without water absorbing agents. Such agents are normally used in toluene since water formed during reaction can deactivate the catalyst inhibiting reoxidation of Cu(I) species [14].

The same prerduced supported copper catalysts used in this work are active also in dimethylcarbonate (DMC) synthesis. In this case, the catalyst was suspended in methanol only and the reaction carried out at 130 °C under 25 bar ($\text{CO}/\text{O}_2 = 5/1$). Under these experimental conditions leaching of the metal was found to be negligible and the catalyst could be repeatedly re-used without any decrease in activity [15]. It is also worth outlining that these catalysts do not contain halide ions, that are considered essential for the activity of homogeneous systems in both DMP polymerization and DMC synthesis, nor they are prepared starting from halogenated precursor.

3.3. Effect of the solvent/amine couple on the polymer properties

Another improvement obtained with the toluene/amine systems is that a significant increase in the polymer yield is obtained, as secondary reaction involving also DMP are lacking.

Moreover, the use of toluene instead of methanol has also a positive effect on the polymer properties. Thus, when the reaction was carried out in methanol/pyridine the average M_w , as determined by GPC was around 5000, whereas in toluene/DBA it reached 16,000 with a narrower distribution. This could be due to the different solubility of PPE in the two solvents, inducing early precipitation in methanol systems. However, the basicity of DBA, aiding deprotonation of the substrate and of oligomers, can play a role in the polymer growing as already observed also in biphasic systems [16].

This new catalytic system appears to be different from the methanol/pyridine one also from the mechanistic point of view. Thus, when the polymerization reaction was carried out in toluene/DBA, the catalyst recovered was no more active.

However, addition of fresh substrate at the end of the first run resulted in a restart of the oxygen uptake, thus suggesting that catalytic deactivation is probably linked to the recovery procedures.

Some experiments were also carried out to investigate the nature of the active metal particles. The catalyst preparation method has a strong influence on the metallic phase morphology. Thus, conventional IW technique allows formation of only two-dimensional particles, at least on titania [10], while the chemisorption-hydrolysis method allows formation of well formed three-dimensional crystallites together with plate-like two-dimensional ones, either on titania, on silica or silica–titania [9,10]. A Cu/SiO₂ sample prepared by IW, therefore supposed to expose mainly two-dimensional particles, was found to be active in methanol/pyridine but failed to react in toluene/DBA.

Moreover, a sample prepared by the CH technique, used in the polymerization reaction in methanol/pyridine, conditions that have been shown to leave only two-dimensional particles [8], was separated and reactivated by reduction but it did not show any activity in toluene/DBA.

This prompts us to suggest that in toluene/DBA mainly three-dimensional particles on the surface of Cu/Si are involved.

The mechanism of DMP polymerization in homogeneous phase has been studied in detail due to both the importance of the industrial process and its resemblance to the mechanism of action of copper protein with a type three active site, e.g. tyrosinase, particular attention being given to the effect of the ligands [17–20].

The formation of a dinuclear phenolate bridged copper(II) complex, after the initial deprotonation of the substrate by the base, is generally accepted [21,22]. The presence of halides as bridging counterions is therefore required to allow the formation of these dinuclear species.

Characterization of catalysts before and after the polymerization reaction and in situ EXAFS and XANES experiments are already in progress with the aim to verify if and how surface metallic particles can be the equivalent of dinuclear copper species.

4. Conclusions

The performance of Cu/SiO₂ in the oxidative coupling of 2,6-dimethyl-phenol has been greatly improved by modifying the solvent/amine couple ac-

ording to the known reactivity of metallic copper species. The use of toluene as solvent and dibutylamine as base allows to reduce the metal leaching to less than 3%, to increase the polymer yield up to 80% and to obtain a higher molecular weight.

Although the mechanism is far to be understood as it is not easily amenable to that proposed for deeply investigated homogeneous systems and the activity is quite low, this catalytic system represents an effective heterogeneous one.

Acknowledgements

The authors gratefully thank the CNR-MIUR for financial support through the “Program Chemistry LAW 95/95-III year” and Ing. Raniero Mendichi of ISMAC-CNR for GPC measurements.

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