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Cu/SiO_2 and Cu/SiO_2–TiO_2 Catalysts

II. Identification of the Active Sites during Polymerisation of 2,6-dimethylphenol in the Presence of Molecular O_2

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8% Cu/SiO_2 and Cu/SiO_2–TiO_2 catalysts, prepared by the chemisorption hydrolysis method and characterised in the preceding paper (Boccuzzi *et al.*, 1999, *J. Catal.*, 184, 316–326) have been tested in the oxidative coupling of 2,6-dimethylphenol, a well-known copper catalysed reaction in the homogeneous phase. All of them proved to be active after reduction of the copper oxide initially present giving ∼75% of PPE and <4% DPQ. Although they lost ∼30% of the metal during the first run, they appeared to be reusable and more active during the second run. From HRTEM and FTIR characterisation before and after the polymerisation reaction, it can be deduced that three-dimensional copper particles are preferentially leached under the reaction conditions, while electron deficient two-dimensional metallic particles can be responsible for the catalytic activity. © 1999 Academic Press

Key Words: **copper catalysts; oxidative coupling; polyphenilene-ethers; oxygen activation.**

1. INTRODUCTION

The ever growing number of patents being filed on the use of heterogeneous copper catalysts witnesses their renewed interest due to their selectivity and low ecotoxicity.

Following our continuous interest in exploring the potentiality of supported copper catalysts, we recently focused our attention on the stability of the metallic phase. Some of us already found evidence of neither sintering nor leaching occurring when working under hydrogenation conditions even with vegetable oil as a medium (1, 2). To have a deeper insight into the behaviour of these systems, we looked at the reactions carried out under oxidative conditions.

Several industrial processes are catalysed by copper salts in the homogeneous phase, among them namely the polymerisation of 2,6-dimethylphenol (DMP) and the synthesis of dimethylcarbonate. To find a heterogeneous alternative for the last two might be worth doing, but reaction conditions are quite demanding for a heterogeneous system to survive. Thus, both of them require the presence of molecular oxygen and of coordinating ligands such as amines that can easily promote leaching of the metal.

Here we report results obtained by using supported copper catalysts in one of these reactions and to show that these systems, on the contrary to what was observed on Cu/Al_2O_3 and Cu/Cr_2O_3 (3), can work under oxidative conditions, even in the presence of coordinating ligands.

We investigated the oxidative coupling of 2,6-DMP to give poly-2,6-dimethyl-1,4-phenylene ether (PPE). PPE is an important engineering plastic utilized in blends produced worldwide on a 300,000 tonnes/year scale (4) (Scheme 1).

The reaction is industrially carried out at 25–50°C, by passing oxygen through a vigorously stirred phenol solution containing a catalyst, typically composed of a copper halide salt and one or more aliphatic amines or pyridine, to give straight-chain PPE by C–O coupling in high yield, whereas the noncatalysed reaction takes place only at 300°C and yields a cross-linked polymer with inferior mechanical properties.

The main by-product of this reaction is a diphenoquinone (DPQ) derived from C–C coupling, whose formation not only decreases the yield, but also degrades the polymer, thus requiring extensive purification. The original system gives 85% of PPE and 3% of DPQ (5) while homogeneous catalysed reactions can give up to 95% of the polymer (5c).

Attempts to heterogenize the catalytic system mainly rely on the use of an excess of oxidizing agents such as silver (6), lead (7), and manganese oxides (8) or heterogeneous copper (II) complexes (9).

The mechanism of this reaction has been studied in detail due to both the importance of PPE and its resemblance to the mechanism of action of copper proteins with a type 3 active site, e.g., tyrosinase. However, some aspects have not been fully elucidated, particularly the nature and structure of the copper intermediate species and the role of oxygen.

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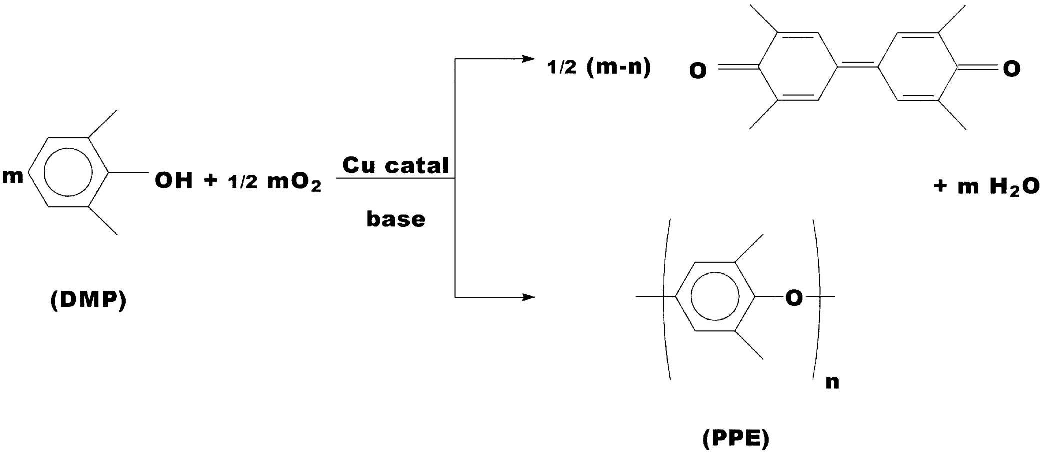


SCHEME 1

Historically, the reaction mechanism was thought to employ mononuclear copper–phenoxo complexes affording phenoxy radicals as the key species. More recent proposals by Challa (10a,b) involve the formation of a dinuclear phenolate-bridged copper (II) complex, after initial deprotonation of the phenol by the base used as cocatalyst.

This complex will then undergo two one-electron transfers from one bridging phenolate to the copper ions, resulting in a dinuclear copper (I) species and phenoxonium cation. This cation may then react with another molecule of phenol, which will result in C–O coupling.

After reoxidation of the copper (I) species by dioxygen the dimer can react further and will ultimately afford the polymer (Scheme 2).

Therefore, it should be more appropriate to call this reaction a dehydrogenation than an oxidation, as no dioxygen is incorporated into the products. Dioxygen is only needed for the reoxidation of copper (I) to copper (II) and the regeneration of the base by the formation of hydroxide.

The role of chloride ions has also been investigated in detail. It has been proposed that copper coordinating counterions such as halides should be present to allow the formation of the μ-halide dinuclear species, required for the reoxidation step (10c,d).

In this paper we will present the results obtained in the presence of two 8% Cu/SiO_2–TiO_2 samples and for the sake of comparison of a catalyst with the same copper loading supported on a silica gel of comparable surface area and porosity and of a Cu/TiO_2 sample already described (11). These results will be described in light of the HRTEM and FTIR characterisation of fresh and used samples.

2. EXPERIMENTAL

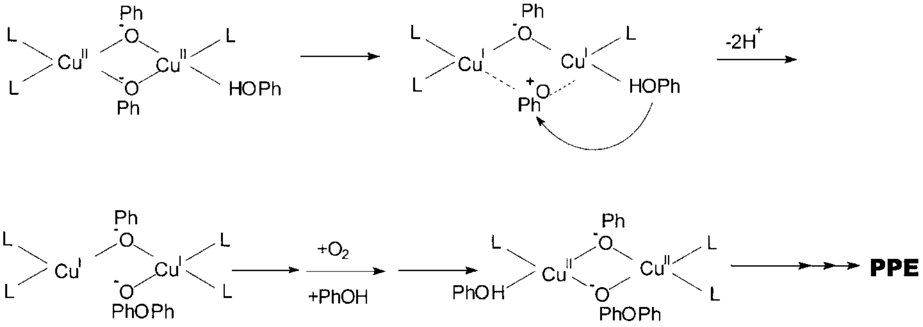
2.1. Materials

2,6-dimethylphenol (DMP, Fluka) was recrystallised from *n*-hexane before use and methanol and pyridine (both from Carlo Erba) were of the highest purity available. O_2 was 99.99% pure.

The catalysts were the Cu/SiO_2, Cu/SiO_2–0.3% TiO_2, and Cu/SiO_2–2.3% TiO_2 samples which were the subject of the preceding paper. They will be hereafter referred to as Cu/Si, Cu/SiTi0.3, and Cu/SiTi2.3, respectively.

2.2. Methods

Electron micrographs and FTIR spectra were obtained as reported in Part I.



SCHEME 2

2.3. *Catalyst Activation and Procedure for 2,6-dimethylpenol Oxidation*

The catalysts (400 mg) were treated under vacuum at 543 K for 20 min and then reduced under H_2 at the same temperature. After cooling under H_2, 400 mg of 2,6-DMP in 10 cc of methanol and 2 cc of pyridine were added under N_2; then O_2 was introduced. Final conversion was determined by GLC using a methylsilicone capillary column.

The O_2 uptake was measured continuously through a gas burette and the initial rate was calculated as the derivate for $t = 0$ of the curves of oxygen uptake against time. These values were taken as a measure of the catalytic activity.

Most of the polymer precipitated during reaction. At total conversion, the reaction mixture was filtered off, the catalyst separated from the polymer by extraction in Soxhlet with methylene chloride, and the copper content determined by AA. The CH_2Cl_2 extract was added to the reaction mixture; the dibenzoquinone content was determined by UV at $\lambda = 415.6$ nm on the resulting solution and the polymer was determined by weight after reprecipitation with hydrochloric acid.

In the recycle experiments, an amount of substrate equivalent to the catalyst recovered was used.

3. RESULTS AND DISCUSSION

3.1. *Polymerization Reactions and Catalytic Behaviour*

Our results are shown in Table 1. Cu/TiO_2 was also investigated for the sake of comparison. The bare support was completely inactive (entries 2 and 5). The oxidation of 2,6-DMP in the presence of the unreduced catalyst took a very long time to reach complete conversion. Selectivity towards PPE was very low, while C–C coupling products were formed in relevant amounts. Moreover, significant leaching of the metal was evident since the beginning of the O_2 absorption (entry 3). On the other hand, all the catalysts examined were found to be active (under the experimental conditions used) when reduced before reaction.

The inactivity of the calcined systems, where all the metal is present as CuO, is in agreement with the fact that, although apparently the true oxidising agent in the original process developed by the General Electric group consists of a copper (II) complex prepared by autooxidation of CuCl in pyridine $(pyCuClOCH_3)_2$, replacement of cuprous chloride by the cupric salt under the same conditions results in an inactive system, indicating that the oxidation of CuCl must yield a product which cannot be described in the usual terms (12). Moreover, in the homogeneous phase Cu(II)-amine complexes are found to be active only in the presence of strong bases as KOH or NaOMe (13).

Therefore, we can suggest that interaction with oxygen in the presence of the substrate and of the nitrogen base makes the reduced catalysts evolve to the suitable configuration, as far as both geometry and oxidation state are concerned.

As shown in Part I (14), all the exposed Cu after the reductive treatment is fully reduced to the metallic state. Part of it consists of three-dimensional crystallites, while the other consists of two-dimensional particles of copper made partially electropositive by the interaction with the oxidic support.

The catalysts used showed comparable selectivity, all of them giving more than 75% yield in the polymer and a very low amount of DPQ (<4%). Moreover, most of the

TABLE 1

Yield of PPE (PPE%), Variation of Metal Content, and Initial Rate (V_{in}) Obtained in the Oxidative Coupling of 2,6-dimethylphenol with Different Copper Catalysts

Entry	Catalyst	PPE yield (%)	Cu loading Before test (wt%)	Cu loading After test (wt%)	ΔCu%[a] (%)	V_{in} ml $O_2 \cdot sec^{-1} \cdot g_{at}\,Cu^{-1}$
1	Cu/Si	78	7.7	5.5	−29	0.5521
	Cu/Si[b]	76	5.5			0.8346
2	SiO_2–TiO_2 0.3%	—[c]				
3	Cu_xO/SiTi0.3[d]	25				
4	Cu/SiTi0.3	76	8.8	6.0	−32	0.1443
	Cu/SiTi0.3[b]	75	6.0			0.3651
5	SiO_2–TiO_2 2.3%	—[c]				
6	Cu/SiTi2.3	75	8.1	5.6	−31	0.1695
	Cu/SiTi2.3[b]	76	5.6			
7	Cu/TiO_2	77	8.7	<2		0.3266

[a] $\Delta Cu\% = [(Cu\ wt\%_{after\ test} - Cu\ wt\%_{before\ test})/Cu\ wt\%_{before\ test}] \times 100$.

[b] Recycled.

[c] No reaction after 24 h.

[d] Unreduced catalyst.

polymer precipitated during reaction, which is indicative of a high degree of polymerisation.

Minor differences were found in activity, Cu/Si giving the fastest reaction, but all the catalysts reached total conversion within an hour. As far as activity is concerned, results cannot be easily interpreted on the basis of metal dispersion or surface area, as all the three system objects of this study show very similar surface features.

The independence of selectivity on the catalyst used can be accounted for by the close similarity observed among the metallic phases, already discussed in Part I.

However, the most interesting feature appears to be the stability of the catalysts under oxidative conditions. All three catalysts have been recovered and reused after the polymerisation reaction. The Cu/TiO_2 system used for the sake of comparison lost most of the metal and could not be reused.

This difference can be ascribed not only to the nature of the supporting oxide, but also to the absence of pores on the surface of the fumed titania used. Work is in progress to elucidate the role of porosity in stabilising the metallic phase.

Copper content determination on the catalysts showed that in all cases about 30% of the metal was lost during the first cycle (Table 1, entries 1, 4, 6). However, the catalysts were very easily re-reduced by H_2 treatment at 523 K and not significant differences in selectivity were observed. To remove some uncertainties on the role of soluble copper on the reaction pathway, fresh substrate was added to the filtrate of one reaction mixture. No reaction occurred under these conditions.

As far as activity is concerned, we wish to underline that a sharp increase in oxygen uptake initial rates was found when reusing the catalyst (Table 1, entries 1, 4). This may suggest not only that the fraction of metal leached from the support is not involved in the reaction pathway, but also that new active sites become available.

3.2. Comparison of Surface Properties of Fresh and Used Catalyst

To have a deeper insight on the nature of the species involved, and in particular to elucidate which one of the two copper species is directly involved in the polymerisation reaction, we have studied by means of FTIR spectroscopy and by transmission electron microscopy the Cu/Si sample before and after the catalytic test. After the reaction and extraction of the products with methylene chloride, the catalyst was dried and re-reduced in 30 mbar of H_2 at 523 K.

3.2.1. TEM studies. In Figs. 1a and 1b electron micrographs of the Cu/Si sample taken before and after the reaction are compared. In the case of the fresh catalyst, copper particles appear well contrasted with respect to the silica carrier (Fig. 1a), and, as previously reported in Part I, their size distribution results in a mean diameter $d_m = 3.5$ nm. Furthermore, high magnification images of the border region of the carrier, where the profile of the supported particles is observable, evidenced that Cu particles almost spherical in shape are present (Fig. 1a, inset).

After the catalytic run, Cu particles appear less easily distinguishable on the support, as they are thinner, and slightly smaller in size—their mean diameter being reduced to 3.0 nm (a histogram of the particle size distribution not reported for the sake of brevity). The analysis of the profile of the particles located at the border of the silica grains revealed that most of the Cu particles are flat, and, in some cases, they appear as a thin layer in close contact with the support (Fig. 1b, inset). The actual presence of copper in such layers was confirmed by the fact that, by prolonged exposure to the electron beam, they are transformed in small spherical-shaped particles. Moreover, these layers were not observed on the bare support, nor did the exposure to the electron beam of its border region result in similar effects.

These features suggest that the observed leaching of a fraction of supported copper occurs through the disruption of the three-dimensional metal particles, in some cases leaving on the carrier only the metal layer in closer contact (and probably stronger interaction) with the silica surface.

3.2.2. FTIR characterisation. Figure 2 shows the experimental FTIR spectra of 10 mbar of CO adsorbed on a fresh sample (Fig. 2a) and on a sample already used in the polymerisation reaction (Fig. 2b), both prereduced in hydrogen at 523 K and the curvefitting of these spectra obtained by superposition of Lorentzian bands; the integrated intensities of the bands are summed up in Table 2.

The analysis of the spectroscopic data concerning the CO chemisorption on the used catalyst in comparison with the fresh one indicates that the overall integrated intensity decreases significantly; however, the changes observed in the individual components are very differentiated: the low frequency components are almost completely depleted while the high frequency component exhibits a small intensity increase. As discussed in Part I, the low frequency components can be assigned to CO chemisorbed at the surface of well-defined three-dimensional small copper particles while the high frequency component, on the basis of its frequency and its behaviour to the reduction of CO pressure, can be assigned to CO adsorbed on two-dimensional, electron deficient copper particles. The increase in the intensity of the high frequency component appears as an indication that by the leaching of the three-dimensional copper particles some new two-dimensional particles are produced.

From the comparison of the used and fresh sample spectroscopic features it can be concluded that in the used samples the copper sites exposed at the surface of the three-dimensional particles are almost completely depleted, while the two-dimensional particles increase.

Therefore, we can conclude that the three-dimensional particles are preferentially leached from the catalyst surface

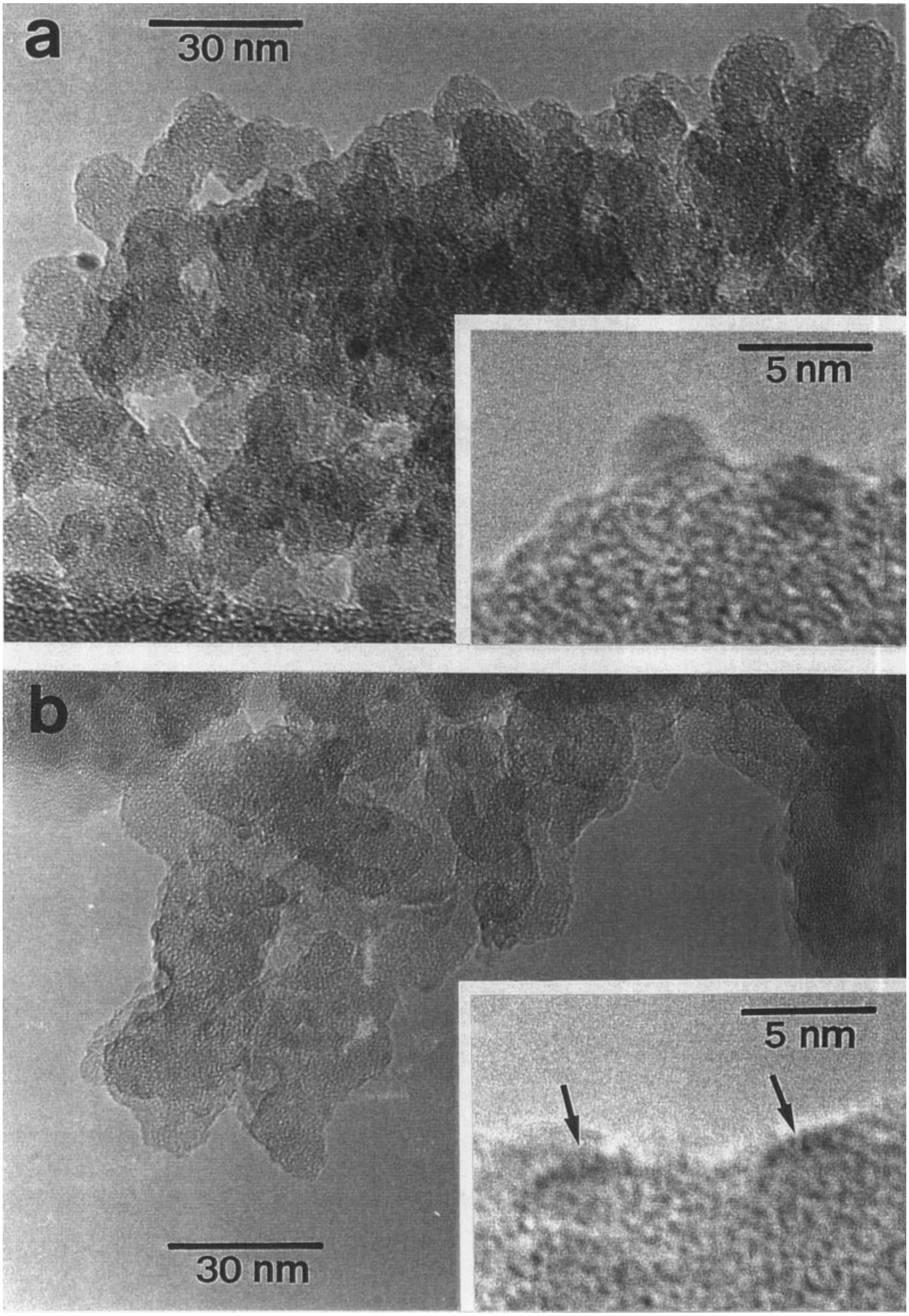


FIG. 1. Electron micrographs (original magnification: ×200,000) of the Cu/Si catalyst: (a) fresh sample, reduced in H_2 at 523 K; (b) after catalytic run, and subsequent washing, drying, and re-reduction in H_2 at 523 K. Insets: particular of the border region of catalyst grains (original magnification: ×500,000); arrows in the inset of (b) evidenced layer structures containing copper.

TABLE 2

Integrated Intensity (I/M, Normalised to the Weight of the Pellet) of the Four Components at 2128, 2110, 2100, and 2070 cm^{-1} Obtained by Fitting the FTIR Spectra of CO (10 mbar) Adsorbed onto the Fresh and Used Cu/SiO_2 Catalyst

	Band at 2128 cm^{-1}		Band at 2110 cm^{-1}		Band at 2100 cm^{-1}		Band at 2070 cm^{-1}	
Cu/SiO_2 catalyst	I/M (cm^{-1})	$\Delta I/M$ %[a]	I/M (cm^{-1})	$\Delta I/M$ %[a]	I/M (cm^{-1})	$\Delta I/M$ %[a]	I/M (cm^{-1})	$\Delta I/M$ %[a]
Fresh	16		17		38		14	
Used	25	+56	7	−60	3	−92	2	−86

[a] $\Delta I/M\ \% = [(I/M_{\text{used}} - I/M_{\text{fresh}})/I/M_{\text{fresh}}] \times 100$.

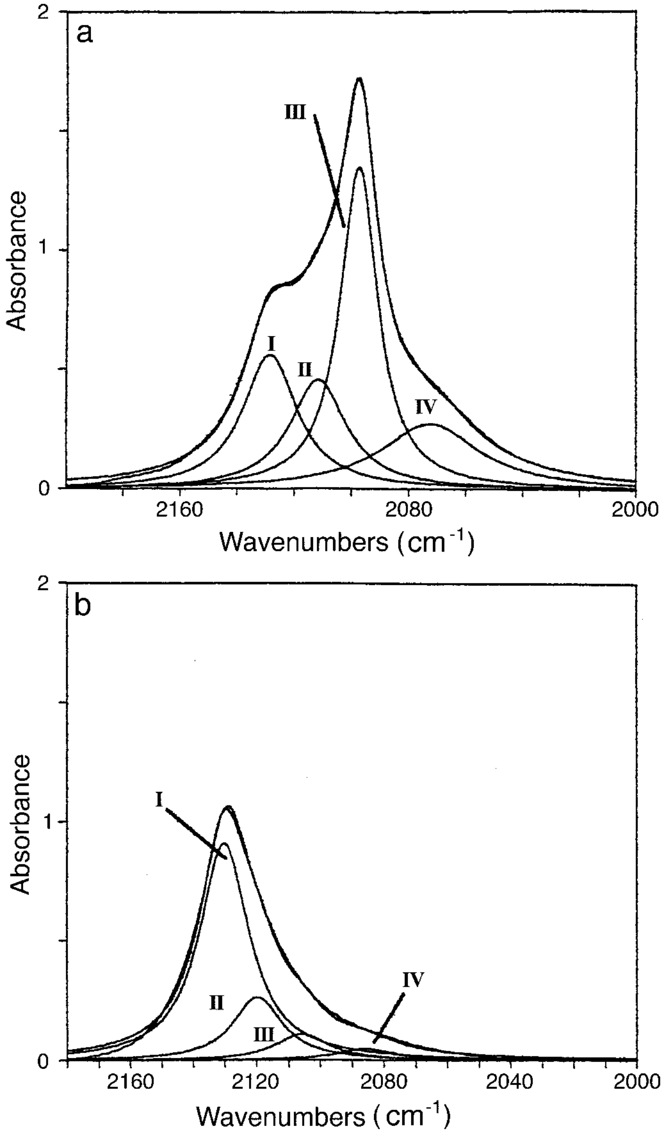


FIG. 2. FTIR spectrum of 10 mbar CO adsorbed on fresh (a) and used (b) Cu/Si catalysts reduced at 523 K. Curves I–IV in both parts are the individual components obtained by a curve-fitting procedure of the experimental spectrum.

during the first cycle. The small increase in the intensity of the high frequency component appears as an indication that by the leaching of the three-dimensional copper particles some new two-dimensional structures are exposed. These could correspond to the layers at the interface between the fully reduced three-dimensional copper particles and the support.

Leaching of these particles is well in agreement with the experience of some of us on the reactivity of metallic copper in the presence of molecular oxygen. It has been shown that a suspension of metallic copper in methanol is quite stable under an oxygen atmosphere up to 60°C, but by adding pyridine the metal could be solubilized already at room temperature through the absorption of O_2 and the formation of $Cu(OMe)_2$ (3).

Figure 3 illustrates the effect of oxygen inlet on the preadsorbed CO on a fresh (Fig. 3a) and on a used (Fig. 3b) Cu/Si sample observed in two experiments made in the same way. On the fresh sample two phenomena are observed: the depletion of the bands assigned to CO adsorbed on the three-dimensional particles and a limited growth of absorption bands in the 2130–2140 cm^{-1} region; the overall integrated intensity of CO absorption bands by oxygen interaction decreases about 32%. On the used sample mainly the growth of the absorption at 2130 cm^{-1} is observed; moreover, after the interaction the overall integrated intensity of CO absorption band increases 16%.

In order to find from these data an indication on the nature of the sites active in the reaction examined some points must be considered, in particular that carbon monoxide is weakly adsorbed at RT on metallic copper sites, irreversibly adsorbed on Cu(I) sites, and does not adsorb at all at RT on Cu(II) sites; moreover the absorption coefficient of CO adsorbed on Cu(I) sites is higher of that of CO adsorbed on Cu(0) sites (15). The decrease in the overall integrated intensity of CO by oxygen interaction on the fresh sample can be taken as an indication that a large fraction of the Cu(0) sites exposed at the surface of three-dimensional particles are fully oxidised to Cu(II) sites, while the increase observed on the used sample can be taken as an indication that the oxidation of the Cu(0) sites of the two-dimensional copper particles gives rise to Cu(I) sites, absorbing CO whose

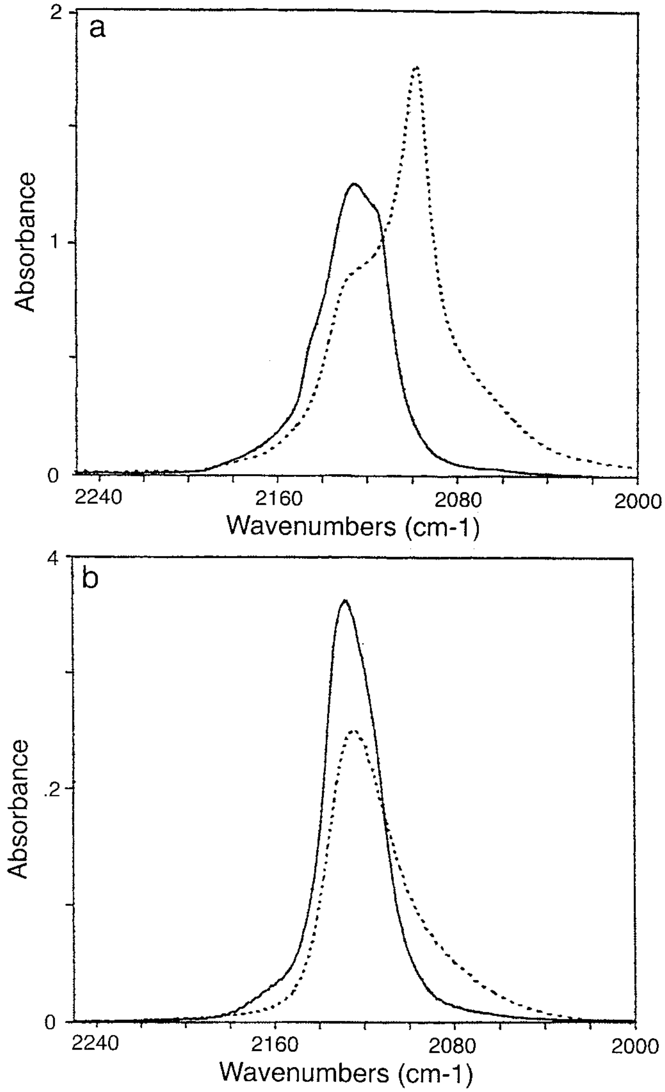


FIG. 3. FTIR spectra of O_2 interaction with CO preadsorbed on fresh (a) and used (b) Cu/Si catalysts reduced at 523 K: (dotted line) spectrum recorded in the presence of 10 mbar CO; (solid line) spectrum recorded 2 min after the inlet of 10 mbar O_2 into the cell.

stretching frequency is almost coincident with that of the Cu(0) sites of the clean two-dimensional particles. The more oxidised nature of the adsorption sites is testified to by the higher resistance of the band to the outgassing at RT (not shown for sake of brevity). The lower propensity of the two-dimensional copper particles to be fully oxidised can be ascribed to the electron deficient nature of these copper sites. We recall here that we have previously observed on Cu/TiO$_2$ samples prepared by wet impregnation a very large effect of the oxygen inlet on the CO absorption band intensity (16) and this phenomenon was related to both an increase in the CO absorption coefficient and to an increase of the exposed copper sites, which on the strongly reduced samples are covered by a titanium suboxide layer. On the Cu/SiO$_2$ sample the increase of the absorption coefficient of the CO absorption band will occur exclusively.

It must be stressed that: (1) the unreduced samples are inactive; (2) the presence of TiO$_2$ does not affect the activity of the catalysts; (3) a substantial part of the metallic phase is lost during the first catalytic run; (4) three-dimensional copper particles are almost lacking on the used catalysts; (5) the catalytic activity of the used samples is higher than that of the fresh ones. The last three points considered appear as an indication that the sites active in the examined reaction are Cu centres on two-dimensional electron deficient reduced copper small particles.

In a previous paper concerning the effect of the catalyst morphology of Cu/TiO$_2$ catalysts on the hydrogenation of the 1,3-cyclooctadiene (16) it was observed that the activity of the sample exposing three-dimensional copper particles was 100 times greater than that of the sample exposing isolated copper sites embedded in the reduced support. The different activity was interpreted taking into account that the small copper particles expose a high fraction of highly uncoordinated copper sites, very efficient in the hydrogen dissociation, whereas the small two-dimensional particles are less efficient in the hydrogen dissociation. In the oxidative coupling reaction presented in this work taking place in the presence of oxygen, the catalytically active copper is the one exposed at the surface of the small two-dimensional particles. It has been shown (17) in a study on monocrystalline copper surfaces that the more reactive oxygen species is a O^--like species while O^{2-}-like species are far less reactive. The first species is formed on defective, isolated sites, while the second one is formed on regular planes. It can be proposed that by oxygen interaction on the three-dimensional particles mainly a regular oxide layer is formed, stabilised by Coulomb interactions between anions and cations, while on isolated sites or on small two-dimensional particles larger amounts of reactive O^- species are formed, possibly by the "catalytic" help of pyridine in the oxygen cleavage with a three-centre mechanism (17, 18). This species could be active and efficient in the H-abstraction from the C–H bond.

The mechanism proposed for the homogeneous catalysed reaction (10) put in evidence the relevance of dinuclear copper species in the catalytic process and particularly their essential role in the re-oxidation step from Cu(I) to Cu(II). The presence of halides as bridging counterions is therefore required to promote formation of these dinuclear species.

In the case of supported copper catalysts, electron deficient two-dimensional metallic particles might be proposed as the equivalent of dinuclear species. Interaction with the support makes them less reactive towards oxygen, thus avoiding their full oxidation to copper (II) oxide, which is inactive.

The key role of polynuclear species is also well established for copper enzymes. The known binuclear Cu proteins hemocyanin and tyrosinase bind O_2 through $2e^-$ reduction to O_2^{2-}, while the fully reduced three-nuclear site is the minimal structural subunit required for biological O_2 bond cleavage and reduction to H_2O (19).

4. CONCLUSIONS

We have studied the polymerization of 2,6-dimethylphenol in the presence of three supported copper catalysts. These have shown to be true heterogeneous catalysts for this reaction, notwithstanding the demading reaction conditions. These catalytic systems do not contain halide ions, nor are they prepared starting from halogenated precursors.

HRTEM and FTIR characterisation of a Cu/SiO_2 sample before and after the catalytic run allowed us to identify the active sites as two-dimensional metallic particles made partially electropositive by interaction with the support. This same interaction avoids the full oxidation of these particles to CuO and therefore its deactivation.

Therefore this kind of supported catalyst may be proposed as a first step towards the heterogenisation of industrial processes catalysed by copper salts in a homogeneous phase like the synthesis of PPE and of dimethylcarbonate.

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