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## Heterogenized polymetallic catalysts Part II. Oxidation of 3,5-di-t-butylphenol by Cu(II), Fe(III) and Pd(II) complexed to a polyphenylene polymer containing $\beta$ -di- and triketone surface ligands; an improved catalyst system $\stackrel{k}{\Rightarrow}$

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#### Abstract

Polyphenylene polymer preparation involves the cyclic trimerization polymerization of acetylated methyl benzoate with diacetyl benzene. Since the methyl benzoate groups do not take part in the polymerization they are present in high concentration. The  $\beta$ -diketone ligands were placed on the surface by reaction of the methylbenzoate group with base and a methyl ketone and the triketone by reaction with base to give the  $\beta$ -triketone. The  $\beta$ -triketones can bind two metal ions in a known geometry that is suitable for bimetallic catalysis of the rapid polyelectron oxidation of catechols. The final catalytic surfaces were prepared by treating the chemically modified polymer with copper(II), iron(II) and palladium(II) acetonitrile complexes with non-coordinating BF<sub>4</sub><sup>-</sup> as the anion. Since the metal ions contain no strongly coordinating ligand, they are very reactive species. These surfaces catalyzed the rapid air oxidation of 3,5-di-tert-butylcatechol (DTBC). The diketone surfaces gave only 3,5-di-tert-butyl-o-quinone (DTBQ) while the triketone surfaces gave ring-cleaved products, confirming the special catalytic effect of the triketone surface. Also, only the triketone catalysts showed any activity for ring cleavage oxidation of DTBQ. These catalysts were much more reactive than previous ones using the same polyphenylene polymer but without the methyl benzoate groups. With these polymers the di- and triketone groups were placed on the surface by chemical modification of the unpolymerized acetyl groups.

Keywords: Polymetallic catalysts; Oxidation; Polyphenylene polymer; Copper complexes; Iron complexes; Palladium complexes

## 1. Introduction

## 1.1. General

In the first paper of this series the air oxidation of 3,5-ditert-catechol (DTBC) catalyzed by polymer supported mono- and bimetallic Cu(II) and Fe(III) species was described [1]. The polymer was a polyphenylene type prepared by the cyclic trimerization of acetyl groups [2]. Diketone surface ligands were placed on the surface by reaction of the acetyl end groups with base and methyl acetate to place  $\beta$ -diketone groups on the surface. The diketone groups were reacted with more base and methyl acetate to then put  $\beta$ - triketone ligands on the surface. Both surfaces were treated with metal ions to give the surface mono- and bimetallic surface complexes. The rigid poylphenylene-type polymer structure was chosen because the surface ligands cannot diffuse together to form bis complexes. Since these surface complex species are coordinately unsaturated, these heterogeneous catalysts should be more reactive than their bis or tris complexed counterparts in homogeneous solution.

These surface complexes were found to be effective catalysts for the air oxidation of DTBC [1]. The expectation that the surface species would be more reactive than their homogeneous counterparts was fulfilled. The monometallic catalyst oxidized DTBC to 3,5-di-tert-butyl-o-quinone (DTBQ). The bimetallic catalyst oxidized DTBC to ring-cleaved products.

The approach described above uses the acetyl moieties, which also take part in the polymerization, as the groups that are modified to give the surface ligands. As the polymerization proceeds, the concentration of acetyl groups continu-

<sup>\*</sup> This paper is dedicated to Professor F. Basolo.

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ously decreases, so that by the time the high polymer is formed, their concentration could be quite low. The approach of the present study involves the use of a group, which does *not* take part in the polymerization, for chemical modification.

#### 1.2. Catalyst system

The group used for the chemical modification is the methyl benzoate functionality. The polymer is prepared by the polymerization of m- or p-acetyl methylbenzoate with m- or p-diacetylbenzene (Eq. (1)). Since the methyl benzoate function is not involved in the polymerization, its concen-



tration should be much higher that the acetyl function used for chemical modification in the previous studies.

As shown in Scheme 1, the chemical modifications now involve the reaction of the methylbenzoate surface species with the anion of a methyl ketone to give 1 and with the dianion of a  $\beta$ -diketone to give the triketone, 3. This reaction sequence places the two types of ligand groups on the polymer surface selectively. The first reaction only puts on the di species while the second reaction only puts on the tri without any contamination from the diketone surface species. Thus, when treated with metal ions, pure 2 and 4 will be formed.

Since it was the organic substrate used in the previous studies, 3,5-di-t-butylcatechol is also used in these studies. A common substrate will permit a more direct comparison between the two catalyst systems.

## 1.3. Previous studies

Iron and copper complexes have received considerable attention because they are the main metals found in biological dioxygen metabolism [3]. Although heme iron systems for dioxygen bonding [4] and dioxygen activation [5] are now fairly well understood, non-heme iron systems are not. Thus the oxidative cleavage of catechol by the high-spin ferric enzymes, pyrocatechase and metapyrocatechase, is one of the most interesting and widely studied biological oxygenating processes [6]. In spite of considerable effort, only three model systems give the activity of the natural enzymes [7-9]. Two of these systems give the intradiol cleavage to cis, cismuconic acid [7,8] while the other gives both types of cleavage, thus more closely duplicating the pyrocatechase activity [9]. Considerable effort has also been put into studies of model compounds for dioxygen binding (haemocyanins) or dioxygen-activating copper proteins such as the tyrosinase monooxygenases which catalyze the orthohydroxylation of phenols [10–18]. All of these copper model systems are bimetallic.

There has also been considerable study of the use of simple copper complexes, which are also usually bimetallic, for the oxidation of DTBC to DTBQ [19-22]. Some copper [23,24] and iron [25] homogeneous catalysts cause the ring cleavage of catechols. Several of the systems studied have been polymeric since catalyst removal in these systems is facilitated [26-28].

## 2. Experimental

### 2.1. Materials

Palladium(II) chloride was purchased from Engelhardt, Inc. Palladium sponge was obtained from Aesar and copper wire (turnings, m2N +) from Johnson Matthey. FeCl<sub>3</sub> and Cu(OAc)<sub>2</sub> were Fisher's reagent grade. Fe(OAc)<sub>2</sub> was obtained from Alfa. 3,5-DTBC, 3,5-DTBQ, *p*-toluenesulfonic acid monohydrate (99%), 18-crown-6 (99.5%), iron powder (~10 $\mu$ , 99.9 +%), triethylorthoformate (98%), *p*acetylbenzoic acid (98%), *m*-acetylbenzonitrile, *p*-diacetylbenzene (99%), NaH (dry, 95%) and Celite (high purity analytical grade) were obtained from Aldrich Chemical Co. 3,5-DTBC was recrystallized from n-hexane and dried under vacuum. Samples of potassium nitrosodisulfonate (Fremy's salt), 4-t-butyl-5-methoxy-1,2-benzoquinone and butylated hydroxyanisole were obtained from Spectrum Chemical Mfg. Corp. The latter was mainly 3-t-butyl-4-hydroxyanisole (3-BHA) with variable amounts of 2-t-butyl-4-hydroxyanisole. Pure samples of 3-BHA were obtained by fractional crystallization of the commercial sample from hot hexane containing approximately 3% acetone. All other chemicals were of reagent grade.

#### 2.2. Physical measurements

<sup>1</sup>H NMR spectra were recorded on a Varian VXR-300 NMR spectrometer. Colorimetric analyses were performed using a Perkin-Elmer model 330 spectrometer. FT-IR spectra were recorded using an IBM FT-IR model #98 spectrometer or an ATI Mattson Genesis Series FT-IR. Mass spectra were run on the HP 5985 GC/MS system of Northwestern University, Evanston, IL. Melting points were determined on a Laboratories Devices Mel-Temp apparatus using a calibrated thermometer.

#### 2.3. Preparation of m- and p-acetyl methylbenzoates

*p*-Acetyl methylbenzoate was prepared by refluxing the acid for 2.5 h in methanol which was saturated with dry HCl gas. After workup by addition of brine and extraction with methylene chloride, the crude product was purified by column chromatography on a silica gel column (Aldrich, 70–230 mesh, 60 Å) using methylene chloride as eluant. The final yield was 80%; m.p. 94–96 °C <sup>3</sup>. *m*-Acetyl benzoic acid was prepared by the hydrolysis of the nitrile and esterified by the same procedure.

#### 2.4. Preparation of catalytic surfaces — general

Two procedures which differed in the order of the curing, chemical modification and coating were used. The one used for the Pd(II) catalytic surfaces followed the order: (i) preparation of prepolymer; (ii) chemical modification; (iii) coating onto Celite; (iv) curing. The order for the remainder of the Celite supported surfaces followed the order: (i) preparation of prepolymer; (ii) coating onto Celite; (iii) curing; (iv) chemical modification.

# 2.5. Polymerization of p-acetyl methylbenzoate with p-diacetylbenzene [2]

In a typical run 60 ml of benzene and 6.0 ml  $(3.6 \times 10^{-2} \text{ mol})$  of triethyl orthoformate (TEOF) were added to a dry 500 ml three-necked round bottom flask containing a stirring bar. Then 1.54 g  $(8.63 \times 10^{-3} \text{ mol})$  of *p*-acetyl methylbenzoate and 1.40 g  $(8.63 \times 10^{-3} \text{ mol})$  of *p*-diacetylbenzene were added to the flask. HCl gas was bubbled slowly through the solution which was stirred at room temperature. The color of the solution turned from yellow to red, then to dark red in 30–40 min. The reaction was stopped before the molecular weight of the polymer became high enough for any precipitate to form. A 150 ml portion of absolute methanol was poured into the flask to precipitate the polymer. After stirring for 10 min, the very light yellow-brown precipitate was filtered and washed with ethanol, several times with saturated sodium carbonate solution, water and finally with ethanol. The product was dried on a vacuum pump overnight. The yield was 0.70 g. The polymer was very soluble in methylene chloride and benzene.

The high molecular weight polymer was prepared by the same procedure except the reaction was run for 1.5-2.0 h to obtain the insoluble polymer. The color of the polymer was orange and the yield was 1.1 g. It was not soluble in any ordinary solvent.

## 2.6. Cyclic trimerization of m- and p-acetyl methylbenzoate

The procedure is the same as that used for the polymerization but in the absence of *p*-diacetyl benzene. After precipitation with methanol, the trimer was purified by column chromatography on a silica gel column (Aldrich, 70–230 mesh, 60 Å) using methylene chloride as eluant.

#### 2.7. Coating of the polymer onto Celite

A 40 g sample of vacuum-dried Celite was placed in a 500 ml round bottom flask containing a stirring bar. A solution of 0.61 g of the low molecular weight pre-polymer dissolved in 20 ml of methylene chloride and 60 ml benzene was added to the flask. The mixture was stirred overnight at room temperature. The solvent was evaporated in a rotary evaporator and the polymer coated Celite was dried under vacuum at 100 °C.

#### 2.8. Curing of the supported polymer

The Celite supported polymer was sprayed with a solution containing 5.1 g of p-toluenesulfonic acid monohydrate in 100 ml of ethanol followed by heating in a vacuum oven at 140–180 °C for several hours. After cooling to room temperature the coated polymer was washed with ethanol to get rid of the residue of p-toluenesulfonic acid and dried under vacuum at room temperature. The polymer had a light red color.

#### 2.9. Chemical modification [1]

#### 2.9.1. Triketone surface ligand

In a typical preparation, a dry three-necked round bottom flask purged with argon was charged with 0.61 g  $(2.54 \times 10^{-2} \text{ mol})$  of sodium hydride, and 10 ml of THF (dried over CaH<sub>2</sub>) were injected through the side neck which was covered with a rubber syringe cap. Then 0.95 ml

<sup>&</sup>lt;sup>3</sup> This compound was characterized by standard <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.<sup>1</sup>H NMR:  $\delta$  2.63 (s, 3H); 3.93 (s, 3H); 7.99 (d, 2H, J = 8.25 Hz); 8.02 (d, 2H, J = 8.20 Hz). <sup>13</sup>C NMR:  $\delta$  26.88, 52.46, 128.19, 129.82, 133.88, 140.21, 165.73, 197.51.

 $(9.3 \times 10^{-3})$  of 2,4-pentanedione was added dropwise. There was a vigorous evolution of hydrogen gas for 5 min. The solution was refluxed (70–80 °C) for 2.5 h and then cooled to room temperature. After stirring for an additional 1.5 h, 0.25 g of 18-crown-6 was added. The solution was now a dull orange–brown. A 4.0 g portion of polymer coated Celite and 30 ml of THF were now added. The solution was refluxed for 24 h and then cooled to room temperature and the solvent removed under vacuum. The dark tan residue was cooled to 0 °C and 50 ml of methylene chloride and 50 g of ice were added to the flask. After the evolution of hydrogen gas ceased, 100 ml of 1 M HCl were added and the mixture was stirred for 30 min. The solid was collected and washed with saturated NaHCO<sub>3</sub>, brine, water and finally with ethanol. The yellowish tan solid was dried under vacuum.

In a similar fashion the high molecular weight polymer was also chemically modified to put  $\beta$ -triketone groups on the surface.

## 2.9.2. Diketone surface ligand

To a dry 250 ml round bottom flask under a stream of argon were added 0.19 g  $(7.9 \times 10^{-3} \text{ mol})$  of NaH and 5 ml of THF followed by 0.6 ml  $(4.8 \times 10^{-3} \text{ mol})$  of pinacoly alcohol (3,3-dimethyl-2-butanone). The reaction was refluxed for 0.5 h to form the anion. Then 4.0 g of polymer coated Celite and 20 ml of THF were added followed by refluxing for 14 h. The solution was cooled to room temperature and the THF was removed under vacuum. To the dark tan residue were added 20 ml of methylene chloride and 15 ml of 1 M HCl followed by stirring for 30 min. The modified polymer coated Celite was collected and washed with brine, saturated NaHCO<sub>3</sub>, water and ethanol. It was dried under vacuum.

A similar procedure was used to modify the high molecular weight polymer.

## 2.10. Metal ion uptake by chemically modified surfaces

The metal species used for these studies were FeCl<sub>3</sub>, [Fe(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>, [Cu(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> and [Pd-(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>. The last three were prepared from the metals and nitrosyl tetrafluoroborate (NOBF<sub>4</sub>) using a modification of a published procedure [29]. Iron powder, copper wire and palladium sponge were the forms of the metals. A typical procedure is that for palladium.

To a degassed 500 ml two-necked round bottom flask containing a stirring bar were added 100 ml of redistilled acetonitrile which was dried over CaH<sub>2</sub>. The acetonitrile was carried through three vacuum purge-degas cycles with argon gas to deoxygenate the solution. The flask was then charged with 10.0 g of the diketone or triketone modified polymer coated Celite. To this was added 1.001 g (9.90×10<sup>-3</sup> mol) of palladium sponge. The flask was once again purged with argon for 5 min and 2.50 g ( $2.14 \times 10^{-2}$  mol) of NOBF<sub>4</sub> were added to the stirred mixture. The flask, which was kept under a slight positive pressure of argon, was periodically vented to release the pressure from the formation of nitrous oxide gas. The mixture was stirred for at least 24 h followed by transfer of the supernatant by cannula to another septum stoppered flask. The solids were then washed with  $3 \times 10$  ml portions of degassed acetonitrile with vigorous stirring. All rinses were combined with the original supernatant liquid and the total volume measured. A 1.0 ml portion was syringed into a beaker and acidified with conc. HCl followed by palladium(II) analysis by the standard dimethylglyoxime gravimetric method. Palladium(II) uptake by the modified polymer coated Celite could then be determined by subtracting the palladium content of the supernatant from the amount of palladium originally used.

The procedures were similar for iron powder and copper wire. In the case of the iron, the powder did not completely dissolve so the unreacted iron power was filtered off and weighed so an accurate determination of the iron taken up by the catalyst surface could be made. Similar procedures were also used to measure iron(II) and Cu(II) uptake by the high molecular weight polymer which was not coated on Celite. Ferric chloride was also used as a surface catalytic species. The modified polymer coated Celite or high molecular weight polymer was stirred with 50 ml of 0.01 M FeCl<sub>3</sub> solution in a closed system at room temperature for 2 days. Iron analysis was carried out by gravimetric analysis as iron(III) oxide [30a], or as  $Fe(SCN)_6^{3-}$  using a colorimetric analysis [30b]. The detailed procedure has been described already [1]. Copper(II) was determined by a standard iodometric analysis [30c].

#### 2.11. Oxidation procedure

To provide good gas liquid mixing, the reactions were run in creased flasks at 25 °C at a constant dioxygen pressure of 1 atm. The progress of the oxidations was followed by dioxygen uptake measured by gas burets thermostated at the reaction temperature. The reaction flask was a 250 ml two-necked coned shaped flask with the sides indented at four places to increase stirring efficiency. The apparatus is similar to that previously described [31]. In a typical run the flask containing 50 ml of reaction mixture was placed in a constant temperature bath and connected to the gas buret. The system was then evacuated for 10 min on the vacuum line with the stirrer running. The stirring was then stopped and the system pressured to 1.0 atm with dioxygen. The mercury in the gas buret and the leveling bulb were then equalized and a reading taken. The stirrer was then turned on to start the run. The pressure was kept constant by continuously leveling the mercury in the gas buret and the bulb with readings being taken immediately after the levels were equalized.

#### 2.12. Product identification

Since the triketone-Fe(III) catalysts gave the most complicated reaction mixtures, the product distribution was determined in this system. The procedure for separating the products has been described already [1]. The products were

CH2

meta or

para

CO<sub>2</sub>CH<sub>1</sub>

HC1 TEOF

readily identified as 3,5-di-t-butyl-1,2-benzoquinone (5)<sup>4</sup>, *cis,cis*-dimethyl 2,4-di-t-butyl muconate (6)<sup>5</sup> and 3,5-di-t-butyl-5-(methylcarboxymethyl)-2-furanone, (7)<sup>6</sup> from comparison of their spectra with those published [32,33].

One of the latter chromatographic fractions contained a mixture of 7 and a product, 8, which was present in the original reaction mixture in 5% yield. Rechromatography of this fraction using silica gel and hexane:acetone (9:1 vol./ vol.) gave two products,  $8a^7$  and  $8b^8$ , as yellow crystals in the ratio 8b/8a = 2. The minor product, 8a, was readily identified as 3-t-butyl-5-methoxy-1,2-benzoquinone by comparison with an authentic sample prepared by oxidation of 3-t-butyl-4-hydroxyanisole with Fremy's salt [34]. The spectral properties of 8b indicated that it also resulted from replacement of one of the t-butyl groups on 5 with a methoxy group.

The products from the runs with monometallic catalysts 2, M = Cu, Fe or Pd, were readily identified as 5 from the <sup>1</sup>H NMR spectra.

The palladium(II) reaction mixtures were worked up by carefully evaporating the solvent in an inert atmosphere. The residue was analyzed by <sup>1</sup>H NMR without any further purification. The only product from the oxidation by the bime-tallic catalyst was  $\mathbf{6}$ .

#### 2.13. Hydrogen peroxide analysis

After oxygen uptake by the reaction mixtures had stopped, they were analyzed for  $H_2O_2$  by the permanganate method [30d]. The reaction mixture was deoxygenated four times by argon-vacuum degas cycles. Then a 20 ml portion of  $H_2SO_4$  (1:5) was injected into the reaction mixture. After stirring for 10 min, a solution containing a large excess of KMnO<sub>4</sub> was added. The volume of oxygen evolved (~30 ml) was recorded.

#### 3. Results

#### 3.1. Preliminary feasibility experiments

These studies tested the surface modification procedure with low molecular weight model compounds that are soluble

<sup>7</sup> 8a: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.24 (s, 9H), 3.82 (s, 3H), 5.73 (d, J=3 Hz, 1H), 6.60 (d, J=3 Hz, 1H). FTIR:  $\nu$ (CO) 1680, 1620 cm<sup>-1</sup>.

<sup>8</sup> **8b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.28 (s, 9H), 3.81 (s, 3H), 5.86 (d, J=2.7 Hz, 1H), 6.53 (d, J=2.7 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 28.082, 35.218, 56.372, 106.08, 132.154, 153.902, 159.343, 181.448, 187.895. FTIR:  $\nu$ (CO) 1680, 1620 cm<sup>-1</sup>. Mass spectrum (DCI) (methane)): *M*H<sup>+</sup> at *m*/*z* 195. M.p. = 83–84 °C.



and can be characterized by spectroscopic techniques. Scheme 2 shows the outline of the studies (TEOF= triethylorthoformate).

The acetylated benzoate esters were trimerized by the usual polymerization procedure (HCl+triethyl orthoformate in benzene). After purification by column chromatography, the <sup>1</sup>H NMR of **9** displayed a new singlet in the aromatic region due to the formation of the new aromatic ring. The ratio of ester hydrogens to aromatic hydrogens was 9/15 as predicted by the structure of the trimer. The <sup>13</sup>C NMR was also consistent with the proposed structure. For the *para* isomer the final confirmation was the mass spectra that gave the predicted parent ion at m/z of 480. As expected, the *para* isomer was less soluble than the *meta* isomer and could be purified by recrystallization.

Next the trimeric methyl benzoate was reacted with 2,4pentanedione and CH<sub>3</sub>Li plus HN(i-Pr)<sub>2</sub> in dimethoxyethane to form the  $\beta$ -triketone groups to give **10**. After purification the ester methyl resonances at 4.0 ppm had completely disappeared. They had been replaced by the enol resonance of the triketone at 5.3 ppm, the keto resonances at 3.4–3.7 ppm and the methyl resonances between 1.65 and 2.05 ppm. The ratio of the intensities of the methyl resonances to the enol plus keto resonances was that expected for the triketone.

#### 3.2. Catalyst characterization

Depending on the polymer system, monitoring the chemical modification was carried out using either <sup>1</sup>H NMR or FT-IR. The NMR technique was suitable for the palladium(II) system since chemical modification was done on the soluble pre-polymer while FT-IR was used for the remaining catalysts for which chemical modification was carried out after curing to give the insoluble high molecular weight polymer.

The initial pre-polymers in the palladium(II) system had a <sup>1</sup>H NMR very similar to the trimer 9. A new benzene resonance is seen at around 7.35 ppm as a singlet. In addition terminal unreacted acetyl groups are seen at 2.60 ppm and

-CO<sub>2</sub>CH<sub>3</sub>

-CO<sub>2</sub>CH<sub>3</sub>

CH<sub>3</sub>C(O)CH<sub>2</sub>C(O)CH<sub>3</sub>

9

<sup>&</sup>lt;sup>4</sup> 5: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.19 (s, 9H), 1.23 (s, 9H), 6.45 (d, J=2.4 Hz, 1H), 6.85 (d, J=2.4 Hz, 1H) FTIR:  $\nu$ (CO) 1650 cm<sup>-1</sup>.

<sup>&</sup>lt;sup>5</sup> 6: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.10 (s, 9H), 1.20 (s, 9H), 3.60 (s, 3H), 3.65 (s, 3H), 5.75 (d, J=1.5 Hz, 1H), 6.25 (d, J=1.5 Hz, 1H). FTIR:  $\nu$ (CO) 1680 cm<sup>-1</sup>.

<sup>&</sup>lt;sup>6</sup> 7: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.98 (s, 9H), 1.23 (s, 9H), 2.81 (d, J = 14.3 Hz, 1H), 2.95 (d, J = 14.3 Hz, 1H), 3.61 (s, 3H), 6.94 (s, 1H). FTIR:  $\nu$ (CO) 1748, 1720 cm<sup>-1</sup>.

2	1	Δ
4	I	υ

Table 1					
Metal ion	uptake by	various	polymer coate	d Celite su	ırfaces

Support	Metal species <sup>a</sup>	Diketone surface uptake (mmol/1g coated support × 10)	Triketone of polymer surface uptake (mmol/1g coated support × 10)	g of polymer
Celite	FeL <sub>6</sub> <sup>2+</sup>	3.2	6.0	0.016
Celite	FeCl <sub>3</sub>	2.8	4.8	0.016
Celite	CuL <sup>2+</sup>	3.8	7.8	0.016
Celite	PdL <sup>2+</sup>	1.25	2.2	ND <sup>b</sup>
None	FeL <sup>2+</sup>	3.0	4.6	0.1
None	FeCl <sub>3</sub>	3.2	5.0	0.1

<sup>a</sup>  $L = CH_3CN$ .

<sup>b</sup> Not determined.

terminal methyl ester group resonances at 3.93 ppm. The only other peaks in the spectrum are aromatic peaks that appear in the range 7.5–8.3 ppm. After modification to give the triketone, the <sup>1</sup>H NMR spectra of the pre-polymer did not contain the methyl ester resonance and new resonances at around 2.05 (-CH<sub>3</sub>), 2.29 (-CH<sub>2</sub>-), and 5.30 and 5.50 (=CH-) ppm appeared. All of this is consistent with the formation of the triketone. The model phenyl triketone compound had resonances at 2.01, 2.30, and 5.31 and 5.81 ppm, respectively. The other peaks are in the aromatic region and are fairly complex, as expected. Close to the mentioned resonances are small resonances that one would expect of isomeric forms of the triketone.

The diketone was made and characterized in a fashion similar to the triketone. In this case an additional advantage was the use of the  $-C_4H_9$  group that could clearly be seen in the spectrum. The <sup>1</sup>H NMR spectra of the modified prepolymer did not display the methyl ester resonance and new resonances appeared at 1.10 ( $-C_4H_9$ ), 2.30 ( $-CH_2-$ ) and 5.80 (=CH-) ppm. The model phenyl diketone displayed very similar resonances.

For the cured modified polymers coated on Celite it was difficult to get useful information from the FT-IR spectra because of the interference by bands from the Celite. For that reason spectra were taken using the uncoated high molecular weight polymer. The ester group of the unmodified polymer exhibited a band at 1721 cm<sup>-1</sup>. The diketone modified polymer gave carbonyl bands at 1701 and 1692 cm<sup>-1</sup> while the triketone modified polymer displayed bands at 1707, 1696 and 1666  $\text{cm}^{-1}$ . In both cases these are the expected bands for successful chemical modification [35]. Further changes occurred upon treatment of the diketone and triketone modified surfaces with  $[Fe(CH_3CN)_6](BF_4)_2$ . In addition to bands due to uncomplexed ligands, the diketone surface had bands at 1570 and 1514 cm<sup>-1</sup>, while the triketone displayed bands at 1567, 1536 and 1502  $\text{cm}^{-1}$ . These bands are those expected if surface metal complexes are present [35].

#### 3.3. Metal ion uptake by modified polymers

The amounts of various metal species taken up by the triketone and diketone modified surfaces are listed in Table

1. In all cases the metal ion uptake by the triketone surfaces is approximately twice that by the diketone surfaces. Since the same polymer sample was used to give both types of chemical modification, this is the expected result if the reactions shown in Scheme 1 are occurring. With the exception of Pd(II) surfaces the amounts of metal ion taken up by the diketone and triketone surfaces were about the same. The differences with the Pd(II) surfaces must result from the different coating-chemical modification procedures.

#### 3.4. Dioxygen uptake studies

The oxygen uptake plots for DTBC displayed no induction periods with triketone catalysts coated on Celite. With the diketone Celite surfaces, no induction periods were observed with  $Fe(CH_3CN)_6^{2+}$ ,  $Cu(CH_3CN)_4^{2+}$  and  $Pd(CH_3CN)_4^{2+}$ catalytic surfaces with a very short induction period with FeCl<sub>3</sub> coated surfaces. Typical plots with  $Fe(CH_3CN)_6^{2+}$ treated surfaces are shown in Fig. 1. Small induction periods were observed for the unsupported catalyst coated with  $Fe(CH_3CN)_6^{2+}$  and  $Cu(CH_3CN)_4^{2+}$  with FeCl<sub>3</sub> giving somewhat longer induction periods.

The kinetic data for the DTBC oxygen uptake studies are listed in Table 2. When the reactions were plotted as first-order reactions in [DTBC], using the stoichiometry,  $1 O_2/2$  DTBC, linear plots were obtained for the initial portion of the reactions with the triketone catalysts, the diketone cata-



Fig. 1. Oxidation of DTBC by polymer supported  $Fe(CH_3CN)_6^{2+}$  in methanol. Reaction mixture contains 0.5 g polymer coated Celite and 0.25 mmol DTBC in 25 ml methanol. Upper curve: triketone polymer; lower curve: diketone polymer.

Table 2	
Kinetic data for the oxidation of 3,5-DTBC by several catalys	ts <sup>a</sup>

Support	Metal species <sup>b</sup>	Ligand	$k_{\rm obs}  imes 10^5  ({\rm s}^{-1})$	$k \times 10^3 (\mathrm{M}^{-1}\mathrm{s}^{-1})$	O <sub>2</sub> taken up (mmol)	H <sub>2</sub> O <sub>2</sub> found (mmol)
Celite	FeL <sub>6</sub> <sup>2+</sup>	triketone	28	93	2.21	0
Celite	$FeL_6^{2+}$	diketone	5.6	35	2.55	1.31
Celite	FeCl <sub>3</sub>	triketone	1.0	4.2	2.66	0
Celite	FeCl <sub>3</sub>	diketone	0.46	3.2	1.63	0.82
Celite	CuL <sub>4</sub> <sup>2+</sup>	triketone	1.4	3.6	2.55	0
Celite	CuL <sub>4</sub> <sup>2+</sup>	diketone	0.19	1.0	2.29	1.21
Celite	PdL <sub>4</sub> <sup>2+</sup>	triketone	32	290	2.51	ND °
Celite	$PdL_4^{2+}$	diketone	0.4	6.4	1.31	ND
None	FeL <sub>6</sub> <sup>2+</sup>	triketone	7.1	31	2.58	ND
None	FeL <sub>6</sub> <sup>2+</sup>	diketone	0.8	5.3	1.52	ND
None	FeCl <sub>3</sub>	triketone	0.9	3.6	2.76	ND
None	FeCl <sub>3</sub>	diketone	0.06	0.38	1.01	ND

<sup>a</sup> 2.5 mmol of 3,5-DTBC in 100 ml methanol at 25 °C using 0.5 g of catalyst coated Celite or 0.05 g of unsupported polymer.

<sup>b</sup>  $L = CH_3CN_2$ 

° Not determined.

lysts with  $PdL_4^{2+}$  and the unsupported catalysts. For the diketone catalysts with  $Fe(CH_3CN)_6^{2+}$ ,  $Cu(CH_3CN)_4^{2+}$ and FeCl<sub>3</sub>, in which H<sub>2</sub>O<sub>2</sub> was detected, the stoichiometry, 1 O<sub>2</sub>/1 DTBC oxidized, was assumed. The observed firstorder rate constants were converted to second-order rate constants (first-order in [DTBC] and first-order in  $[M^{n+}]$ ) by dividing by the  $[M^{n+}]$  which would be present if the metal ion were in a homogeneous solution of the same volume as the reaction mixture (100 ml). Data for the oxidation of DTBQ are shown in Table 3. Since the ring cleavage of DTBQ is a two-electron oxidation, the stoichiometry,  $1 O_2/$ 2 DTBQ, was used in plotting the data. In all cases the diketone surfaces were completely unreactive and the rates for the triketone surfaces were considerably slower than those for DTBC oxidation. In all the runs in Table 3, the theoretical limit of 1.25 mmol of O<sub>2</sub> was not reached. Rates of DTBQ oxidation could also be calculated approximately from the last stages of the oxidation of DTBC when all the DTBC had been converted to DTBQ. The rates were within a factor of two of the more accurate determination starting with DTBO. This result indicates the oxidation of DTBC occurs in two steps: formation of DTBQ followed by ring cleavage.

#### 3.5. Product distributions



As shown in Eq. (2), the only product for all the diketone containing surfaces was DTBQ. A coproduct with the Cu and Fe surfaces was  $H_2O_2$  in a 1  $H_2O_2/1$  DTBQ ratio.

The detailed product distribution for the DTBC oxidation was previously determined with  $FeCl_3$  treated triketone surfaces [1]. In the present studies the products were separated and identified for the  $Fe(CH_3CN)_6^{2+}$  containing triketone surfaces. The product distribution given in Eq. (3) is at



the point where  $O_2/DTBC = 0.5$  while the triketone dioxygen uptake curve in Fig. 1 leveled off at  $O_2/DTBC$  molar ratios of about 1. The <sup>1</sup>H NMR spectra of the total reaction solution indicated that the Cu(CH<sub>3</sub>CN)<sub>4</sub><sup>2+</sup> treated triketone surfaces gave similar reaction mixtures. The Pd(CH<sub>3</sub>CN)<sub>4</sub><sup>2+</sup> treated triketone surfaces gave only **6** as product. The oxidation of DTBQ by all the triketone surfaces also gave only **6** as product.

In the previous paper an unknown, which resulted from replacement of a t-butyl group by a methoxy group, was reported. Repeated chromatography of this fraction separated two products in a ratio of 2/1, *both* of which resulted from replacement of a t-butyl by a methoxy group. The minor product was determined to be 3-t-butyl-5-methoxy-1,2-benzoquinone by comparison with an authentic sample. The spectral properties of the major product were consistent with 5-t-butyl-3-methoxy-1,2-benzoquinone. Thus the coupling constant of 2.7 Hz can be best explained by this structure. The m.p. of 83–84 °C is in the range previously reported for this compound: 78–80 °C [36], 79–80 °C [37] and 86–88 °C [38]. However the color of the compound was reported to be a dark red rather than the light yellow found for the unknown and the <sup>1</sup>H NMR and IR <sup>9</sup> were different from those

<sup>&</sup>lt;sup>9</sup> <sup>1</sup>H NMR: δ 1.24 (s, 9H), 3.77 (s, 3H), 6.01 (d, J = 1.7 Hz, 1H), 6.11 (d, J = 1.9 Hz, 1H). IR:  $\nu$ (CO) 1708, 1667 cm<sup>-1</sup>.

n	1	2
4	1	4

Metal species b	Ligand	$k_{\rm obs}  imes 10^6  ({\rm s}^{-1})$	$k \times 10^4 (\mathrm{M}^{-1}\mathrm{s}^{-1})$	O <sub>2</sub> taken up (mmol)
FeL <sub>6</sub> <sup>2+</sup>	triketone	1.4	5	1.02
FeL <sup>2+</sup>	diketone	0	0	0
FeCl <sub>1</sub>	triketone	0.9	4	0.70
FeCl <sub>1</sub>	diketone	0	0	0
CuL <sup>2+</sup>	triketone	0.4	1	0.86
CuL <sup>2+</sup>	diketone	0	0	0
$PdL_4^{2+}$	triketone	25	230	ND °
$PdL_4^{2+}$	diketone	0	0	0

Table 3 Oxidation of 3,5-DTBQ by catalysts supported on Celite <sup>a</sup>

\* 2.5 mmol of 3,5-DTBC in 100 ml methanol at 25 °C using 0.5 g of catalyst coated Celite.

<sup>b</sup> L = CH<sub>3</sub>CN.

<sup>c</sup> Not determined.

reported [38]. The isomer, 4-t-butyl-5-methoxy-1,2-benzoquinone, could be eliminated since the <sup>1</sup>H NMR of an authentic sample was different from the unknown <sup>10</sup>. The other three isomers, in which the aromatic hydrogens are in adjacent positions on the aromatic ring, have not been reported.

## 4. Discussion

Part 1 of this series firmly established that bimetallic catalysts, 4, based on the triketone surface ligand, 3, have a very specific catalytic action for DTBC oxidation which the monometallic catalysts, 2, based on the diketone surface ligand, 1, do not possess [1]. Thus, while 2, M = Cu or Fe, catalyzes the air oxidation of DTBC to quinone, 5 (Eq. (2)), the bimetallic catalyst, 4, M = Cu or Fe, causes ring cleavage to give 6 and 7. The most likely mechanism for this special reactivity is complexation of each oxygen in the intermediate DTBQ to one of the metal ions in the bimetallic catalyst followed by a simultaneous two-electron transfer, with one electron being transferred to each of the two metal ions. This scheme is outlined in Eq. (4). The monometallic catalyst can only oxidize by a one-electron transfer and thus give a free radical which would be a high energy species in this system. This result was particularly important because analogous monometallic homogeneous catalysts gave no reaction and bimetallic homogeneous catalysts gave only DTBQ. Thus the coordinately unsaturated heterogeneous catalysts are much more effective oxidants than their completely coordinated



solution counterparts. The product studies in the present study confirm and expand on the results of Part 1. Thus, as shown

in Eq. (2), the monometallic catalysts, 2, gave only DTBQ as oxidation product. In Part 1, with Fe and Cu catalysts, the other product was suspected to be hydrogen peroxide on the basis of dioxygen uptake. The hydrogen peroxide analysis in the present work confirms it is the other product so the overall reaction is:  $O_2 + DTBC \rightarrow DTBQ + H_2O_2$ . This result is not surprising as this overall stoichiometry has been observed in the oxidation of catechol itself by homogeneous Cu(II) catalysts [39] and  $H_2O_2$  is often a product of the autoxidation of Cu(I) [40]. This stoichiometry is used in calculating the rate constants with these monometallic catalysts. The dioxygen uptake indicates hydrogen peroxide is not formed with the Pd(II) monometallic catalyst or with any of the bimetallic catalysts. With the latter catalysts the absence of H<sub>2</sub>O<sub>2</sub> was confirmed by analysis. The reason must relate to the fact that reduced species that can be oxidized by two-electron steps will react with  $H_2O_2$ . Pd(0), Fe(II) and Cu(I) dimers can be oxidized in two-electron steps. The product distributions with the bimetallic Fe and Cu catalysts, shown in Eq. (3), are identical to those found in Part 1. As shown in Eq. (4), 6 is believed to be the main initial product. The furanone product, 7, is almost certainly formed by half hydrolysis of 6, very likely during workup, followed by addition of the acid across the double bond. When the workup was carried out by careful evaporation of the solvent in the absence of moisture, as was done in the Pd(II) and DTBQ oxidations, the only product was 6. The origins of 8a and 8b are uncertain. They could arise from a radical side reaction since they do not appear in the Pd(II) and DTBQ oxidations where radical species are unlikely. In any case, further speculation is unwarranted until 8b is positively identified.

The present paper describes studies aimed at developing an improved catalyst system. As shown in Eq. (1), the new system involves the aromatic polymerization of acetyl aromatics containing methylbenzoate groups which do not take part in the polymerization. The methylbenzoate groups can be cleanly converted either to  $\beta$ -di- or triketone surface ligands by the reactions shown in Scheme 1. The feasibility of this approach was demonstrated by the studies with a model system outlined in Scheme 2. The trimer, 9, was prepared without any loss of the methylbenzoate functions. The meth-

 $<sup>^{10}</sup>$  <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.32 (s, 9H), 3.90 (s, 3H), 5.79 (s, 1H), 6.30 (s, 1H).

ylbenzoate groups were quantitatively converted to  $\beta$ -triketone ligands to give **10** by the same reactions as those used to chemically modify the polymer. In addition <sup>1</sup>H NMR and FT-IR studies on the polymers before and after chemical modification confirm that the desired chemical changes have been achieved with the actual catalytic systems. In addition these studies demonstrate that metal ion uptake gives the surface complexes, **2** and **4**.

The next step is to demonstrate that the new catalysts actually do have increased activity over those used in the first paper of this series. Since a second improvement of the catalyst involves coating the metal ions as the reactive acetonitrile complexes with tetrafluoroborate as the counterion rather than the less reactive chloride or acetate, a direct comparison cannot be made in most systems. Only in the case of FeCl<sub>3</sub> was the same metal species used in both studies. An indication of the success of the new chemical modification procedure is metal ion uptake. In the previous study, the diketone surface took up 0.036 mmol per gram of polymer coated Celite while the triketone surface absorbed 0.063 mmol per gram [1]. The corresponding amounts, listed in Table 1, for the surfaces used in this study are 0.28 and 0.48 mmol, respectively. Thus the surfaces prepared by the procedures shown in Scheme 1 absorb about 8 times more FeCl<sub>3</sub> than those prepared by procedures used previously [1]. This is the expected result since the methylbenzoate groups are not involved in the polymerization as are the acetyl groups. The most important comparison is that of reactivity towards DTBC. Because of the long induction periods observed in the previous study, no rate constants were calculated from the data [1]. These induction periods were of the order of 80 h for the triketone surface coated with FeCl<sub>3</sub> and even longer with the FeCl<sub>3</sub> coated diketone surface. With FeCl<sub>3</sub> coated triketone surfaces there is no induction period and with the diketone surfaces the induction period is only about 5 h. Thus the newer catalysts display much higher reactivity than the original ones.

The second catalyst improvement involves the use of the weakly complexing acetonitrile ligand and the non-complexing tetrafluoroborate counterion. The effect of this change can be determined from the data in Table 2 for the FeCl<sub>3</sub> and  $Fe(CH_3CN)_6^{2+}$  oxidations. The most meaningful comparison is with the second-order rate constants, k, since this value corrects for the different amounts of metal ion present. For the triketone surfaces, the value of k (9.3 × 10<sup>-2</sup> M<sup>-1</sup> s<sup>-1</sup>) for the Fe(CH<sub>3</sub>CN)<sub>6</sub><sup>2+</sup> system is over 20 times the value of  $k (4.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})$  for the FeCl<sub>3</sub> system. For the diketone surfaces the difference is a factor of over 10. However, as shown in Table 1, the amount of metal taken up by the catalyst surface does not depend greatly on the identity of the metal species. FeCl<sub>3</sub>, Fe(CH<sub>3</sub>CN)<sub>6</sub><sup>2+</sup> and Cu(CH<sub>3</sub>CN)<sub>4</sub><sup>2+</sup> all give the same metal ion uptake within a factor of two. The Pd(CH<sub>3</sub>CN)<sub>4</sub><sup>2+</sup> uptake was somewhat less but this surface was prepared in a fashion which was quite different from the other three and the amount of polymer on the Celite was not determined.

A comparison of the rate differences for the acetonitrile complexes of Fe<sup>2+</sup>, Cu<sup>2+</sup> and Pd<sup>2+</sup> is of interest because such comparisons for the same coordination environment are rare. The values of k for the triketone surfaces were: Pd<sup>2+</sup>  $(2.9 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}) > \text{Fe}^{2+} (9.3 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1})$  $> \text{Cu}^{2+} (3.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})$ . The lower value for Cu<sup>2+</sup> almost certainly reflects the lower redox potential of the Cu(II)-Cu(I) couple. Since Fe(III) and Pd(II) have about the same redox potentials in aqueous solution, their similarities in rate is not surprising. However, as discussed below, these comparisons may be greatly oversimplified since the reactions could proceed by different mechanisms.

The most surprising result of the present studies is the small differences between the triketone and diketone surfaces for the Fe and Cu oxidations of DTBC to DTBQ. The maximum differences in k are about a factor of 3. In light of the fact that, in homogeneous solution, analogous monometallic complexes gave no oxidation and bimetallic complexes were required for oxidation of DTBC to DTBQ, this is indeed an unexpected observation. The bimetallic complexes might be expected to form surface complexes such as 11 [41] or 12 [42] while the monometallic would be expected to form 13.



In a fashion analogous to that show in Eq. (4), 11 or 12 would be expected to give a concerted two-electron transfer which would be much more facile than a one-electron transfer in 13. The results indicate this is not the case. The difference between the mono- and bimetallic catalysts is dampened because the monometallic system would give a relatively stable 3,5-di-t-butyl-o-benzosemiquinone radical by a oneelectron transfer. Such a radical intermediate has been postulated in the catalytic air oxidation of DTBC by several metal acetylacetonates  $(M(acac)_2; M = Mn, Co, Ni, Fe)$  to give DTBQ [43]. On the other hand there is a report of a stabilized 3,5-di-t-butylsemiquinonate radical bonded to Cu(I) [44]. This radical is formed by the one-electron transfer from 13 to Cu(II). Oxidation of the complexed radical would give the observed product, DTBQ. The reaction series is shown in Eq. (5). Based on the absence of a large rate enhancement, such a one-electron transfer may be the rate determining step even in the oxidation of the bimetallic complexes, 11 and 12.



The reason for the apparent lack of the concerted two-electron transfer analogous to that shown in Eq. (4) is unclear. It

could be that in the particular system, the steric requirements for formation of 11 and/or 12 are not favorable while they are favorable for formation of the DTBQ complex in Eq. (4). On the other hand Pd(II) behaves in the expected fashion. The bimetallic catalyst oxidizes DTBC about 50 times faster than the monometallic. The reason for this result could relate to the larger size of palladium(II) which results in better 'steric matches' in the bimetallic intermediates, 11 and/or 12. However the differences with the Cu(II) and Fe(III) oxidations could simply be the fact that Pd(II) is a very different oxidant than the other two metal species. Thus, Pd(II) is only a two-electron oxidation as a monomeric species so it is incapable of the one-electron transfer shown in Eq. (5). However Pd(II) is capable of oxidizing DTBC by the two-electron route shown in Eq. (6).

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The oxidation by the bimetallic catalyst must proceed by the concerted two-electron transfer analogous to that shown in Eq. (4). However, in the case of Pd(II), the Pd(II) reduction product would be a Pd(I) dimer which is a well known oxidation state in palladium chemistry [45]. There have been several recent examples of Pd(I) dimers [46–51]. The reaction scheme is shown in Eq. (7). Thus, although the Pd(II)



monometallic catalyst can oxidize DTBC by the non-radical two-electron transfer shown in Eq. (6), the concerted twoelectron transfer shown in Eq. (7) must be the more facile process. The formation of a Pd(I) dimer as reduction product in Eq. (7) has at least one practical advantage. In other studies in this laboratory it was found that the bimetallic Pd(II) catalytic species was much more stable to eventual decomposition to Pd(0) resulting in many more turnovers than the monometallic catalysts [52]. This reflects the fact that the Pd(I) dimer in Eq. (7) is much more stable to decomposition to Pd(0) than a monomeric Pd(0) complex.

In contrast the kinetic results for DTBQ oxidation, listed in Table 3, are straightforward for all four metal oxidants. The bimetallic species oxidized the DTBQ at appreciable rates while the monometallic species were completely unreactive. These results clearly demonstrate the importance of bimetallic catalysis and support the product distribution results which showed that ring cleavage only occurred with the bimetallic catalysts. For most bimetallic catalysts the value of k was about an order of magnitude slower than the k for DTBC oxidation. This is in keeping with the ring cleav-

age being a higher energy process than DTBC oxidation. An unexpected result was the relative magnitudes of the values of the second-order rate k for the  $Fe(CH_3CN)_6^{2+}$  and  $FeCl_3$ systems. They are effectively the same while for DTBC oxidation the  $Fe(CH_3CN)_6^{2+}$  catalyst was faster by a factor of over twenty. The reason for this difference in relative rates is not obvious but is probably related to differences in mechanism between the DTBC and DTBQ oxidations. A less dramatic result is the fact that k for the FeCl<sub>3</sub> oxidation is four times that for the  $Cu(CH_3CN)_4^{2+}$  oxidation while they have almost the same values for the DTBC oxidation. The higher redox potential of the FeCl<sub>3</sub> system could be more important in the higher energy ring cleavage reaction. Due to the low value of k for the  $Fe(CH_3CN)_6^{2+}$  oxidation,  $Pd(CH_3CN)_4^{2+}$ becomes by far the most active catalyst for DTBQ oxidation. Finally Pd(II) is a two-electron oxidant and thus can, in principle, cause ring cleavage without proceeding through high energy radical species. However the bimetallic process shown in Eq. (7) must be the most facile route even for Pd(II).

In order to test the effect of dispersion, a few runs were carried out using a whole polymer for comparison with polymer-coated Celite catalysts. As can be seen from the data in Table 1, a 0.1 g sample of whole polymer absorbed about the same amount of metal species as a 0.016 g sample coated on Celite. In the oxidation reaction, not only were induction periods observed, but the value of k for the whole polymer was 3–8 times slower than the polymer-coated Celite. Since the second-order rate constant k is normalized for the amount of metal species present, the metal present in the whole polymer is used much less effectively then when coated on Celite. Thus, from several viewpoints, the polymer-coated Celite is, by far, the most effective catalyst system to date.

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