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Oxidation of pinane using transition metal acetylacetonate complexes immobilised on modified activated carbon

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Abstract

The performance of a new solid catalyst is studied. Copper and cobalt acetylacetonate complexes are chemically anchored to functionalised activated carbon. These catalysts are active and highly selective to 2-pinane hydroperoxide in the oxidation of pinane at room temperature and atmospheric pressure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon materials are widely used as catalysts or catalyst supports for a great variety of reactions. The desirable performance of catalysts of these materials for certain applications can be achieved by modifying physical and chemical surface properties such as surface area, porosity, hydrophobicity, surface charge or degree of graphitisation [1–5].

Carbon materials can satisfy most of the desirable requirements for a suitable support: chemical inertness, stability, mechanical resistance, high surface area and good porosity. This has motivated other researchers to use them as supports for metallophthalocyanine complexes, which proved to be active for the liquid phase oxidation of cycloalkanes at room temperature and atmospheric pressure [6,7]. The physico-chemical properties of the supports used to immobilise these complexes influences the catalytic performance.

Little research has been done concerning the use of modified activated carbon supports to heterogenise homogeneous catalysts for liquid phase processes. When complexes are simply impregnated on the solid supports the major disadvantage is the possible leaching of the complexes into solution resulting in catalyst deactivation. This can be overcome by topologically or chemically anchoring the complexes on the support. Interesting developments are emerging in the design of porous solid materials containing covalently attached transition metal complexes [8–10]. Thomas designed successfully inorganic molecular sieve catalysts with grafted active centres [11]. Recently, Zefirov et al. topologically anchored metallophthalocyanine complexes on NaA zeolite, which proved to be active for liquid phase hydroxylation of benzene with H_2O_2 [12].

Transition metal acetylacetonate complexes have been reported as having interesting redox properties

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[13]. Neves et al. encapsulated these complexes in zeolite Y [14]. In the present work we describe a technique for the covalent attachment of these organometallic complexes to activated carbon supports. The catalytic performance of these materials was tested in the oxidation of pinane at room temperature and atmospheric pressure. This reaction was previously studied in more detail in the presence of zeolite encapsulated metallophthalocyanine complexes [15,16].

2. Experimental

2.1. Materials

The starting carbon material (C_0) was a commercially available activated carbon (NORIT GAC 1210). Free Cu(II) and Co(II) acetylacetonate complexes ($Cu(II)(acac)_2$ and $Co(II)(acac)_2$) and hexanediamine were purchased from Aldrich. The solvents used for catalyst preparation were purchased from Merck and dehydrated with molecular sieves (Linde 4A) before use.

Cis-pinane (97–98% pure) was obtained from α-pinene by reduction with diimide.

2.2. Catalyst synthesis

2.2.1. Oxidation of activated carbons with nitric acid

The oxidised activated carbon is obtained by refluxing 18 ml of 65% HNO_3 solution g^{-1} of carbon. After 3 h reflux, the modified activated carbon is separated by filtration and washed with distilled water until neutral pH and dried at 90°C (code C_1).

2.2.2. Anchoring of hexanediamine (hxd) on the oxidised activated carbon via thionyl chloride

The pre-oxidised carbon C_1 is refluxed with $SOCl_2$ (0.1 mol $SOCl_2$ g^{-1} carbon) for 1 h. Afterwards, the remaining $SOCl_2$ solution is distilled off. The carbon obtained is refluxed with 300 ml of 5×10^{-2} M toluene solution of hxd g^{-1} of carbon for 6 h. The solid material is consecutively washed with ethanol and dried at 80°C for 2 h (C_2).

2.2.3. Reaction of $Cu(II)(acac)_2$ and $Co(II)(acac)_2$ complexes with the modified activated carbon

Modified carbon C_2 is refluxed with 20 ml of 7×10^{-5} M chloroform solution of $Cu(II)(acac)_2$ or $Co(II)(acac)_2$ g^{-1} of carbon for 16 h. Finally, the material is washed with ethanol and dried at 80°C for 2 h ($Cu(II)(acac)_2$hxd-C and $Co(II)(acac)_2$hxd-C, respectively).

2.2.4. Adsorption of $Cu(II)(acac)_2$ and $Co(II)(acac)_2$ complexes on nitric acid oxidised activated carbon

The pre-oxidised carbon C_1 is refluxed with 20 ml of 7×10^{-5} M chloroform solution of $Cu(II)(acac)_2$ or $Co(II)(acac)_2$ g^{-1} of carbon for 16 h. The catalyst is finally washed with ethanol and dried at 80°C for 2 h ($Cu(II)(acac)_2$-C and $Co(II)(acac)_2$-C, respectively).

2.3. Catalyst characterisation

Textural characteristics were obtained from physical adsorption of nitrogen at 77 K on a Micromeritics ASAP 2010 V1.01 B instrument.

The contents of oxygenated surface groups for the carbon samples C_0 and C_1 were evaluated by titration with bases of increasing strength according to the classical Boehm method [3,17]. Carbon samples, C_0 and C_1, were shaken for 24 h in 0.05 N solutions of three different bases of increasing strength ($NaHCO_3$, Na_2CO_3 and NaOH) and subsequently acidified with 0.05 N HCl solution.

The point of zero charge (PZC) values were determined by mass titration [18].

The catalysts were characterised by temperature programmed desorption and gas chromatography/mass spectrometry (TPD-MS) analysis. TPD analysis were carried out on a MICROMERITCS TPD/TPR 2900 instrument by heating the samples in a fixed bed reactor, in flowing He (25 cm^3/min) at 10°C/min until 950°C. The evolution of released decomposed products was monitored by mass spectrometry with a FISONS MD800 GCMS instrument. The effluent stream was fed to a mass spectrometer through a heated line and full range mass spectra were recorded.

FTIR spectroscopy of the powered samples was carried out on a Bio-Rad FTS 155 spectrometer. The spectra were taken with a resolution of 4 cm^{-1} and running 250 scans.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a XSAM800 (KRATOS, Manches-

ter, UK) X-ray spectrometer. Non-monochromatic radiation from a Mg anode was used (main ray has $h\nu$=1253.6 eV). Pressure in the analysis chamber was in the range of 1×10^{-9} Torr and a power of 130 W was used.

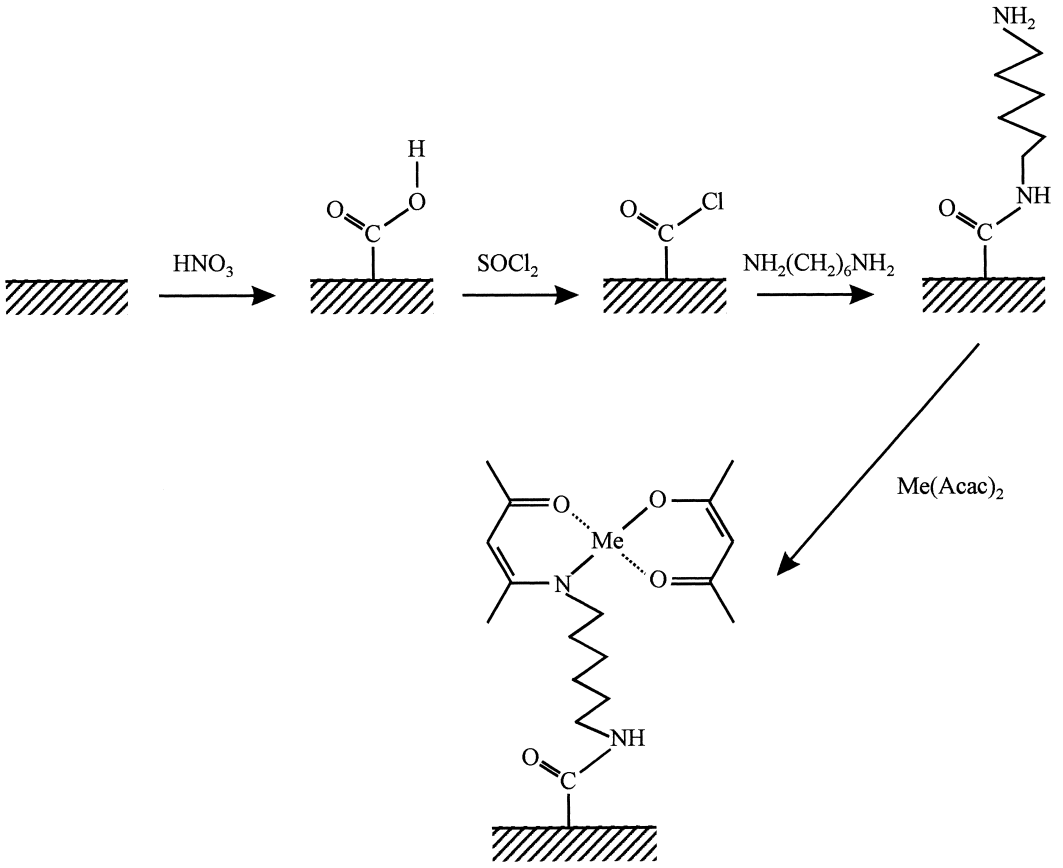
2.4. Catalytic experiments

Oxidation reactions of pinane were carried out at room temperature and atmospheric pressure using *t*-BHP as oxidant and a mixture of acetone and *t*-butanol (9:1 volume ratio) as solvent. In a typical experiment, pinane and the oxygen donor were used in a 1:8 molar ratio with 10 mg of catalyst. Samples were treated with aqueous sodium sulphite and analysed by GC and GCMS on a 30 m×0.25 mm DB-1 column from J & W.

3. Results and discussion

3.1. Catalyst preparation

The modification of the surface of activated carbon NORIT is done by oxidation with nitric acid providing acid carboxylic groups [19]. The conversion of carboxylic acid into the corresponding acyl chloride by heating with thionyl chloride is a well-known reaction. By this means, through reaction with acyl chloride groups, hexadiamine is chemically bounded to the carbon providing surface groups containing aliphatic carbon chains with terminal primary amines, as previously referred by Jansen and van Bekkum (Scheme 1) [2]. Acetylacetonate complexes are tethered by Schiff condensation reaction with the primary amines, similarly to the way these complexes are im-



Scheme 1.

Table 1
Nitrogen adsorption data[a]

Activated carbon	S_{BET}	S_{ext}	S_m	V_m	TPV
C_0	1037	313	724	0.32	0.60
C_1	928	345	583	0.25	0.56

[a] BET areas (S_{BET}, m^2/g), external surface areas (S_{ext}, m^2/g), micropore areas (S_m, m^2/g), micropore volumes (V_m, cm^3/g) and total pore volumes (TPV, cm^3/g).

Table 2
PZC values and Boehm titration results for the carbon samples

Consumption of base after hydrolysis (meq/100 g of carbon)	NaOH	Na_2CO_3	$NaHCO_3$	PZC
C_0	35	10	–	7.8
C_1	205	160	90	2.4

mobilised in zeolites in the work done by Neves et al. [14].

3.2. Catalyst characterisation

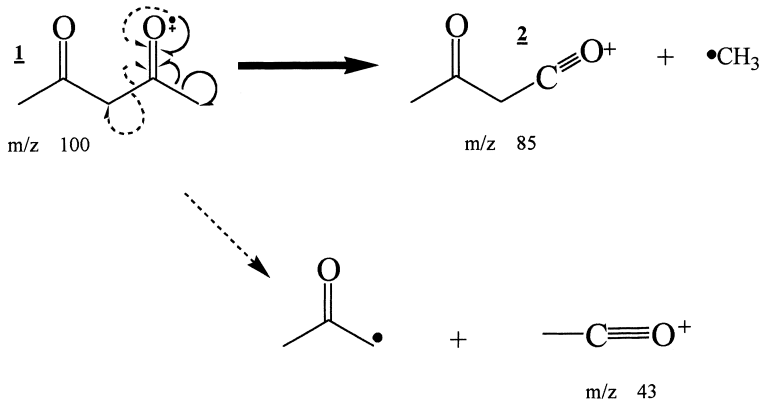
The BET specific surface area, micropore area, micropore volume and the total pore volume decrease upon nitric acid oxidation of activated carbon (Table 1). An effect that may account for this result is the formation of macropores upon oxidation with nitric acid. The titration according to the method of Boehm shows a significant increase in the consumption of base after treatment, which reflects an increase in the number of acidic surface oxides (Table 2). This is in agreement with the significant decrease of the PZC value that reflects the changing ratio between acidic and basic surface groups on oxidised activated carbon C_1 (Table 2). Hence, this carbon has a high acid strength. The surface acidity results from the presence of acidic surface functions such as carboxylic, lactone and phenolic groups that are formed upon oxidation with HNO_3 [19]. According to Boehm, $NaHCO_3$ neutralises carboxylic groups, Na_2CO_3 neutralises carboxylic and lactonic groups and NaOH neutralises carboxylic, lactonic and phenolic groups [3]. Table 3 shows the contents of these surface oxides of the carbon samples. The high concentration of carboxylic acid and lactone groups accounts for its low PZC value.

Table 3
Content in surface oxides on C_0 and C_1 according to the Boehm titration method [3]

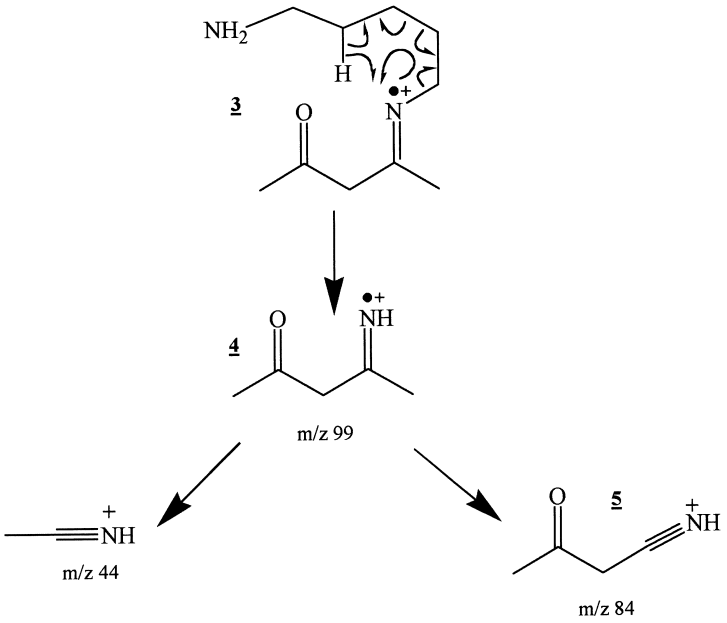
meq/100 g	Phenolic	Lactonic	Carboxylic	Total
C_0	25	10	–	35
C_1	45	70	90	205

Catalyst samples prepared by impregnation of the complexes or by chemical reaction as described above, were submitted to thermal programmed desorption in He flow, in the temperature range 100–900°C.

Significant peaks were obtained at *m*/*z* 100, 85 and 43 for the adsorbed complexes. These peaks may be ascribed to the acetylacetonate **1** molecular ion (*m*/*z* 100) and to its subsequent fragmentation according to Scheme 2. Acetylacetonate **1** is likely to be formed by ligand exchange of the acac complex with surface carboxylate groups.



Scheme 2.



Scheme 3.

On the other hand, the catalyst samples bearing the chemically bonded complexes exhibit significant mass spectra peaks at *m*/*z* 99, 84 and 42, which do not appear in the mass spectra of the adsorbed complexes. These peaks are consistent with the fragmentation shown in Scheme 3. The ion corresponding to *m*/*z* 99 is likely to be formed by a McLafferty fragmentation in the mass spectrometer, of imine **3** which, on its turn, might result from the splitting of the amide bond to the carbon surface.

Figs. 1 and 2 compare the TPD/MS profiles for the impregnated (outlined symbols) and chemically

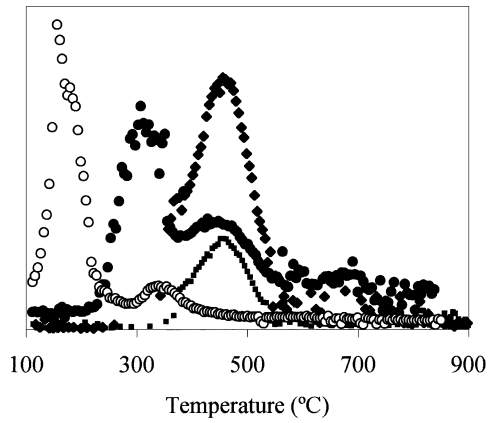


Fig. 1. TPD-GCMS profiles for the impregnated (outlined symbols) and covalently bonded (filled symbols) copper complexes. (○, ●) *m*/*z* 85 (**2**); (■) *m*/*z* 99 (**3**) and (◆) *m*/*z* 84 (**4**). Signal intensities in arbitrary units.

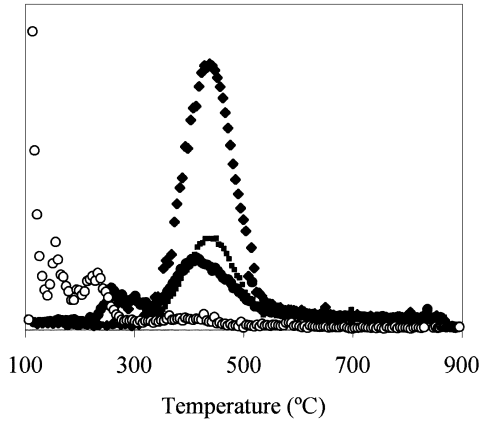


Fig. 2. TPD-GCMS profiles for the impregnated (outlined symbols) and covalently bonded (filled symbols) cobalt complexes. (○, ●) *m*/*z* 85 (**2**); (■) *m*/*z* 99 (**3**) and (◆) *m*/*z* 84 (**4**). Signal intensities in arbitrary units.

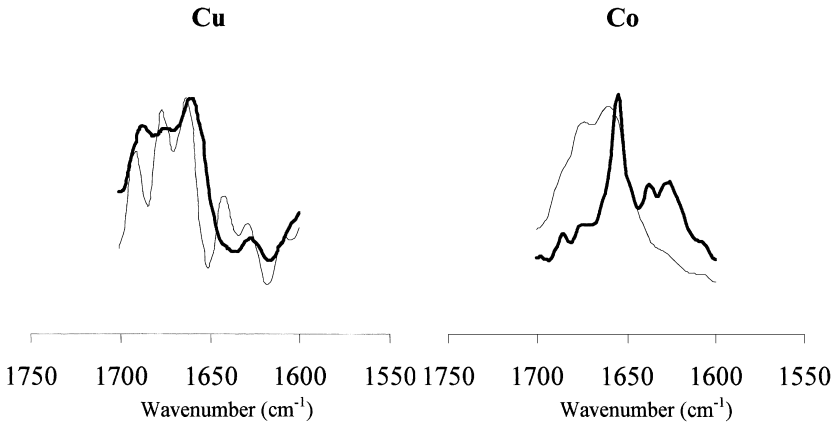


Fig. 3. DRIFT spectra (absorbance scale) of the impregnated (thin line) and covalently bonded (thick line) complexes.

bonded complexes (filled symbols) for the copper and cobalt catalysts, respectively. The TPD profiles of the impregnated samples were recorded for the ion at *m*/*z* 85 and are dominated by a strong desorption band in the temperature range 100–250°C in the case of the Cu complex (Fig. 1, empty circle) and in the range 100–200°C for the Co complex (Fig. 2, empty circle). For the chemically bonded samples, the TPD profiles were recorded for ions at *m*/*z* 99, 84 and also at *m*/*z* 85. For both Cu and Co complexes, the TPD profiles exhibit significant desorption bands, which can be ascribed to acetylacetonate (*m*/*z* 85 ion: Scheme 2; filled circle: Figs. 1 and 2). However, these desorption bands arise at a temperature range much higher (250–550°C) than that observed for the impregnated samples. In particular, are observed two different bands: a first band in the temperature range 250–350°C and a second band in the temperature range 350–550°C.

A possible explanation for these two TPD bands may be as follows:

1. The band in the lowest temperature range corresponds to a low energy decomposition, probably due to decomplexation prior to the splitting of the amide bond.
2. On its turn, the band in the highest temperature range corresponds to a higher energy decomposition, probably involving splitting of the amide bond to the carbon surface, followed by decomplexation to give 2,4-pentanedione **1** and imine **3**. This is consistent with the TPD profiles recorded for ions at *m*/*z* 99 and 84 (Scheme 3) exhibiting bands in the same temperature range (350–550°C, Figs. 1 and 2).

The FTIR spectra of adsorbed and bonded $Cu(acac)_2$ and $Co(acac)_2$ complexes on the activated carbon supports are shown in Fig. 3. Samples C_1 and C_2 were used to take the backgrounds that were subtracted from the measured adsorbed and bonded sample spectra, respectively. The spectra of the bonded and adsorbed samples are different The former clearly shows a band at 1658 cm^{-1} that does not appear in the spectra of the adsorbed complexes. This band may be assigned to the new C=N bond resulting from the Schiff condensation between the complexes and the amines.

Samples C_2, $Cu(II)(acac)_2$ hxd-C and $Co(II)(acac)_2$ hxd-C, when analysed by XPS, present charge effects (shifts 1.4, 1.4 and 1.6 eV, respectively) what means that they are less conducting than C_1 and the adsorbed samples. These results may suggest the presence of thicker insulating involving layers on the surface of the activated carbons. Table 4 shows the charge deviations and the graphitic/aliphatic carbon ratios of the different samples obtained by curve fitting the XPS C 1s region. $M(acac)_2$ tethered samples decrease significantly the graphitic/aliphatic ratio. This is another indication of the existence of aliphatic carbon (derived from hexanediamine) attached to the surface of the activated carbon supports.

Fig. 4 compares the XPS Cu 2p and Co 2p signals, respectively, of the tethered and adsorbed complexes. Multiplet structures (associated to the existence of

Table 4
XPS analysis of the catalyst samples and support materials, charge deviations and the graphitic/aliphatic carbon ratios

	C_1	C_2	$Cu(acac)_2$-C	$Cu(acac)_2$hxd-C	$Co(acac)_2$-C	$Co(acac)_2$hxd-C
Shift (eV)	–	1.4	–	1.4	–	1.6
C_1/C_2	0.92	0.14	0.89	0	1.96	0.15

unpaired electrons) are present in the case of the adsorbed $Cu(acac)_2$ samples but absent in the case of the bonded $Cu(acac)_2$ samples. Multiplet structures have also a greater relative importance in spectra of adsorbed $Co(acac)_2$ than in spectra of covalently bonded species; but the difference between the two cases is less pronounced than in the copper containing samples. These differences may result from Schiff condensation between the acetylacetonate complexes and the pendant amine ends of the aliphatic carbon chains.

3.3. Oxidation experiments

The oxidation of *cis*-pinane with *t*-BHP in the presence of $M(II)(acac)_2$hxd-C at room temperature and atmospheric pressure yields mainly 2-pinane hydroperoxide and no 2-pinanol is formed.

Selectivity to 2-pinane hydroperoxide observed for $Co(II)(acac)_2$hxd-C and $Cu(II)(acac)_2$hxd-C is high: 93 and 84%, respectively, for 91% conversion.

The oxidative transformation involves free radical autoxidation pathways, similar to what is observed with zeolite encapsulated phthalocyanine complexes under the same reaction conditions [15,16]. The homolytic decomposition of *t*-BHP by Co(II) and Cu(II) with generation of *t*-butoxy, *t*-butylperoxy radicals and molecular oxygen is a well-known fact [20]. Similarly to what was observed in the presence of zeolite encapsulated phthalocyanine complexes, *t*-BHP is probably adsorbed and subsequently decomposed by the complexes and pinane is oxidised by reaction with *t*-Bu(per)oxy radicals followed by addition of oxygen. With zeolite encaged complexes was also observed that catalytic activity depends on the oxygen donor used, having been observed the order $t\text{-BHP} \gg O_2 > H_2O_2$ [16]. This result suggests that, for an efficient addition of oxygen, the hydrocarbon must be activated by *t*-Bu(per)oxy radicals.

No pinane hydroperoxide is decomposed to pinanol most likely due to the limited access of pinane hydroperoxide to the active sites.

In the presence of modified activated carbons C_1 and C_2 and, on the other hand, in the absence of catalyst the conversion of pinane is significantly lower than that observed with the tethered catalysts (Fig. 5). The activity of these catalysts, when reused after purifying procedures, declines the second time they are used. In a third use, their activity remains practically unchanged. These results indicate that Schiff condensation between acetylacetonate complexes and amines was carried out successfully conferring these catalytic materials a greater stability towards leaching of the complexes. The additional catalytic activity observed for the first run is most likely due to the presence

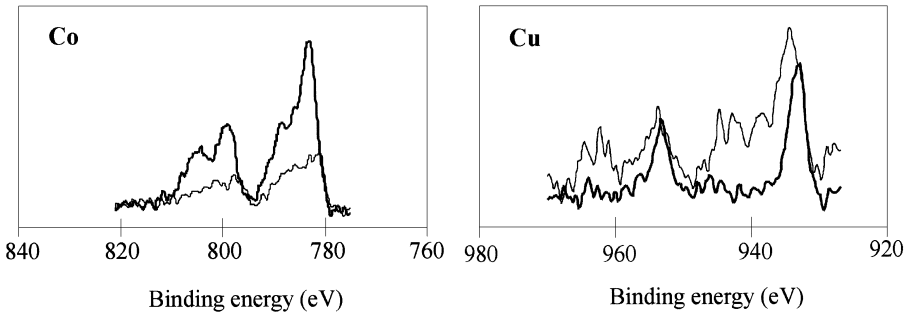


Fig. 4. XPS Cu 2p and Co 2p signals of the adsorbed (thin trace) and covalently bonded complexes (thick trace). Intensities in arbitrary units.

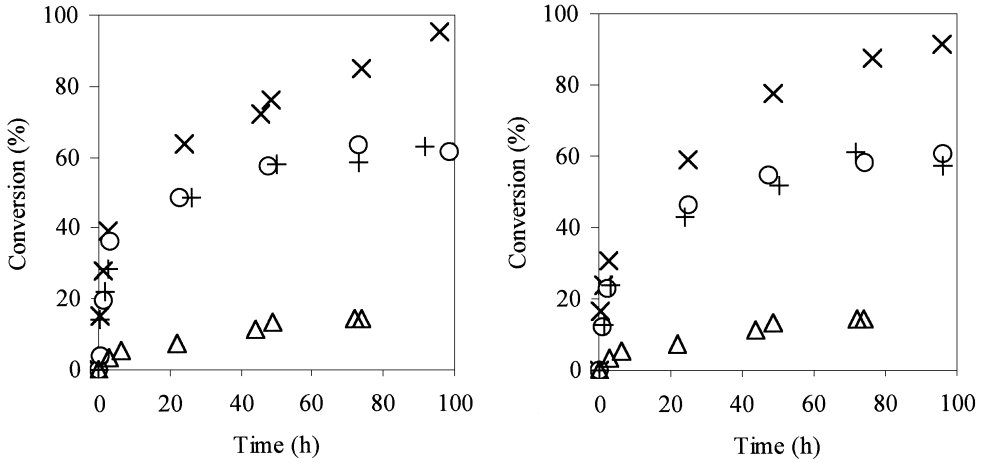


Fig. 5. Pinane conversion profiles for the oxidation reactions carried out in the presence of the catalyst samples Cu(II)(acac)$_2$-C and Co(II)(acac)$_2$-C, compared with that of the uncatalysed reaction. Effects of catalyst reuse: (×) first use; (○) second use; (+) third use and (△) uncatalysed reaction.

of adsorbed complexes that were not totally removed during the catalyst preparation. Eventually, they are leached out from the catalyst and therefore present in less amounts in further runs.

4. Conclusions

The results show that it is possible to covalently attach transition metal acetylacetonate complexes to activated carbon supports by in situ Schiff condensation between the complexes and amine groups.

These solid materials are interesting for liquid phase oxidations since they reveal good stability towards leaching of the complexes into solution. They are active for the oxidation of pinane at room temperature and atmospheric pressure. 2-Pinane hydroperoxide is formed with remarkable selectivity.

References

[1] M. Molina-Sabio, M.A. Muñecas-Vidal, F. Rodriguez-Reinoso, in: F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, K.K. Unger (Eds.), Characterisation of porous solids II, Stud. Surf. Sci. Catal. 62 (1991) 329.
[2] R.J. Jansen, H. van Bekkum, Carbon 32 (1994) 1507.
[3] H.P. Boehm, Carbon 32 (1994) 759.
[4] B. Stöhrm, H.P. Boehm, R. Schlögl, Carbon 29 (1991) 707.
[5] I.F. Silva, J. Vital, A.M. Ramos, H. Valente, A.M. Botelho do Rego, M.J. Reis, Carbon 36 (1998) 1159.
[6] R.F. Parton, P.E. Neys, P.A. Jacobs, R.C. Sosa, P.G. Rouxhet, J. Catal. 164 (1996) 341.
[7] R.C. Sosa, R.F. Parton, P.E. Neys, O. Lardinois, P.A. Jacobs, P.G. Rouxhet, J. Mol. Catal. A 110 (1996) 141.
[8] A. Carmona, A. Corma, A. Iglesias, A. San José, F. Sánchez, J. Organomet. Chem. 492 (1995) 11.
[9] A. Carmona, A. Corma, M. Iglesias, F. Sánchez, Inorg. Chim. Acta 244 (1996) 79.
[10] R.A. Sheldon, I.W. Arends, H.E. Lempers, Catal. Today 41 (1998) 387.
[11] J.M. Thomas, J. Mol. Catal. A 115 (1997) 371.
[12] N.S. Zefirov, A.N. Zakharov, Can. J. Chem. 76 (1998) 955.
[13] Y. Ishii, J. Mol. Catal. A 117 (1997) 123.
[14] I. Neves, C. Freire, A.N. Zakharov, B. de Castro, J.L. Figueiredo, Colloids and Surfaces A: Physicochem. Eng. Aspects 115 (1996) 249.
[15] A.A. Valente, J. Vital, in: H.U. Blaser, H. Baker, R. Prins (Eds.), Heterogeneous catalysis and fine chemicals IV, Stud. Surf. Sci. Catal. 108 (1997) 461.
[16] A.A. Valente, J. Vital, J. Mol. Catal. A 156 (2000) 163.
[17] H.P. Boehm, E. Diehl, W. Heck, R. Sappok, Angew. Chem. Int. Edit. 3 (1964) 669.
[18] C. Leon y Leon, Ph.D. Thesis, Pennsylvania State University, PA, USA, 1992.
[19] P. Vinke, M. van der Eijk, M. Verbree, A.F. Voskamp, H. van Bekkum, Carbon 32 (1994) 675.
[20] R.A. Sheldon, J.K. Kochi, Metal-catalysed Oxidations of Organic Compounds, Academic Press, New York, USA, 1981, p. 34.