the bond length between the Th^{4+} nearest cations neighbors and the oxygen anions in the surrounding of Cu^{2+} (S), and consequently the average $Cu^{2+}(S)O^{2-}$ bond length must appear higher than $3^{1/2}a/4$.

Thus, taking into account this electrostatic perturbation of the thoria lattice by copper, the crystallographic model (with I and S sites) is clearly coherent with the observed variation of $A_\parallel$ ESR parameter. Furthermore, this model shows that Cu^{2+} S ions appear slightly more "isolated" than Cu^{2+} I ions. This conclusion is also in good accordance with the ESR saturation measurements (Figure 6).

Conclusion

Copper–thorium oxides prepared by coprecipitation of thorium and copper hydroxides by ammonium hydroxide, at low copper contents (Cu/Th < 0.01), are single-phase systems, with the thoria structure. Cu^{2+} ions are present in this structure, probably with an 8-fold coordination in interstitial (I) and in substitution (S) positions; I Cu^{2+} species can be introduced in the ThO_2 lattice at a low calcination temperature (below 673 K), whereas S Cu^{2+} species appear only after calcination at higher temperatures. This information was deduced from ESR spectra of both species, which showed that both Cu^{2+} ions are isolated in the thoria lattice. The introduction of copper into I and S crystallographic sites produces a small axial distortion of the thoria cubic symmetry. From the **g** tensor and **A** tensor values, the paramagnetic electron appears a little more localized on the S copper ion than on I one.

When Cu/Th ratio is higher than 0.01, a new ESR signal (B) appears, and copper ions can no longer be considered as isolated ions. These results will be discussed in the following article.[22]

Preparation and Characterization of Copper–Thorium Oxide Catalysts. 2. ESR Study of Copper(II) Ion Pairs and Correlation with the Selective Hydrogenation of Isoprene

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CuThO oxides prepared with an atomic ratio Cu/Th > 0.01 were extensively studied by electron spin resonance (ESR) and X-ray photoelectron spectroscopies (XPS). The XPS analysis of these solids showed that the thoria surface is enriched with copper. The X-ray diffraction patterns for Cu/Th > 0.25 revealed two distinct phase systems, ThO_2 and CuO. ESR studies evidenced two signals of monomeric Cu^{2+} species (M_1 and M_2) and a well-resolved D signal ($\Delta m_s = 1$) of Cu^{2+} ion pairs, accompanied by a weak signal at half magnetic field intensity ($\Delta m_s = 2$). From the $\Delta m_s = 2/\Delta m_s = 1$ intensities ratio and from the fine splitting observed for the D signal, the distance between the Cu^{2+} ions in the pair have been calculated. These copper–thorium oxide catalysts are active for selective hydrogenation of isoprene at 373 K after reduction of the oxide phase at 523 K. A correlation between this activity and the relative intensities of M_1, M_2, and D signals was established.

Introduction

Solid solutions of isolated Cu^{2+} ions in the thoria lattice can be prepared by coprecipitation of the hydroxides by aqueous ammonium hydroxide, followed by a calcination treatment in air.[1] This single-phase system had been characterized at very low copper contents (below Cu/Th = 0.01), mainly by ESR techniques.

At higher copper contents, we had observed noticeable modifications in the ESR spectra of the Cu^{2+} ions with respect to those obtained at low copper contents. All these phenomena will be discussed and achieved with XPS characterization of the solid surface, after calcination in air, to study the copper distribution on the surface of the catalysts.

This work is a part of a larger study of copper-based catalysts in which the Cu^{2+} ions were associated with other cations (Zn^{2+}, Al^{3+}, or Cr^{3+}).[2-4] Then, the present purpose is to extrapolate our previous approach to the new and relatively well characterized copper–thorium system. In that way, some catalytic results concerning the selective hydrogenation of isoprene by the reduced CuThO catalysts, at low and high copper contents, have been also reported, to demonstrate the different catalytic behavior of the various copper species characterized by ESR in the calcined compounds. Further ESR and XPS investigations
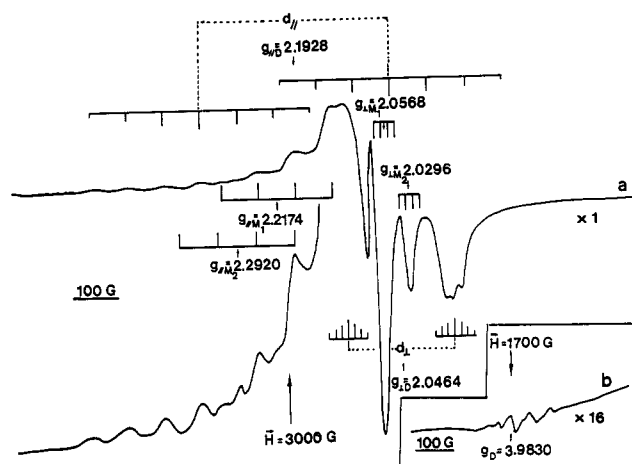
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Figure 1. ESR signals (X-band) observed at room temperature with the Cu/Th = 1.5 sample: (a) signal for $\Delta m_s = 1$ (allowed transition); (b) signal for $\Delta m_s = 2$ (forbidden transition).

concerning the reduced state of these CuThO catalysts will be published elsewhere.[5]

Experimental Section

Preparation of the Catalysts. The solids were prepared by precipitation of the hydroxides by aqueous ammonium hydroxide from copper and thorium nitrates, as previously described.[1]

ESR Spectra. X-band ESR spectra were recorded as previously.[1] Q-band spectra were recorded on a Varian E9 spectrometer, at 35 GHz, without microwave saturation; 100-kHz modulation with 1-G amplitude was used. The intensities of the transitions were obtained by double integration. The contributions for ^{63}Cu and ^{65}Cu were not resolved in the spectra obtained with the present atomic ratios Cu/Th, so a single isotope was assumed in the calculations.

XPS Measurements. The surface atomic composition Cu/Th of the catalysts has been deduced from XPS studies.

A Leybold-Heraeus LHS 10 spectrometer with an Al Kα anticathode ($h\nu$ = 1486.6 eV) was used to record the XPS spectra. The samples were crushed to a fine powder and spread thinly on an indium support; the spectra were taken in a high vacuum (10^{-8} Torr) at room temperature.
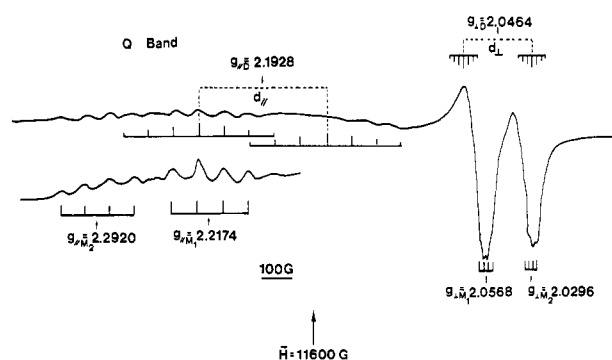
For a homogeneous solid, the surface atomic ratio Cu/Th is given by the formula

$$\frac{I_{Cu}}{I_{Th}} = \frac{Cu}{Th} \frac{\sigma_{Cu}}{\sigma_{Th}} \frac{\lambda_{Cu}}{\lambda_{Th}} \frac{T_{Cu}}{T_{Th}}$$

where I_{Cu} and I_{Th} are the areas of two photoelectron peaks (here $Cu_{2p3/2}$ and Th_{4f} lines) of the analyzed elements, $\sigma_{Cu,Th}$ represent the photoelectron cross sections of the $Cu_{2p3/2}$ and Th_{4f} levels taken from Scofield tables[6] ($\sigma_{Cu_{2p3/2}}$ = 227 528 barns and $\sigma_{Th_{4f}}$ = 581 400 barns at 1487 eV). $\lambda_{Cu,Th}$ is the escape depth of the photoelectron, proportional to the kinetic energy $(E_{Cu,Th})^{0.77}$ (ref 7), and $T_{Cu,Th}$ is the transmission factor of the analyzer, proportional in our case to the kinetic energy $E_{Cu,Th}$. Then, we have

$$\frac{I_{Cu}}{I_{Th}} = \frac{Cu}{Th} \frac{\sigma_{Cu}}{\sigma_{Th}} \left(\frac{E_{Cu}}{E_{Th}}\right)^{1.77} = 0.11 \frac{[Cu]}{[Th]}$$

Catalytic Test. The catalytic hydrogenation of isoprene was carried out at 373 K in an all-glass grease-free flow apparatus, previously described[8] and equipped with two parallel microreactors to obtain catalytic activities relative to a reference catalyst (Cu/Th = 0.1). The reaction conditions were 100 mg of catalyst, a total pressure of 1 atm, 40–60 mL min^{-1} of hydrogen, and 20 Torr of

Figure 2. ESR signal observed at 35 GHz (Q-band) at room temperature with the Cu/Th = 1.5 sample.

Table I. ESR g and A Anisotropic Tensors Values for Cu^{2+} Ions in CuThO Compounds (Cu/Th > 0.25)

Cu/Th > 0.25	$g_\parallel$	$g_\perp$	g_{iso}	$A_\parallel$, G	$A_\perp$, G	A_{iso}, G
M$_1$ signal	2.2174	2.0568	2.1639	82.8	13.5	59.7
M$_2$ signal	2.2920	2.0296	2.2045	80.1	13.0	57.7
D signal ($\Delta m_s = 1$)	2.1928	2.0464	2.144	80.5	14.0	58.3
D signal ($\Delta m_s = 2$)	g = 3.9830					

isoprene. Before the catalytic test, the catalysts were reduced in a flow of pure hydrogen at 523 K. The reaction products were analyzed by gas chromatography.

Results

ESR Results. As previously mentioned,[1] a new B spectrum appears when the Cu/Th atomic ratio is greater than 0.01, whereas the relative intensities of A$_1$ and A$_2$ signals decrease and totally disappear for Cu/Th = 0.25. Then, the B spectrum is always observed with an invariable shape when Cu/Th increases from 0.25 to atomic ratios as high as 4; for example, the B spectrum for Cu/Th = 1.5 is given in Figure 1a.

To obtain better information about the B spectrum, Q-band analysis of the Cu/Th = 1.5 sample was performed (Figure 2). X-band and Q-band ESR spectra clearly demonstrate the existence of three signals (Table I):

One signal, D, corresponds to Cu^{2+}–Cu^{2+} pairs.[9] Indeed, the seven components (1-2-3-4-3-2-1) of the hyperfine splitting with two identical nuclei of spin $^3/_2$ clearly visible for $g_\parallel$ (Figures 1 and 2) and the weak signal observed just at half the normal magnetic field intensity (Figure 1b) are characteristic of the existence of copper(II) ion pairs.[10-13] The weak signal corresponds to the forbidden transition (Δm_s = 2), whereas the signal observed at the normal magnetic field corresponds to the allowed transition (Δm_s = 1). Both signals (Δm_s = 1 and Δm_s = 2) will be assigned D signal.

Two signals M$_1$ and M$_2$, probably produced by two monomeric Cu^{2+} species, are slightly different from the former A$_1$ and A$_2$ species[1] (see, for example, the $A_\parallel$ values).

The study of these spectra versus the calcination temperature (Figure 3) shows that the resolution is enhanced at higher temperatures. As previously discussed,[1] ESR line narrowing can be correlated with a more isolated magnetic

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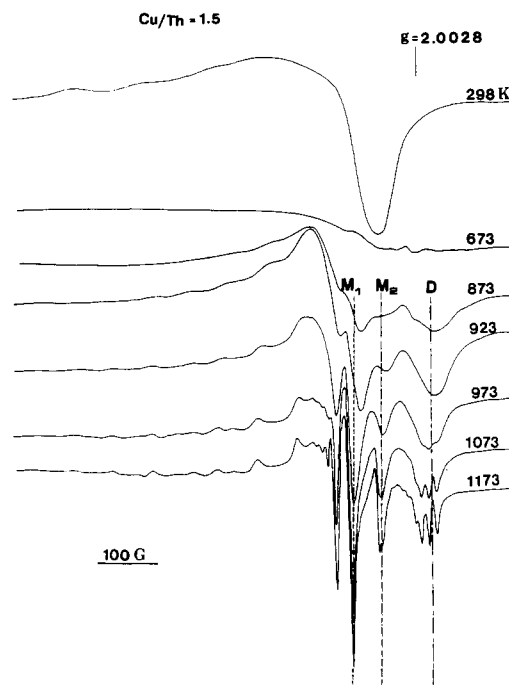(12) Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177.

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Cu/Th = 1.5

g = 2.0028

298 K

673

M₁ M₂ D 873

923

973

1073

1173

100 G

Figure 3. ESR signals (X-band) observed at room temperature with the Cu/Th = 1.5 sample after raising calcination temperature treatments in air, from 673 to 1173 K. Here, M_1, M_2, and D denote characteristic lines of the corresponding spectra of monomer and dimer species.
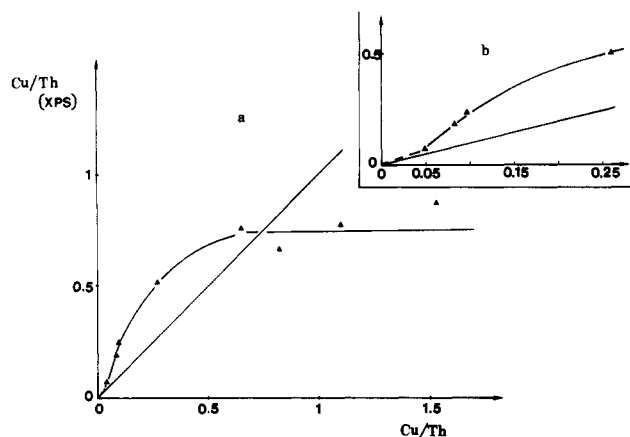

- A₁
○ A₂
■ D
▲ M₁
△ M₂
☆ Activity

a.u.
Intensity of
esr signal

0.1 0.2 0.3 0.4 0.5   1.0   Cu/Th

Figure 4. Relative intensities variations for A_1, A_2, M_1, M_2, and D ESR signals (with independent arbitrary units), versus the chemical atomic ratio Cu/Th. The relative catalytic activities (reference Cu/Th = 0.1; $v = (1.2 \pm 0.2) \times 10^{-4}$ mol min^{-1} g^{-1}) are also reported.

character of the observed species, and thus a redistribution with a better dispersion of Cu^{2+} ions by migration in the thoria lattice does occur at higher temperatures. Line narrowing may also result from relaxation of Cu^{2+} ions by precipitated ThO_2, which involves a better crystalline material upon higher calcination temperature. In all the cases, the dimeric and both monomeric species can be observed, for Cu/Th > 0.01. Separation of the ESR lines attributed to the different species (A_1, A_2, M_1, M_2, D) is not easy. However, by following some lines that characterize these species, versus the calcination temperature, it seems evident that the M_1, M_2, and D signals vary in a similar manner (Figure 3). Thus, it is possible to report the relative intensities of the A_1, A_2, M_1, M_2, and D signals (with independent arbitrary units) versus the copper/ thorium atomic ratio for the different samples (Figure 4);

Cu/Th
(XPS)

Figure 5. (a) Surface atomic composition Cu/Th (derived from XPS intensities ratios measured for $Cu_{2p3/2}$ and Th_{4f}) versus the chemical atomic ratio Cu/Th (the theoretical line for a homogeneous solid is drawn). (b) Same variations with an expanded scale.

Table II. Relative Catalytic Activities as a Function of Cu/Th Ratio (Cu/Th = 0.1 as a Reference)

catal Cu/Th	0.04	0.06	0.08	0.1	0.25	0.5
activity		0.15	0.47	1.0	0.98	1.56

here also, the M_1, M_2, and D intensities seem to be correlated: these signals rapidly increase from Cu/Th = 0.01 to a maximum value, reached for Cu/Th = 0.25; then, a significant decrease in the intensities is observed, and a complete disappearance of the signals occurs for Cu/Th > 4.

XPS Results. The surface compositions determined from XPS data are compared in Figure 5 with the corresponding samples compositions. The 45° diagonal line corresponds to the hypothetical situation of homogeneous compounds. The results clearly indicate the presence of three domains that can be correlated with the ESR results (Figure 4):

(i) Cu/Th < 0.01 corresponds exclusively to the A_1 and A_2 species previously described.[1] It is difficult to record $Cu_{2p3/2}$ XPS spectra for Cu/Th < 0.01; however, it appears that the distribution of copper can be considered almost homogeneous at this low copper content.

(ii) 0.01 < Cu/Th < 0.25 corresponds to the simultaneous existence of A_1, A_2, M_1, M_2, and D species until Cu/Th = 0.25, and only M_1, M_2 and D species above this atomic ratio; the experimental values of the surface compositions are clearly located above the theoretical line, which indicates that the surface of the samples is enriched in copper, as compared to the samples mean compositions.

(iii) For higher atomic ratios (Cu/Th > 0.25), a deviation and a plateau are observed, until Cu/Th = 1.5. This phenomenon, which is often observed for supported catalysts,[14,15] can be correlated here with the additional formation of crystallites of copper oxide on the thoria. The distribution of these new copper species (undetectable by ESR) on the surface of the catalysts remains nearly constant for this range of atomic ratios (the CuO crystallites grow up with an approximately constant surface coverage, and the surface atomic ratio Cu/Th calculated from XPS remains constant). These observations correlate the structural investigations of the samples series: just above Cu/Th = 0.2, the X-ray diffraction analysis begins to show

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Table III. Selectivity in the Isoprene Hydrogenation

catal Cu/Th	3-methyl-1-butene, %	2-methyl-1-butene, %	2-methyl-2-butene, %	isopentane, %
0.06	28	60	12	<1
0.08	29	58	13	<1
0.1	30	57	13	<1
0.25	29	58	13	<1
0.5	14	48	23	15

the existence of CuO crystallites, in addition to ThO$_2$ and the relative intensity of the CuO diffraction diagram increases drastically with the sample copper content. Furthermore, the pH evolution[1] during the "coprecipitation" was also in accordance with the formation of two-phase systems in this Cu/Th domain.

Catalytic Activity and Selectivity. Table II reports the relative activity values for the different samples:

For low Cu/Th ratios (<0.01), the hydrogenation activity is neglectible.

For intermediate ratios (0.01 < Cu/Th < 0.25), the catalytic activity clearly increases. A reference activity has been chosen for the Cu/Th = 0.1 catalyst: (1.2 ± 0.2) × 10^{-4} mol g^{-1} min^{-1}, measured for this catalyst, was reported as unit relative activity in Table II. In the experimental conditions previously described, hydrogenation of isoprene is very selective in monohydrogenation products (Table III).

For higher Cu/Th ratios (for example, 0.5), the catalytic activity slightly increases, but the selectivity is poor: a significant amount of isopentane was detected (15%).

Discussion

The formation of copper ion pairs is often observed by ESR.[9-13,16-20] In particular, in the case of copper-based catalysts, copper pairs existence is a frequent feature;[13,16-19] however the corresponding spectra are often less resolved than in the present case; the reasons are the good dispersion of Cu^{2+} ion pairs in the thoria lattice (low copper content) and probably the high symmetry of this cubic lattice. Then, a correlation between the Cu^{2+} species corresponding to CuThO ESR spectra (M$_1$, M$_2$, and D) and the catalytic properties can be attempted. In a similar view, the catalytic interest of oxide precursors (Cu^{II}OCu^{II})$^{2+}$ pairs, which gave after reduction active sites Cu^{I} for methanol synthesis, had been recently evidenced for supported copper-zinc catalysts,[18,19] but precise calculations of the ESR spectroscopic parameters of these copper(II) pairs was not possible in that case, because of existence of strong copper-copper magnetic interactions that strongly broadened and obscured the ESR signals.

In a general way, the most visible ESR characterization of Cu^{2+} pairs existence is the presence of a weak signal at half normal field intensity, which is produced by forbidden transitions at $\Delta m_s = 2$.[10,11] The intensities ratio I_{rel} of the signals respectively observed at $\Delta m_s = 2$ and $\Delta m_s = 1$ is theoretically correlated with the distance r between both Cu^{2+} ions in the pair,[20] by the equation

$$I_{rel} = \frac{I_{\Delta m_s=2}}{I_{\Delta m_s=1}} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2$$

where A is a constant [$A = (21 \pm 2) \times 10^{-6}$], with r in nanometers and ν in gigohertz. In our case, $I_{rel} = (6 \pm 1.5) \times 10^{-4}$ and $r = 0.56 \pm 0.03$ nm. This significant uncertainty (25%) in the I_{rel} value takes into account the approximate subtraction of the most intense lines of M$_1$ and M$_2$ monomer signals (Figure 3).

The dimer spectrum (Figure 1a) gives a direct experimental evaluation of $d_\parallel$ ((420 ± 60) × 10^{-4} T) and $d_\perp$ ((240 ± 10) × 10^{-4} T). These parameters are defined by[13]

$$d_\parallel = \frac{2D}{g_\parallel\beta} \qquad d_\perp = \frac{D}{g_\perp\beta}$$

where β = Bohr magneton, $g_\parallel$ = 2.1928, and $g_\perp$ = 2.0464. From these values, we can derive estimations of the zero-field splitting constant D ((4.6 ± 0.7) × 10^{-25} J for the parallel components and (4.3 ± 0.2) × 10^{-25} J for the perpendicular ones).

If we assume that D is due only to dipolar interactions with no contribution from anisotropic exchange,[20] by using the equation

$$D = 10^{20}\frac{(2g_\parallel{}^2 + g_\perp{}^2)\beta^2}{2r^3}$$

where D is in joules and r in nanometers, we obtain $r = 0.50 \pm 0.06$ nm (parallel components) and $r = 0.51 \pm 0.03$ nm (perpendicular components). This last estimation is the most accurate; nevertheless a good correlation is observed with the r value previously deduced from I_{rel}.

In conclusion of this ESR investigation, formation of localized Cu^{2+} pairs in the lattice of ThO$_2$, mainly characterized by dipolar interactions, is evident: the distance between both ions is 0.51 ± 0.03 nm, which is about the unit cell dimension of the thoria lattice (a = 0.56 nm). However, distribution of these copper dimers cannot be uniform in the thoria bulk, because the XPS results (Figure 5) show an important surface enrichment with copper in the Cu/Th domain between 0.01 and 0.25, which is the domain of the copper(II) pairs formation. Moreover, a simple calculation from the specific areas shows that the total contents of copper cannot be localized at the surface of the thoria, even for the small contents of copper.

Yet, the presence of a large amount of copper(II) pairs near the thoria surface in the oxide precursor state of the catalysts is very probably correlated to the catalytic activity in the hydrogenation reactions: indeed, the catalytic activities are negligible for Cu/Th < 0.01 (domain for the exclusive formation of A$_1$ and A$_2$ species, without any copper ion pairs; Table II, Figure 4), and for Cu/Th > 0.01, the conversion rate for selective hydrogenation of isoprene follows the evolution of the ESR signal intensity (M$_1$, M$_2$, and D). Then, the formation of active copper sites by reduction of the copper(II) ion pairs of M$_1$ and M$_2$ species can be invoked to explain the appearance of very selective catalytic sites in the hydrogenation of isoprene until Cu/Th = 0.25. This correlation can be compared with similar observations on copper-based catalysts active in methanol synthesis.[18]

For higher Cu/Th ratios, the catalytic activity still increases, but a significant drop in the hydrogenation selectivity is clearly observed. This behavior is certainly correlated with the formation of a large amount of copper oxide during the preparation step of the catalysts. Such CuO clusters on the surface of thoria would prevent accessibility to the previous selective sites. Furthermore, the ESR signals of the copper(II) ion pairs or M$_1$ and M$_2$ species, probably correlated with these selective sites, also decrease in this Cu/Th domain, and totally disappear above Cu/Th = 4, which allows us to suppose also a net

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decrease in the corresponding selective catalytic sites concentration.

To elucidate the potential catalytic role of M_1, M_2, and D species, ESR and XPS studies of CuThO catalysts in the reduced state are in progress.[5]

Importance of Energetics in the Design of Small Bandgap Conducting Polymers

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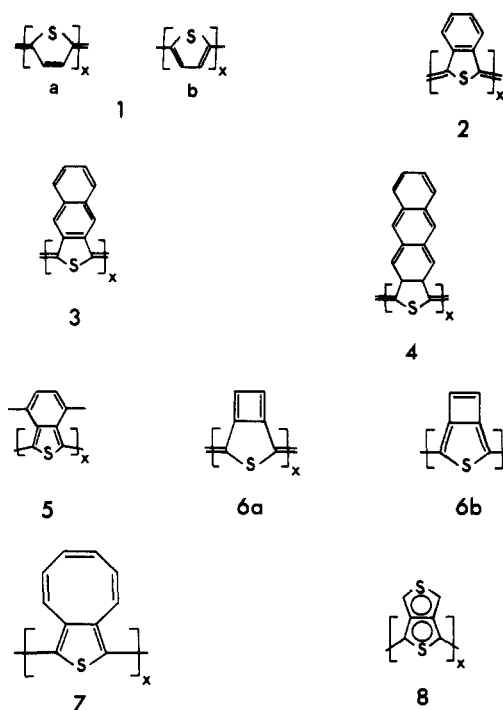*Allied-Signal Co., Corporate Technology, Morristown, New Jersey 07960-1021*

With a combination of semiempirical quantum chemical methods applicable for geometry optimization and energy band structure calculation, several heteroatomic conjugated polymers based on polythiophene have been studied with the goal to correlate the chemical composition and topology of the unit cells with energetics and bandgaps. In the theoretical design of small E_g polymers the relative stability of structural isomers of a given polymer plays a crucial role. We have found for the materials investigated in this work that the structure having the larger bandgap among structural isomorphs is the more stable one. The combination of MNDO and Hückel crystal orbital methods provide a firm theoretical basis to the synthesis of small-bandgap conducting polymeric materials.

Introduction

The synthesis of conjugated polymers exhibiting high electrical conductivity has drawn considerable interest in recent years.[2] Concomitant with the synthesis of conducting polymers, electronic structure calculations have been developed for understanding electrical and optical properties of these materials.[2-16] Many of the theoretical calculations on conducting polymers have dealt with the understanding of the electronic structure of small energy bandgap (E_g) polymers. Such calculations may help in designing new small E_g polymers. Recently Dougherty et al.[9,10] have also studied possible small E_g polymers.

Chart I

Several theoretical calculations concerning small E_g have put emphasis on calculating the E_g of polymers without taking energetics into consideration.[9-16] However, determining the relative stability between structural isomers or conformers of a given polymer becomes a crucial matter in those cases where alternative structures possess essen-

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