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PYROLYSIS AND HYDROPYROLYSIS OF AMBERLITE IRC50 AND SOME OF ITS METAL-EXCHANGED FORMS

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ABSTRACT

As a model for part of the structure of low-rank coals, a cation exchange resin (Amberlite IRC50) and several of its metal-exchanged forms were studied by differential thermal analysis in nitrogen and in high-pressure hydrogen, and also by simultaneous thermogravimetry and mass spectrometry. The pyrolysis temperatures decreased in the sequence: Na > Ba > Ca > Zn > Co > Bi > Sn > Pb > Fe > Ni. The presence of high-pressure hydrogen complicated the results for the reducible metals.

Because the peak temperature of the lead form was similar to those of iron, nickel and tin, which are known to catalyse hydrogenation reactions, it is concluded that lead is worthy of investigation as a potential catalyst for coal hydrogenation. The combination of nickel and cobalt, and of lead and iron appear to act synergistically in hydrogen, so they too may be effective catalyst combinations. Since sodium, potassium and calcium occur commonly in low-rank coals, they may inhibit the onset of decomposition reactions during processing at typical coal-processing temperatures of about 400 °C.

INTRODUCTION

The weak cation exchange carboxylate resin Amberlite IRC50 has been studied here as a model compound for one of the functional groups known to occur in low-rank coals, viz. carboxylate groups.

Low-rank coals, such as lignites, generally contain significant proportions of carboxylate groups and associated hydrogen and metal cations. Some of the latter catalyse certain coal hydrogenation reactions. In order to study the reactions of carboxylate groups independent of other reactions which occur in coal, it is expedient to select suitable model systems.

A study [1] of the metal salts of octadecanoic acid showed that the pyrolysis and hydropyrolysis temperatures, determined by TG or DTA, varied from about 300 °C for the tin(II) salt to 500 °C for the potassium and sodium salts. The strength of the metal–carboxylate bonding appeared to be the parameter controlling the onset of reaction.

In this study the Amberlite resin was treated with a solution of a salt of various metals to produce metal-exchanged forms. The highly condensed

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polymeric structure of the resin has some similarities to the structure of low-rank coals, which also have metal ions ionically bonded to carboxylate groups attached to large molecular structures [2]. The effect of the nature of the cation on the decomposition reactions was investigated by DTA and simultaneous TG–MS, as an aid in understanding some of the reactions which take place in lignite processing.

EXPERIMENTAL

Preparation of exchanged resins

Na^+ form

A 100-g sample of the hydrogen ion form of Amberlite IRC50 (supplied by BDH) was treated with a solution of 17 g of sodium hydroxide in about 200 cm^3 of distilled water. After stirring intermittently for 2 h the resin was filtered off, re-treated with a fresh sodium hydroxide solution, filtered again, thoroughly washed with water, and desiccated.

Ca^{2+} and Ba^{2+} forms

Damp H-form resin (6 g) was treated with 100 cm^3 of saturated calcium hydroxide solution. The resin was filtered, re-treated with a fresh batch of calcium hydroxide solution, filtered again, thoroughly washed, and desiccated over silica gel. The barium form was prepared by an analogous process using barium hydroxide solution.

Sn^{2+} form

About 5 g of the dried hydrogen form of the resin was soaked in 50 cm^3 of a solution (100 mol m^{-3}) of anhydrous tin(II) chloride in methanol (to inhibit hydrolysis of the tin ions).

Other forms

About 5 g of the damp sodium form of the resin was soaked in a solution of an appropriate salt of the desired metal (100 mol m^{-3}). It was soaked, washed and filtered three times, and finally desiccated. The salts used were: $ZnSO_4$, $Pb(CH_3COO)_2$, $Ni(CH_3COO)_2$, $CuSO_4$, $Fe(NO_3)_3$, $CoSO_4$ and $Bi(NO_3)_3$.

Mixed ion forms

Two mixed ion forms were prepared using (1) an aqueous mixture of $CoSO_4$ (100 mol m^{-3}) and $Ni(CH_3COO)_2$ (10 mol m^{-3}); and (2) $Fe(NO_3)_3$ (100 mol m^{-3}) and $Pb(NO_3)_2$ (10 mol m^{-3}).

Differential thermal analysis (DTA)

Some DTA experiments were done with nitrogen at atmospheric pressure flowing at 95 cm^3 min^{-1}, using a Stone 202 DTA instrument with sample holder 11BR2 and ring-shaped Platinel thermocouples, with platinum dishes holding 6.5–9.5 mg of sample. The exchanged resins were desiccated over P_2O_5 before DTA. The heating rate was 10 °C min^{-1}.

For the high-pressure DTA experiments, sample holder 15-BR2 was used. A 4–10-mg sample was weighed onto a 4-mg aluminium foil dish, and placed on the ring thermocouple (Platinel 2). An empty aluminium dish was placed on the reference thermocouple ring.

For the DTA experiments in hydrogen, the sample chamber was flushed twice with hydrogen at 8 MPa pressure before filling to the operating pressure of 8.0 MPa. The heating rate was set to 10 °C min^{-1}, but because of the absorption of hydrogen by the platinel thermocouples, they had to be recalibrated (using Analytical grade KNO_3, $KClO_4$, K_2SO_4 as standards). The actual heating rate was found to vary from 25 °C min^{-1} at 100 °C to 10 °C min^{-1} at 600 °C.

Thermogravimetry–mass spectrometry (TG–MS)

The thermobalance was a Stanton-Redcroft Model TG-770. A 2–5-mg sample was heated at 10 °C min^{-1} in an atmosphere of helium flowing at 70 cm^3 min^{-1}. The modifications to the hangdown tube and the interface with the Extranuclear SpectrEL quadrupole mass spectrometer (Model No. 275-50) have been described by Parker and Patterson [3]. Briefly, the gas flows from the thermobalance via an alumina capillary (about 50 mm long), whose tip is just above the sample pan, and 1.6 m of teflon tubing to the leak valve of the mass spectrometer. A small proportion of the gas is sampled by the mass spectrometer via the leak valve; the remainder is removed by a rotary vacuum pump.

The ion signals, sample mass and temperature were recorded by a microcomputer. After each run, the TG, DTG and the ion signal of selected mass numbers were plotted as a function of temperature. One major mass number was chosen for each product of interest. Each ion has a different sensitivity.

RESULTS AND DISCUSSION

The DTA curves of the resin salts in flowing nitrogen, at atmospheric pressure, are shown in Fig. 1, and the DTA in hydrogen at a pressure of 8.0 MPa in Fig. 2. Typical reactions which occurred are shown in Fig. 3; the TG–MS results in flowing helium are given in Figs. 4–10. All samples lost

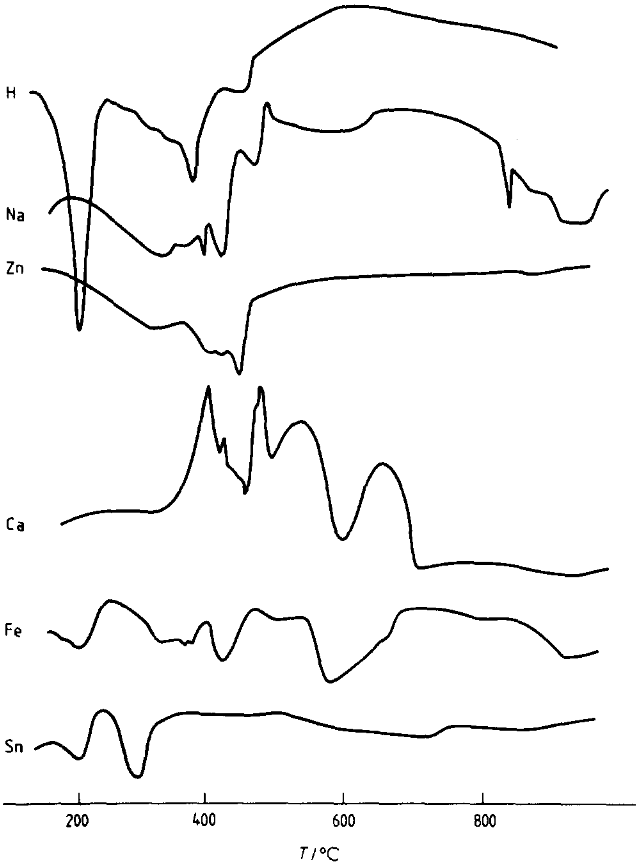


Fig. 1. DTA of some Amberlite IRC50 salts in dynamic nitrogen (95 cm^3 min^{-1}), at heating rate 10 °C min^{-1}: H^+ form, 9.5 mg; Na^+ form, 6.5 mg; Zn^{2+} form, 7.8 mg; Ca^{2+} form, 9.3 mg; Fe^{3+} form, 6.6 mg; Sn^{2+} form, 9.5 mg.

water below 100 °C. The results of different techniques will be discussed together for each form of the ion-exchange resin.

H^+ form

An endothermic reaction occurred at about 200 °C in nitrogen (Fig. 1). Water ($m/z = 17$) was the only species detected by MS during this reaction (Fig. 4), and the mass loss calculated from the TG (8.7%) was approximately that expected from the dehydration–cyclization reaction (10.5%) reported by Marinov and Mitov [4] (Fig. 3a).

The absence of this reaction in the metal-exchanged samples was used diagnostically to indicate that most, if not all, of the hydrogen ions had been exchanged for metal cations.

Between 400 and 500 °C there was a 75% mass decrease accompanied by a complex thermal effect. During this pyrolysis reaction CO ($m/z = 28$), CO_2

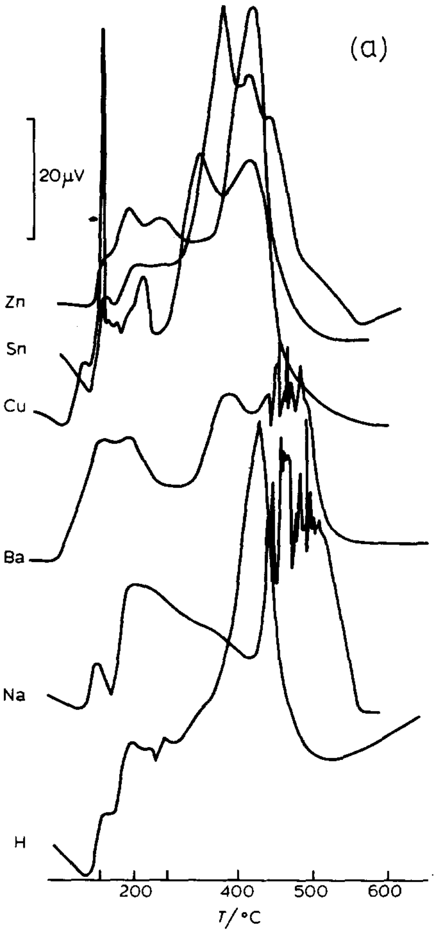


Fig. 2. DTA in hydrogen at 8.0 MPa pressure of Amberlite IRC50: (a) Zn^{2+} form, 4.5 mg; Sn^{2+} form, 7.1 mg; Cu^{2+} form, 4.5 mg; Ba^{2+} form, 4.1 mg; Na^{+} form, 5.9 mg; H^{+} form, 6.2 mg.

($m/z = 44$) and many organic species were detected by MS ($m/z = 15$, 29, 39, 41, 43, 56, 67, 68, 86, 91, etc.). The char remaining after TG was 16% of the original mass.

Na^{+}, K^{+} and Ca^{2+} forms

Pyrolysis occurred at about 500 °C—the highest pyrolysis temperature of all the exchanged forms tested. Considerably more CO than CO_2 was detected by MS, along with numerous organic fragments including methane ($m/z = 15$) and ethane ($m/z = 29$). During the reaction, a 44% mass decrease occurred, indicating that some char remained.

At 830 °C there was a sharp endothermic peak on DTA (Fig. 1) due to the melting of sodium carbonate: cf. melting point [5] of pure Na_2CO_3 851 °C.

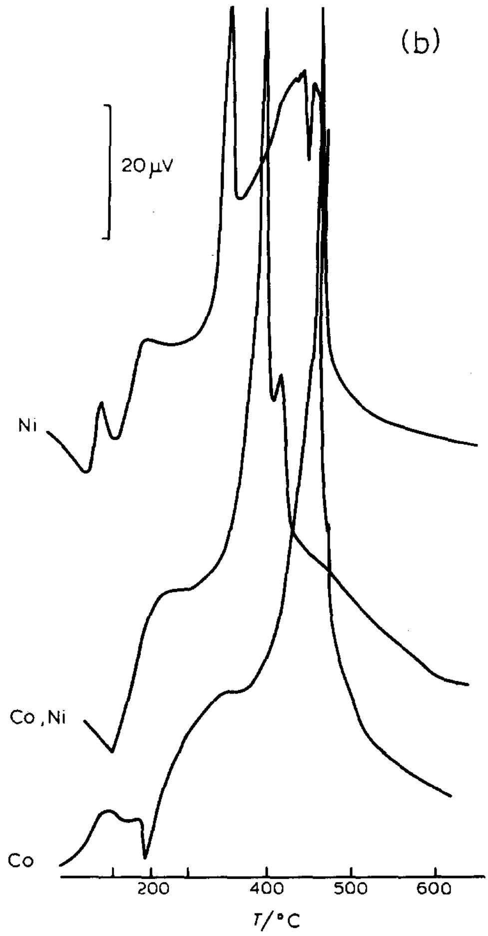


Fig. 2. (b) Ni^{2+} form, 4.8 mg; mixed Cu^{2+}, Ni^{2+} form, 4.4 mg Co^{2+} form, 5.8 mg.

This was followed by the endothermic decomposition of sodium carbonate, during which CO and a little CO_2 were detected by MS. This implies reaction with the remaining carbonaceous material, none of which remained after the run (visual observation).

The reactions of the sodium-exchanged Amberlite appear to be as shown in Fig. 3b, followed by the decomposition of sodium carbonate:

$$Na_2CO_3 + C \xrightarrow{800\,^\circ C} Na_2O + 2\,CO$$

$$Na_2CO_3 \xrightarrow{800\,^\circ C} Na_2O + CO_2$$

In hydrogen (Fig. 2a) the exothermic decomposition reaction was very complex. The reactions of the potassium and calcium forms were similar to those of the sodium form.

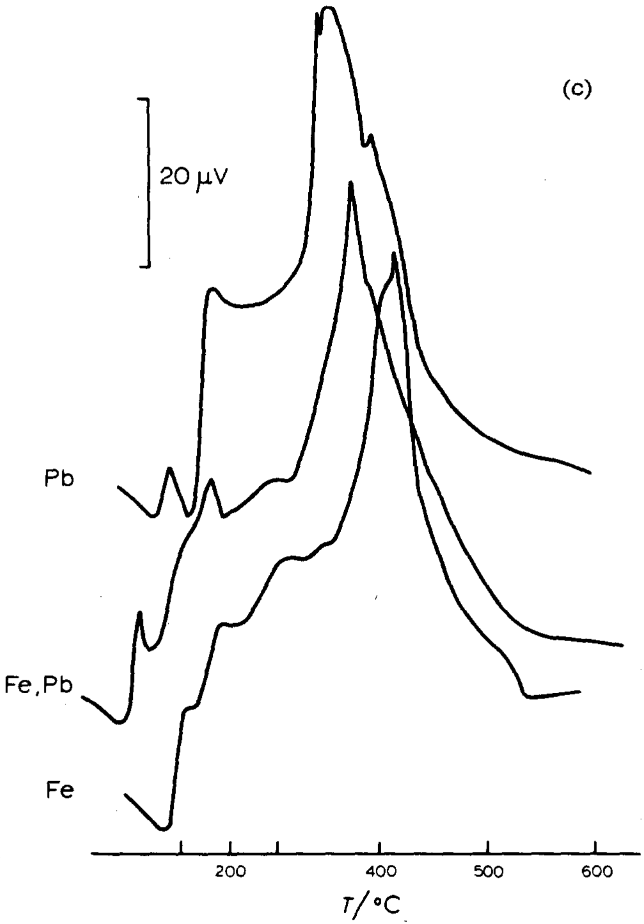


Fig. 2. (c) Pb^{2+} form, 7.1 mg; mixed Fe^{3+}, Pb^{2+} form, 3.8 mg; Fe^{3+} form, 4.4 mg.

Zn^{2+} form

The zinc-exchanged resin decomposed in a single step (TG) at about 450 °C (Fig. 5). Carbon dioxide was the main gaseous product, although some carbon monoxide was also detected by MS along with many organic fragments. The experimental results are consistent with the reaction shown in Fig. 3c.

Ba^{2+}, Pb^{2+}, Bi^{3+} and Sn^{2+} forms

The DTG of the barium form gave peaks at 390 and 450 °C (Fig. 6). During the smaller, first peak, CO_2 and some CO were evolved. The peak in organic products such as methane and ethane occurred at 480 °C. The separation into stages appears to have been caused by the low decomposition temperature allowing the intermediate ketone to be stable for a time (Fig. 3d).

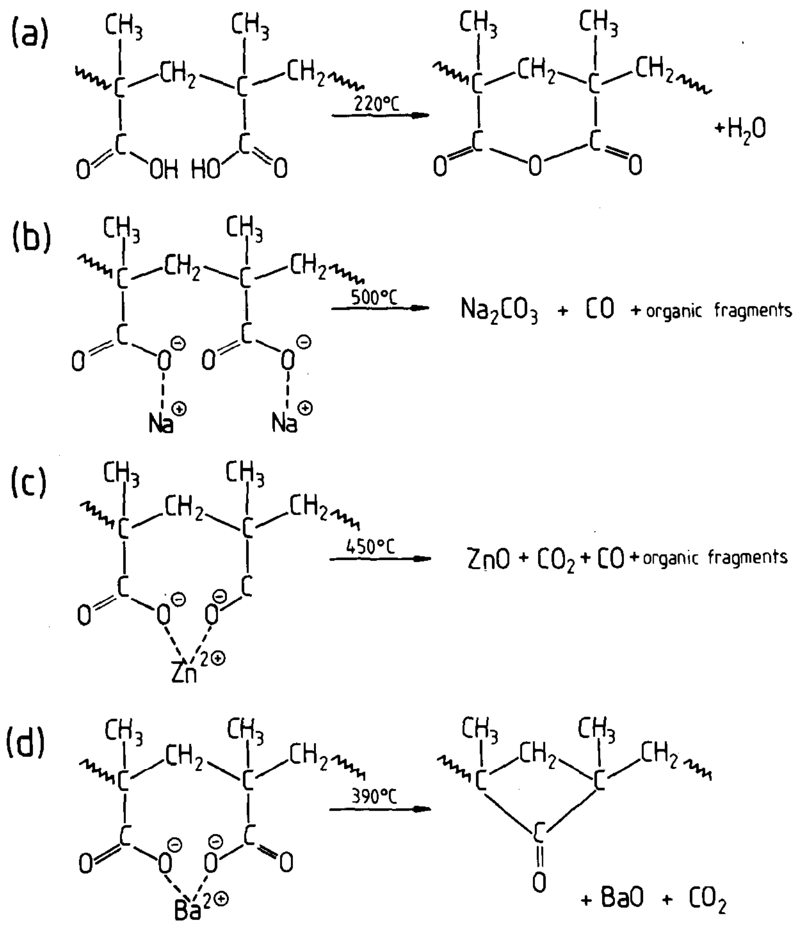


Fig. 3. Decomposition reactions of Amberlite IRC50: (a) H^+ form; (b) Na^+ form; (c) Zn^{2+} form; (d) Ba^{2+} form.

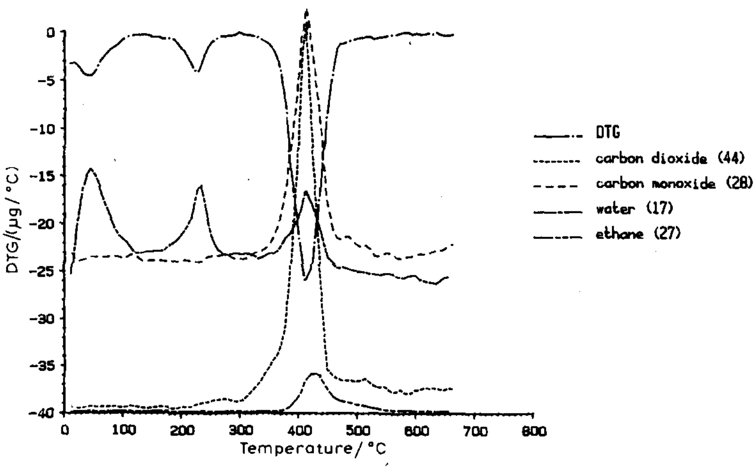


Fig. 4. TG–MS of Amberlite (H^+).

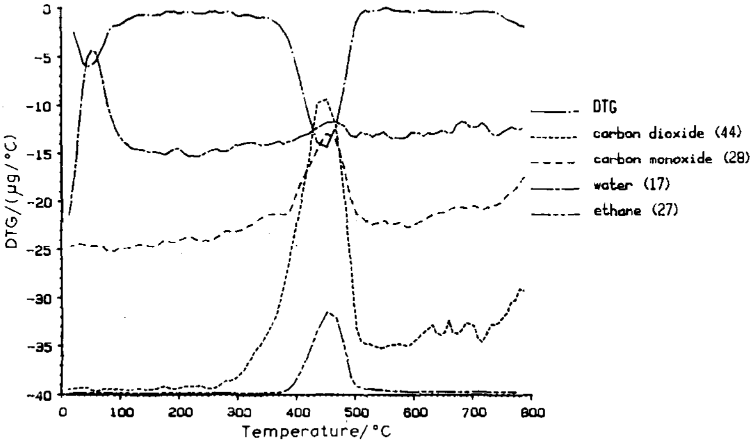


Fig. 5. TG–MS of Amberlite (Zn^{2+}).

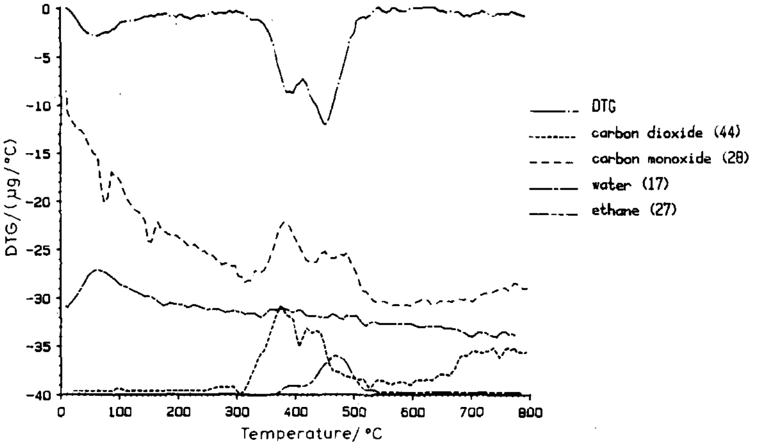


Fig. 6. TG–MS of Amberlite (Ba^{2+}).

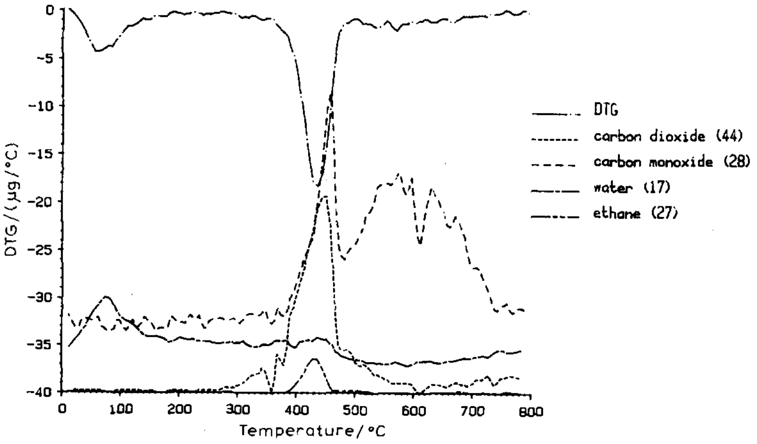


Fig. 7. TG–MS of Amberlite (Co^{2+}).

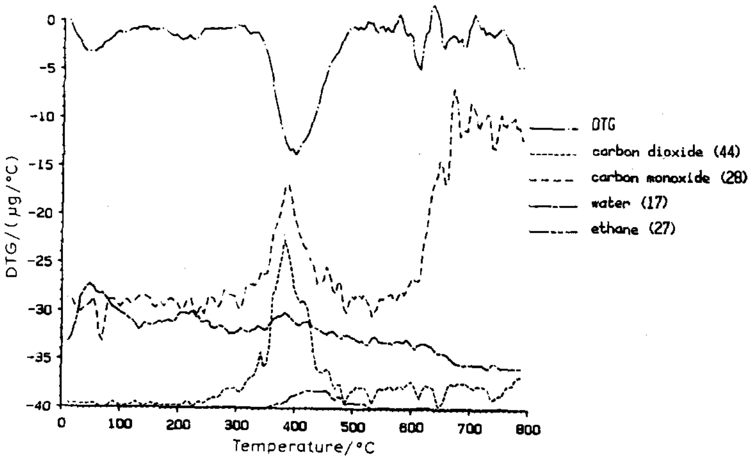


Fig. 8. TG–MS of Amberlite (Fe^{3+}).

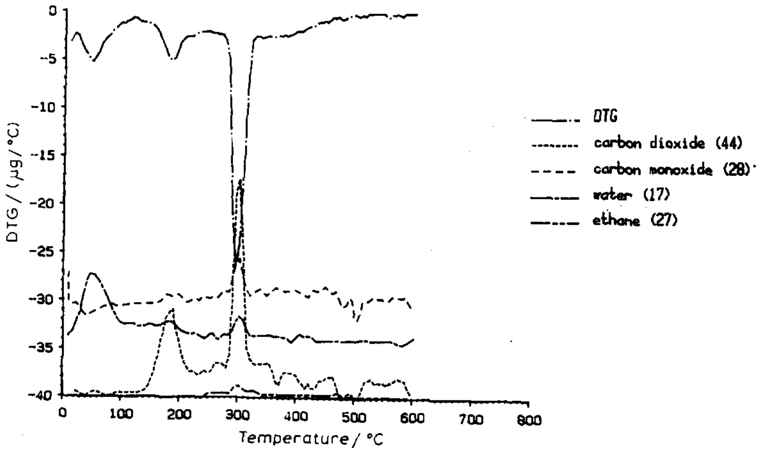


Fig. 9. TG–MS of Amberlite (Cu^{2+}).

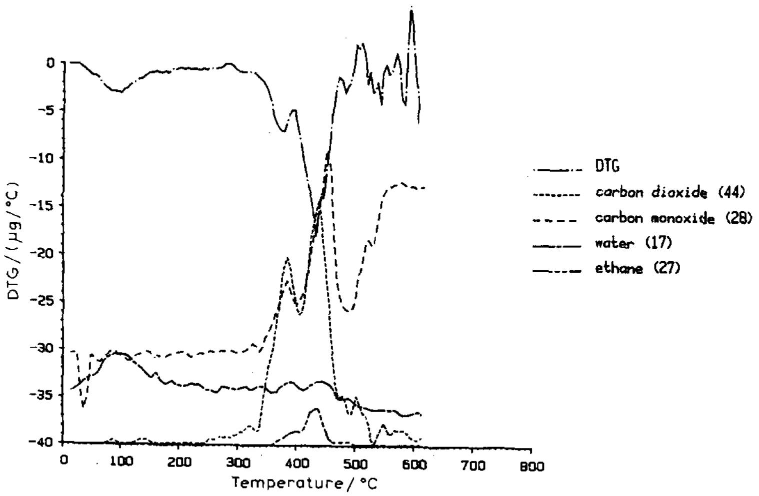


Fig. 10. TG–MS of Amberlite (Co^{2+}, Ni^{2+}).

The DTA of the Ba form in hydrogen gave a broad peak at 380 °C and a complex multipeak at 430–465 °C.

Splitting also occurred with the lead and bismuth forms. A slight shoulder was discernible with the tin(II) form. The low exothermic peak temperature of the Pb form in hydrogen suggests that lead may be an effective catalyst of coal hydrogenation.

Tin is known to be one of the most effective catalysts of coal hydrogenation. This metal is molten under reaction conditions (MP = 232 °C) and it may be that it acts as a temporary trap for organic radicals, which therefore do not polymerize so readily and are more likely to be hydrogenated. Since lead is in the same group of the periodic table as tin, and its melting point is 327.5 °C, it may react in a similar way to tin. Lead is also considerably less costly than tin, and that would be an advantage if it is found to be an effective catalyst.

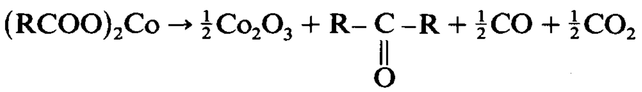
Ni^{2+} *form*

The nickel form gave similar TG–MS results to barium except that the MS showed further evolution of CO from 500 to 700 °C due to reaction of the nickel oxide with the char.

The DTA of the nickel form in hydrogen showed a sharp peak at 340 °C which may be due to reduction of nickel(II). The main peak was at about 420 °C (Fig. 2b).

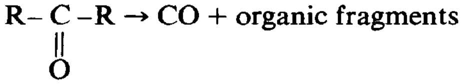
Co^{2+} *form*

The cobalt form gave results similar to those of the nickel form, except that the MS peaks for CO_2 and CO were of comparable size (Fig. 7). In this case the oxide formed was of higher oxidation state



$$\mathrm{(RCOO)_2Co} \rightarrow \tfrac{1}{2}\mathrm{Co_2O_3} + \mathrm{R}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R} + \tfrac{1}{2}\mathrm{CO} + \tfrac{1}{2}\mathrm{CO_2}$$

where the resin is represented as $(RCOO)_2^{2-}$



$$\mathrm{R}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R} \rightarrow \mathrm{CO} + \text{organic fragments}$$

CO evolution at 500–730 °C indicates reduction of the oxide by the char.

Fe^{3+} *form*

The main DTG peak was broad, and occurred at 400 °C (Fig. 8), accompanied by the evolution of similar quantities of CO and CO_2. At 600–800 °C further CO was produced by the sequential reduction of iron oxide by the carbonaceous residue. Samples of the iron resin heated to 400 or 500 °C in nitrogen for 45 min and cooled overnight, were shown by XRD to contain Fe_3O_4, FeO and Fe. After treatment at 600 °C, Fe and Fe_3C were detected. The reaction sequence inferred for this sample is as follows

$$(RCOO)_3Fe \rightarrow \tfrac{1}{2}Fe_2O_3 + \tfrac{3}{2}CO + \tfrac{3}{2}CO_2 + \ldots$$

$$\tfrac{1}{2}Fe_2O_3 + \tfrac{1}{6}C \rightleftarrows \tfrac{1}{3}Fe_3O_4 + \tfrac{1}{6}CO$$

$$\tfrac{1}{3}Fe_3O_4 + \tfrac{1}{3}C \rightleftarrows FeO + \tfrac{1}{3}CO$$

$$FeO + C \rightleftarrows Fe + CO$$

$$Fe + \tfrac{1}{3}C \rightleftarrows \tfrac{1}{3}Fe_3C$$

Unlike the case of iron(III) octadecanoate [1] there appeared to be little indication of splitting of the main decomposition reaction of the Amberlite (Fe).

After the sample had been heated to 900 °C in N_2, it was cooled to ambient temperature. When exposed to air, it glowed red hot as the iron carbide was oxidized by air.

Cu^{2+} form

The behaviour of the copper form was quite different from all the others. Its first sharp decomposition step was at 180 °C, when copper(II) reduced to copper(I) and carbon dioxide was produced (Fig. 9). The second sharp peak occurred at 300 °C. Some CO_2 and possibly CO were detected, but organic fragments may also contribute to the peaks at $m/z = 28$ and $m/z = 44$. The following reactions are inferred.

$$(RCOO)_2Cu \xrightarrow{180\,^\circ C} (RCOO)Cu + CO_2 + \text{organic fragments}$$

$$(RCOO)Cu \xrightarrow{300\,^\circ C} Cu + CO_2 + \text{organic fragments}$$

After DTA in hydrogen, elemental copper was the clearly visible sole product.

Mixed Co^{2+}, Ni^{2+} form

A sample which had been ion-exchanged in a solution containing cobalt and a small amount of nickel, gave two main DTG peaks: at 390 and 440 °C (Fig. 10). The lower peak appears to be due to the nickel-containing fraction: the nickel-exchanged resin peaked at 370 °C with CO_2 as the predominant gaseous product. The second and larger peak at 435 °C must be due to the cobalt component reacting more or less independently, evolving comparable amounts of CO and CO_2: the cobalt-exchanged resin had its main DTG peak at 440 °C and evolved comparable quantities of CO and CO_2.

The mixed Co^{2+}, Ni^{2+} form also evolved CO at temperatures above 500 °C due to reduction of the oxides by the char.

In hydrogen (Fig. 2b) the main peak temperatures were between those of the cobalt form and the nickel form. This indicates that the reactions occurring in hydrogen are quite different from those occurring in an inert atmosphere.

Mixed Fe^{3+}, Pb^{2+} form

The TG–MS results of this mixed-ion form (mainly Fe^{3+} with a little Pb^{2+}) appear at first glance to be similar to those of the iron form, with the main DTG peak at 400 °C, and comparable amounts of CO and CO_2 being evolved. However, there is also a small peak at 200 °C accompanied by evolution of CO_2. This peak is much lower than for lead on its own, so may indicate some synergism between the iron and lead.

In hydrogen (Fig. 2c) the single main peak temperature is between those of the iron form and the lead form.

The combination of iron and a small amount of tin has been found to enhance the rate of hydroliquefaction reactions of brown coal [6]. The present results indicate some interaction between nickel and cobalt, and between lead and iron, in hydrogen. Therefore, those combinations of catalytic ions merit further study in lignite hydroliquefaction.

CONCLUSIONS

The peak temperatures of the pyrolysis reaction of the ion-exchanged Amberlite IRC-50 in inert atmosphere decreased in the order: Na > Ba > Ca > Zn > Co > Bi > Sn > Pb > Fe > Ni. This trend appears to be related to the ionic bond strength between the cation and anion, and is similar to that found for salts of octadecanoic acid [1]. In high-pressure hydrogen (8.0 MPa) the reactions were somewhat more complex in the case of the nickel, barium and bismuth forms. The copper form was anomalous in that the cation was reduced even in inert atmosphere.

Ishii et al. [7] showed that the lower the temperature of the exothermic DTA peak, the higher the conversion of coal, as measured by high-pressure catalytic hydrocracking in a 500-cm^3 autoclave at 400 °C. Therefore, the low peak temperature of the lead form of the Amberlite resin means that lead is worthy of investigation as a catalyst for coal hydroliquefaction. Iron, nickel and tin are known catalysts for hydrogenation.

As with the octadecanoates the nature of the solid products was determined by their thermodynamics. The sodium, potassium and calcium forms were the most stable. Since these three ions are usually the main ones inherent in low rank coals, it may be that they inhibit the onset of reactions during coal processing at about 400 °C.

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