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On the interaction between pyridine and coal as studied by CP/MAS ^{15}N n.m.r.

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The interaction between pyridine-^{15}N and both fresh and oxidized coal was studied by means of CP/MAS ^{15}N n.m.r. In fresh bituminous coal, pyridine interacts only weakly through physical adsorption and hydrogen-bonded complex formation. On the other hand, in oxidized bituminous coal and fresh subbituminous coal the presence of both pyridinium ions and physically sorbed pyridine was observed. The occurrence of proton transfer to pyridine suggests that strongly acidic functions are generated during coal oxidation.

(Keywords: pyridine; coal; CP/MAS ^{15}N n.m.r.)

The interaction of good coal solvents such as pyridine[1], with the coal matrix presents a complex problem which has attracted considerable attention[2-6]. Recently, n.m.r. techniques have been used in several ways to study such interactions[2-4]. One approach has been to use magnetic nuclei in the solvent molecules as probes to monitor solvent molecular motion[3,4]. For instance ^{2}H n.m.r. spectra of deuterated benzene and pyridine sorbed in coal show evidence of both severely restricted and freely rotating molecules[3]. Also, ^{13}C n.m.r. spectra of pyridine and aniline soaked coals show that most solvent molecules are involved in rapid anisotropic molecular motion with only weak magnetic coupling between coal protons and solvent protons[4]. On the other hand, examination of the coal matrix by ^{1}H n.m.r. in the presence of deuterated pyridine has shown that in the swollen coal the matrix constituents have increased mobility, and that as a consequence of the swelling process proton–radical interactions are reduced[2].

In order to further elucidate the interactions between coal and pyridine, the authors have examined the ^{15}N n.m.r. spectrum of coal containing small quantities of pyridine-^{15}N. Because acid–base interactions cause larger charge-density changes around nitrogen than carbon, and because of the large chemical shift range of nitrogen[7], ^{15}N n.m.r. can be expected to be more sensitive than ^{13}C n.m.r. This has been demonstrated using both high resolution[8] and solid state[9-11] ^{15}N n.m.r. techniques for pyridine on catalytically active solids.

EXPERIMENTAL

Recent work has shown that bituminous coal such as Illinois No. 6 strongly sorbs ≈10% w/w of pyridine[6]. In the experiments reported here, 250 mg of powdered coal were heated under vacuum at 110°C for 4 h. About 25 μl of pyridine-^{15}N was distilled onto the coal sample which was then sealed, the sample all the while remaining under vacuum. In order to ensure a uniform distribution of pyridine in the sample, the sealed ampoule was placed in an oven at ≈100°C for at least 8 h. For certain samples, the amount of pyridine used was doubled, and the time of heating was increased to 3 days. For the n.m.r. experiments, the coal samples were removed from the ampoules and packed in Delrin spinners in a dry atmosphere.

^{15}N n.m.r. spectra were obtained at 18.25 MHz on a Bruker CXP 180/90 n.m.r. spectrometer. For most spectra, CP/MAS conditions were used[12-14] with rf amplitudes of 32 kHz, and spinning rates of ≈3 kHz. Cross-polarization times of 1–10 ms were used with recycle times of 2 s. A sweep width of 20 kHz was used to collect 300 point free induction decays which were zero-filled to 4K before Fourier transformation. Between 5000 and 10 000 scans were required for adequate signal to noise ratios.

Powder patterns were obtained for static samples by using the pulse scheme of Rance and Byrd[15] with dipolar decoupling. ^{15}N n.m.r. shifts are reported with respect to the NO_3^- line of solid NH_4NO_3. Coal samples studied include both fresh and oxidized samples of Devco hvA coal, Illinois No. 6 coal and Whitewood subbituminous C coal (see *Table 1*). Fresh refers to the state of the coal 'as received'. Physical and chemical testing (rheological properties, chemical analysis, F.T.-i.r., etc.) indicated that these samples had not been subjected to detectable weathering after mining. The oxidized samples were prepared by exposing crushed samples (300 μm) to a stream of air in a drying oven for various periods of time.

RESULTS AND DISCUSSION

The CP/MAS ^{15}N n.m.r. spectrum of pyridine-^{15}N sorbed in fresh Illinois No. 6 coals is shown in *Figure 1a*. There is a single, broad line at 73.7 ppm, with a width of ≈10 ppm. Doubling the amount of pyridine, or increasing the time of heating from 8 h to 3 days did not change the spectrum markedly. Neat pyridine has its resonance at 58 ppm, whereas the aqueous pyridine line occurs at 80 ppm[7]. In other solvents, including alcohols, ethers, etc., the nitrogen n.m.r. line falls between about 56 and 88 ppm[7]. Therefore the 73.7 ppm line for pyridine in coal may be attributed to pyridine molecules physically sorbed in the coal pores. The width of the line suggests that there is a distribution of chemical environments

Table 1 Analysis of coal samples

	Illinois No. 6			Devco		Whitewood
		Oxidized			Oxidized	
	Fresh wt%	a wt%	b wt%	Fresh wt%	c wt%	Fresh wt%
Ash	11.0	10.8	9.9	1.3	1.1	7.7
Volatile matter	37.1	35.1	34.7	33.9	32.6	35.9
Fixed carbon	51.9	54.1	55.4	64.8	66.3	56.3
Carbon	71.8	68.9	67.1	85.6	83.6	67.9
Hydrogen	5.1	4.4	4.1	5.4	5.4	4.7
Sulphur	2.6	2.4	2.3	0.7	0.7	0.1
Nitrogen	1.7	1.6	1.6	2.2	1.9	0.8
Oxygen (by difference)	7.8	11.9	15.0	4.8	7.3	18.8

a 24 h at 105°C
b 96 h at 105°C
c 192 h at 105°C

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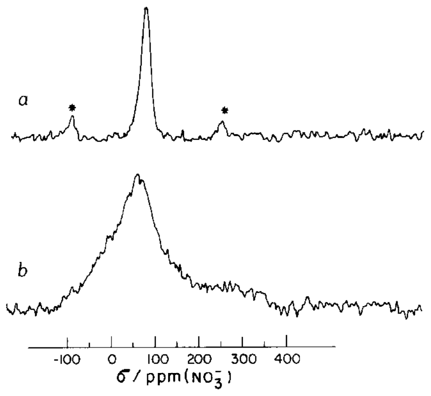

Figure 1 ^{15}N n.m.r. spectrum of pyridine–^{15}N sorbed on Illinois No. 6 coal: a, with magic angle spinning; stars mark spinning sidebands; b, static powder pattern

and the range of chemical shift values covers relatively weak interactions of pyridine–^{15}N with a variety of chemical functionalities. Stronger interactions such as with Lewis or Bronsted acids are absent.

Examination of the ^{15}N powder pattern for this sample (*Figure 1b*) reveals that it cannot be characterized by a single set of shielding parameters. The extremities of the pattern suggest values of $+360$ and -98 ppm for σ_{zz} and σ_{xx} respectively. From the average shift of 73.7 ppm, a value for σ_{yy} of -41 ppm can be obtained. These values, which are maxima, compare with eigid lattice values for pyridine–^{15}N of -313, -94 and 469 ppm for σ_{xx}, σ_{yy} and σ_{zz}[16]. The difference between these and the values observed for pyridine–^{15}N in coal can be attributed to anisotropic molecular rotation, as the pyridine interacts only weakly with the coal and the rigid lattice values for free and sorbed pyridine should be similar. The σ_{zz} out of plane component changes rather less than the in-plane components, suggesting a greater degree of in-plane motional averaging. Of course, different degrees of motional averaging will give a distribution of averaged shielding parameters. Hence there is much more intensity in the powder pattern near the average shift value than expected for a powder pattern with the shielding parameters suggested by its extreme values[17].

The other bituminous coal examined, Devco coal, also shows a single line for its sorbed pyridine (*Figure 2a*). On the other hand, for pyridine in subbituminous coal, two lines are evident. One occurs at ≈ 74 ppm, as for the other coals and again can be attributed to sorbed pyridine. The second line occurs at 158 ppm, and this line must be assigned to the pyridinium ion, which in solution absorbs between 161 and 183 ppm[7].

For comparison purposes, ^{15}N spectra were also measured for several pyridinium salts enriched to $\approx 10\%$ in pyridine–^{15}N. In the case of pyridinium nitrate, the shielding tensor was general, with $\sigma_{xx} = 44$, $\sigma_{yy} = 96$ and $\sigma_{zz} = 360$ ppm, which leads to a $\bar{\sigma}$ of 167 ppm. For pyridinium iodide, where in-plane motional averaging occurs[18], the shielding tensor was axially symmetric, with $\sigma_{(\mathrm{perpendicular})} = 86$ ppm, $\sigma_{(\mathrm{parallel})} = 354$ ppm so that $\bar{\sigma} = 175$ ppm.

The observation of pyridinium ions implies that a proton has been transferred completely, so that the proton donor must be a sufficiently strong acidic moiety. The degree of proton transfer in pyridine–acid systems depends on a number of factors, including the acid pK$_a$, the dielectric constant of the solvent and the relative concentrations[19–21]. For instance, in benzene solution, the degree of proton transfer was estimated to be $\approx 50\%$ for acids with pK$_a$ values of ≈ 1.2[20]. On the other hand, in pure solid pyridine–acid adducts, the degree of proton transfer was complete for acids with pK$_a$ values less than ≈ 1.5[21]. The behaviour of surface bound acid functions is rather less certain. The results obtained for pure, simple systems do suggest that proton transfer to pyridine should occur only for acidic groups with pK$_a$ values rather less than 4, e.g. carboxylic acid functions on condensed aromatic ring systems, or on aromatic rings with other oxygen containing substituents.

^{15}N n.m.r. spectra were also examined for pyridine sorbed on oxidized coal. *Figure 2c, d* and *e* show spectra for fresh Illinois No. 6 coal and coal samples which were oxidized for 24 h and 96 h respectively. The oxidized coal samples show intensity at 150 ppm which increases with time of oxidation. This implies that air oxidation at elevated temperature produces a significant quantity of strong carboxylic acid functions. The behaviour of pyridine–^{15}N treated Devco coal, both fresh and oxidized, was completely parallel to that observed for the Illinois No. 6 coal.

The details of the oxidation process as it occurs in coals suitable for metallurgical coking has been the subject of a number of recent studies[22–27]. Although there is some evidence that fresh Illinois No. 6 coal does not contain carboxylic acid functions[28], most (but not all studies[22–27] agree that such groups are produced during oxidation of coking coals. On the other hand, there is evidence for carboxylic acid functions in fresh coals of lower rank[28–29]. All these findings are in agreement with the results presented here.

As the relative ^{15}N n.m.r. line intensities for sorbed pyridine and the pyridinium ion are virtually independent of cross-polarization times between 1 and 5 ms, the intensities (after taking into account spinning sidebands) can be used to give a quantitative estimate of the carboxylic acid groups ionized by pyridine. The fresh Whitewood subbituminous coal had 0.25 mM/g of such groups, the fresh Illinois No. 6 or Devco bituminous coals had none. Air oxidation produced 0.22 mM/g, after 24 h, or 0.48 mM/g after 96 h for the Illinois No. 6 coal, with similar results for the Devco coal. From acid titration measurements the concentration of acid groups with a pK$_a < 4$ has been estimated to be 1.4 mM/g for Rawhide subbituminous coal, and 1 mM/g for Illinois No. 6 coal[28]. These results are in general agreement with our ^{15}N n.m.r. results considering that pyridine is protonated only by strong acids with pK$_a \leqslant \approx 2$. In conclusion, these results suggest that ^{15}N n.m.r. of sorbed pyridine–^{15}N is quite a sensitive probe for strong surface acid groups in coal.

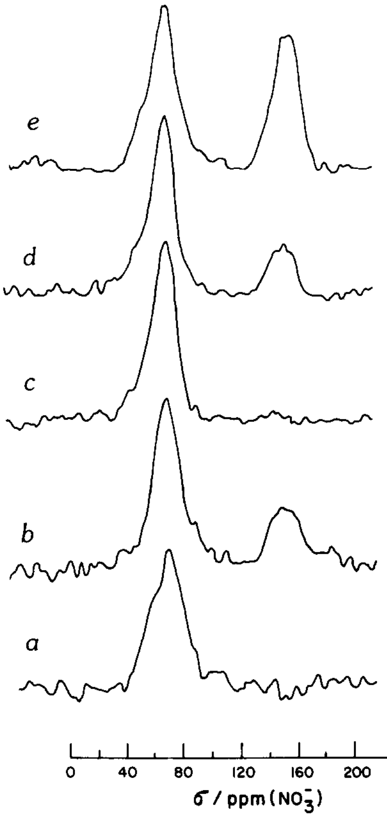

Figure 2 CP/MAS ^{15}N n.m.r. spectrum of pyridine–^{15}N sorbed on coal samples: a, Devco coal; b, Whitewood coal; c, Illinois No. 6 coal–fresh sample; d, Illinois No. 6 coal–oxidized 24 h; e, Illinois No. 6 coal–oxidized 96 h

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Regional News

Fuel and energy research in Australia

There is an abundance of fuel and energy resources in Australia, but nonetheless there are many pressing problems due to the nature and location of our fuels, and the needs of our domestic and export markets. Our indigenous reserves of natural oil are likely to supply some 60% of our liquid fuel needs up to 2000. Thereafter, pressing needs for new discoveries of oil, or for the establishment of synthetic liquid fuel industries, will be felt. On the other hand, we have substantial reserves of natural gas, mainly located on the North-west shelf (off the northern coast of Western Australia) some 3000 km from the major energy markets of Victoria, New South Wales, and Queensland. Oil shale is another resource of large magnitude, with readily recoverable material capable of supplying at least 100 years of Australia's liquid fuel need at current usage rates. Coal is a major resource, used to generate 80% of our electricity and to provide coke for the metallurgical industry. Coal is also an important export, Australia currently being the world's largest exporter of coal. In spite of the heavy demand, Australia uses <0.1% per annum of its known reserves of coal.

Australia also makes significant use of biomass as a fuel, hydropower, and solar energy. There is also scope for the use of wind and tidal power, and the major deposits of uranium ore are well known. Fuel and energy research in Australia is influenced to a great extent by the resource and demand situation outlined above. The need to ensure continuity in liquid fuel supplies has prompted much research into the production of synthetic oil. Over the past ten years this research has been principally concerned with the use of coal and oil shale as feedstocks. Major research, both of a fundamental and process development nature, into hydrogenation, pyrolysis and synthesis processes has been carried out: much of this work is now complete. For example the Australian Coal Industry Research Laboratories (ACIRL) have finished their PDU studies of coal hydrogenation, and the CSIRO has completed its pilot-plant development of flash pyrolysis. However the BHP Company Ltd is continuing its work on coal hydrogenation, and CSIRO industry studies on oil shale retorting and oil upgrading continue to be well-supported, as does research on synthesis reactions. In this latter area industrial, government and university researchers are active.

As noted above natural gas is plentiful, but remotely located. Therefore new research is under way on means of converting methane to liquid fuels, either by reformation and synthesis, or by new methods employing partial oxidation or pyrolysis to produce intermediates that are readily compressed and transported, and readily converted to liquid fuels.

Research on coal now has two principal foci: reduced costs and increased effectiveness in mining, preparation, and transportation, especially with export markets in view; and improvements in combustion behaviour in power plant, with particular emphasis on the behaviour of the ash. University, government and industrial laboratories are active in coal utilization research, with combustion for power generation as one of the main concerns. Combustion test pilot plants have been operated for many years by the CSIRO and the State Electricity Commission of Victoria, and recently the Electricity Trust of South Australia and ACIRL have built test combustors. The principle aim in the eastern states of Australia is to characterize the local bituminous coals for market and to solve operational problems, in order to strengthen local and export sales opportunities. In Victoria, South Australia and Western Australia research emphasis is on the problems of local use of coals which may produce corrosive and fouling ashes.

Other important energy research includes advanced methods of oil exploration, safety in mines, and environmental control associated with fuel preparation and use. An indication of the range of research in hand can be got from the distribution of funds released at the end of 1985 to support selected applied research topics, under the National Energy Research, Development and Demonstration Program (NERDDP). The funds are:

Research area	$10^6\$\mathrm{A}$
Coal mine safety and productivity	2.9
Coal mine site technology	3.8
Fuel resources assessment	1.1
Coal utilization (carbonization and combustion)	1.3
Synthetic liquid fuels	3.9
Solar, wind and nuclear	3.2
Energy conservation	1.9
Economic, social and environmental issues	1.2

In the present short account it is not possible to note all matters of significance. However a good account of coal research in Australia can be found in various papers presented at the 1985 International Conference on Coal Science, Sydney. More general coverage of energy research is given by the annual Compendia of Australian Energy Research, Development and Demonstration Projects published by the Commonwealth of Australia, Department of Resources and Energy, Canberra.

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