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ESR Examination of Ultramarines and Their Activities as Catalysts in Thiophene Hydrodesulfurization

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The catalyzed reaction between thiophene and hydrogen has been studied over the range 17 to 400°C using a flow system. Catalysts were made by the partial extraction of sulfur from blue, pale blue, pink, or white ultramarine by hydrogen at 450°C.

The original ultramarines, freshly activated catalysts, and well-used catalysts have been studied by esr spectroscopy. The results are interpreted, and are related to various color changes that occur. Catalytic activity is proportional to the extent of sulfur extraction during activation, and appears to be unrelated to the concentration of sulfur free radicals in the catalyst.

Products of the hydrodesulfurization of thiophene at 400°C were hydrogen sulfide and mixtures of C_3- and C_4-hydrocarbons. The corresponding reaction using-2-methylthiophene gave propane and ethane as the major hydrocarbon products. The cracking reaction that follows the initial desulfurization step probably proceeds by a mechanism involving carbonium ions.

Ultramarine has been used by Dudzik and Kinastowski (*1*) as a catalyst for both the dehydrogenation and dehydration of isopropanol (322–410°C), and for the dehydrogenation of tetrahydronaphthalene (538–599°C). Brief mention has been made of its activity for hydrodesulfurization, cracking, and oxidation (*2*) but no detailed product compositions were quoted for the reactions studied. In the latter work, it was concluded that the active centers for most of these reactions were associated with the sulfur free radicals present in the ultramarine. More recently, Dudzik, Cvetanović and Preston have examined the cracking activity of related substances, namely molecular sieves containing trapped sulfur free radicals, and have observed that paramagnetic sulfur-impregnated sieves were much more active than either the pure sieves or sulfur-impregnated sieves which exhibited only weak paramagnetism or were diamagnetic (*3*).

The objects of the present work were (i) to examine the esr spectra of a range of ultramarines, and (ii) to determine the products formed during thiophene hydrodesulfurization over these materials. The ultramarines chosen for study were the normal highly paramagnetic blue form, which was the type used by Dudzik and Kinastowski (*1*), a diamagnetic white material, a pale blue variant with properties intermediate between those of the blue and the white, and lastly a pink ultramarine which was more acidic and less paramagnetic than the blue. In this way it has been possible to assess the relevance or otherwise of paramagnetism to the catalytic desulfurization activities of these solids.

EXPERIMENTAL METHODS

Ultramarines. Powdered samples of each of the four ultramarines used were supplied by Reckitts (Colours) Ltd. of Hull. Blue ultramarine had the formula

$$Na_{7.19}Al_{5.44}Si_{6.56}O_{24}S_{4.25};$$

impurities consisted of potassium and

calcium (each <1%), magnesium and iron (each <0.1%), uncombined clay 4.2%, and free moisture 1.6%. The sample gave an intense esr spectrum ($\sim 10^{21}$ spins g^{-1}) consisting of a single line at $g = 2.028$, which agrees with values reported elsewhere in the literature (*4*). The other ultramarines had been prepared from the blue form. The pale blue and the white materials were prepared by chlorination of blue ultramarine in a nonaqueous suspension; this procedure brought about partial decationization. The pink variant was prepared by first heating together a mixture of blue ultramarine and ammonium chloride, and then subjecting the product to dry hydrochlorination; this gave a material in which sodium ions had been partially exchanged for hydrogen ions, and hence it was more acidic than the others.

Apparatus. A standard flow system was used. Hydrogen, initially at 1.2 atm pressure, was dried by passage through a trap containing Type 5A molecular sieve. It then passed either through a saturator at 20°C containing thiophene or 2-methylthiophene, or through a bypass. The resultant 12:1 hydrogen:thiophene mixture, or 36:1 hydrogen:methylthiophene mixture then passed through the tubular Pyrex reactor contained in an electric furnace. Flow rates were in the range 20 to 40 ml min^{-1}. The catalyst, which weighed 0.2 g, completely filled a 2-cm section in the center of the reactor tube; it was kept in place by plugs of glass wool and glass lugs. Gases leaving the reactor were analyzed for hydrogen sulfide by conventional wet methods, whereas hydrocarbons were condensed out of the stream and removed for analysis by gas–liquid chromatography or by mass spectrometry.

RESULTS

The various ultramarines as supplied were not catalytically active. However, when samples of each ultramarine were heated in a hydrogen stream, hydrogen sulfide was evolved and catalytic activity developed. This process of sulfur removal occurred at 20°C and above for the blue and for the pale blue ultramarines, but temperatures above 320°C were required for the appreciable removal of sulfur from the pink and from the white variants. The rate of sulfur removal was slow, and so a standard activation temperature of 450°C was adopted. At this temperature, hydrogen sulfide evolution ceased when hydrogen had been passed for about 5 hr. The amount of sulfur removed, as a percentage of that originally present, was: blue ultramarine, 8 to 15% (4 samples); pale blue ultramarine, 25% (1 sample); white ultramarine, 48% (1 sample); pink ultramarine, 48% (2 samples). This process of sulfur removal was accompanied by changes in color and in paramagnetism as described in Table 1.

Catalysts derived from white and from pink ultramarine were some two to three times more active than those derived from blue ultramarine. At the standard reaction temperature of 400°C the activities were

TABLE 1

CHANGES IN COLOR AND IN PARAMAGNETISM OBSERVED DURING THE PREPARATION AND USE OF CATALYSTS

Original ultramarine		Activated catalyst		Used catalyst[a]	
Color	(Spin conc)10^{-19} (spins g^{-1})	Color	(Spin conc)10^{-19} (spins g^{-1})	Color	(Spin conc)10^{-19} (spins g^{-1})
Blue	100	Blue	100	Greyish-blue	95
Pale blue	40	Pale blue	40	Grey	40
Pink	1	Pale violet	1	Blue-grey	15
White	0	White	0	Blue-grey	5

[a] These colors refer to catalysts used for short periods (<10 hr); all catalysts used for long periods were dark grey.

sufficient to bring about the hydrodesulfurization of 3 to 8% of the thiophene that passed through the reactor. The reaction exhibited an activation energy of about 2.4 kcal mole^{-1} over the range 17 to 300°C for catalysts derived from blue and from pink ultramarine: this value compares with values in the range 5 to 12 kcal mole^{-1} reported by Dudzik (*2*). The low value obtained in this work suggests that some diffusion process may be rate-determining, the transport of thiophene to catalytically active sites situated in the pores of the ultramarine is one possibility.

Further changes in color and in paramagnetism occurred as catalysts were used. These are also recorded in Table 1.

Products formed in addition to hydrogen sulfide are shown in Table 2. Mass spectrometry was used to show that no methane or alkyl sulfides were formed.

The simplest reaction was obtained using catalysts derived from pink ultramarine, the products of thiophene desulfurization being solely propane and propene with the former in large excess. Reactions over the other catalysts gave mixtures of C_3- and C_4-hydrocarbons, and the percentage of unsaturated material in the product varied from 4 to 72%, depending upon the ultramarine used.

The hydrodesulfurization of 2-methylthiophene also gave propane as the major product (see Table 2). Ethane was also observed, but its concentration was low except when catalyst freshly prepared from blue ultramarine was used. Trace quantities of C_4-hydrocarbons ($<1\%$) were observed by glc and, in addition, minute quantities of C_5-hydrocarbons were detected by mass spectrometry.

For reactions at 400°C the molar yield of hydrogen sulfide was equal to the molar loss of thiophene by reaction, and so the sulfur-content of the catalyst remained stationary. However, when a catalyst prepared from pink ultramarine was used at a temperature below the minimum activation temperature, for example at 320°C, no hydrogen sulfide was eluted from the reactor, and the sulfur-content of the catalyst increased. Subsequent treatment of the catalyst in pure hydrogen at 400°C resulted in the production of hydrogen sulfide, the amount formed being equivalent to the quantity of sulfur taken up by the catalyst in the preceding experiment.

TABLE 2

TYPICAL PRODUCT COMPOSITIONS OBTAINED BY THE CATALYTIC HYDRODESULFURIZATION OF THIOPHENE (T) OR OF 2-METHYLTHIOPHENE (2MT) AT 400°C

Ultramarine from which catalyst was formed	Reactant	Products (%) *n*-Butane	1-Butene	2-Butene	Propane	Propene	Allene	Ethane
Pink	T	0	0	0	96	4	0	0
Blue	T	3	4	1	78	14	0	0
Pale blue	T	8	5	14	56	17	0	0
White	T	0	7	17	28	38	10	0
Pink	2MT	tr[c]	tr	tr	97	0	0	3
Blue[a]	2MT	tr	tr	tr	60	0	0	40
Blue[b]	2MT	tr	tr	tr	96	0	0	4

[a] Fresh catalyst.

[b] Well-used catalyst.

[c] tr = trace $<0.5\%$.

DISCUSSION

Part 1. Esr Spectra and Color Changes

Blue ultramarine is a nonstoichiometric substance, related to the zeolites, which contains sulfur. Its structure (*5*) consists of an open framework of SiO_4 tetrahedra, the corners of which are shared, in which a little less than half of the silicon atoms have been replaced by aluminum. This substitution confers a negative charge on the formal $M_{12}O_{24}$-unit which is neutralized by the presence of sodium ions distributed randomly throughout the cage structure. In fact, an excess of sodium ions is always observed, and the resultant positive charge is neutralized by the sulfur clusters which take on polysulfide ion character. Morton has shown recently *(6)* that both the blue color and the paramagnetism of blue ultramarine are attributable to the presence of S_3^- radicals in an unrestricted environment in the crystal.

The information recorded in Table 1 is interpreted as follows: The process of chlorination whereby the pale blue and the white variants were made brings about partial decationization. This probably occurs by a charge-transfer process involving chlorine atoms and polysulfide ions [Eq. (2)]:

$$Cl_2 \rightarrow 2Cl\ (ads). \qquad (1)$$

$$Cl\ (ads) + S_3^- \rightarrow Cl^- + S_3. \qquad (2)$$

Some or all of the sodium chloride so formed is removed from the ultramarine by the solvent. Such a neutralization of S_3^- units would cause the material to become diamagnetic and the blue color would be completely discharged; both effects are observed.

The first stage of the preparation of pink ultramarine was the reaction of the blue form with ammonium chloride. This gives a violet material which, like the blue, is a commercial pigment. The reflectance spectrum of the violet material contains a strong maximum at about 445 mμ, a weak maximum at 570 mμ, and a percentage reflectance in the red region that was high by comparison with that recorded for the original blue ultramarine. Subsequent treatment to give pink ultramarine was achieved using anhydrous hydrogen chloride instead of chloride, thus giving a product that was more acidic than the blue or the white materials. It appears that this dry hydrochlorination (like the decationization) was accompanied by the removal of the blue coloration but that the constituent responsible for the pink coloration remained. The relatively weak esr spectrum of the pink material was asymmetric. The *g*-factors (2.050 and 2.030) are closely similar to values reported for S_3^- present in the highly restricted environment of the potassium chloride crystal ($g = 2.0026$, 2.0319, and 2.0499). Hence, the constituent responsible for the pink coloration may be S_3^- ions which, because of their location, are hindered from taking part in the charge-transfer process described in Eq. (2) above.

Remarkably, the intensities of esr spectra before and after the activation of a given ultramarine were the same although an appreciable quantity of sulfur had been removed during activation. This indicates that, whatever the nature of the disruption of the sulfur clusters caused by the action of hydrogen, opportunities do not arise for the removal of paramagnetic sulfur entities by combination to give diamagnetic ions or molecules.

The pink ultramarine was the only material to change color on activation. The change to a pale violet material was not accompanied by an increase in the intensity of the esr spectrum, although the signal became less asymmetrical. We interpret these changes as showing that a proportion of the S_3^- in restricted locations moved to unrestricted positions during the activation process.

Carbon deposition occurred as catalysts were used for hydrosulfurization, and this probably accounted for the grey color of used catalysts. The development of a light-blue color when catalysts derived from white ultramarine were used is difficult to understand, as is the increase of paramagnetism with use observed in catalysts derived both from white and from pink ultramarine. Apparently, S_3^- clusters became negatively charged as the catalyst was used but the source of the negative charge is unknown. The processes occurring may be similar to those observed in sulfur-impregnated Type A molecular sieves, where it has been shown that very long sulfur chains (typically 600 atoms) acquire biradical character at 400°C *(3)*.

Part 2. Reaction Mechanism

The ultramarines became active catalysts when they were partially desulfurized in a hydrogen stream. Increases in the *cracking* activity of sulfur-impregnated molecular sieves as a result of hydrogen treatment have been reported (*3*) but the origin of the effect is uncertain. However, it is unlikely that the two systems are comparable in this respect especially since there are no reports of sulfur removal from the sieves during activation by hydrogen. There is no doubt that, in the case of the ultramarines, hydrogen activation caused disruption and perhaps the complete removal, of some sulfur clusters, and the simultaneous formation of sites possessing a high degree of reactivity towards thiophene. The catalytic cycle of events is considered to be as follows ($x > y > 0$):

$$\ldots S_x \ldots + (x - y)\,H_2 \rightarrow \ldots S_y \ldots + (x - y)\,H_2S, \quad (3)$$

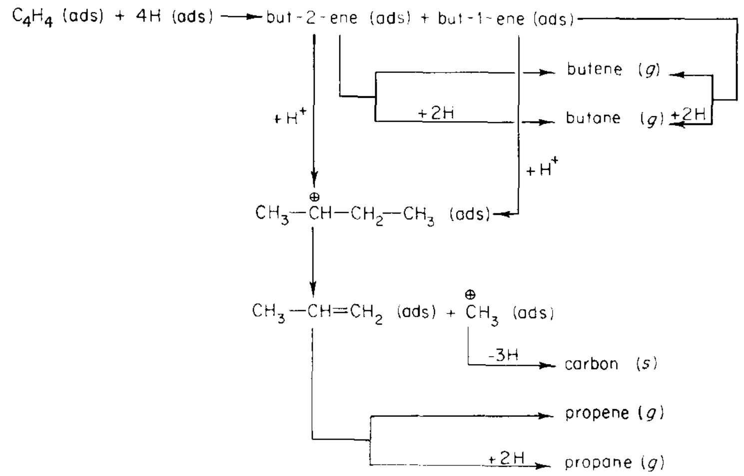
$$\ldots S_y \ldots + C_4H_4S \rightarrow \ldots S_{(y+1)} \ldots + C_4H_4\ (\text{ads}), \quad (4)$$

$$C_4H_4\ (\text{ads}) \xrightarrow{\text{hydrogen}} \text{hydrocarbon products}, \quad (5)$$

$$\ldots S_{(y+1)} \ldots + H_2 \rightarrow H_2S + \ldots S_y \ldots. \quad (6)$$

Thus, the (hydrodesulfurization) activity of the ultramarines appears to depend upon the amount of uncharged sulfur removed, and is therefore lower for highly paramagnetic ultramarines, whereas the (cracking) activity of the sieves is enhanced (*3*) by the presence of sulfur free radicals.

The conversion of adsorbed-C_4H_4 to hydrocarbon products is envisaged to occur as follows:



The formation of C_3-hydrocarbons as the major product, and as the sole product over the more acid catalyst, suggests strongly that the mechanism involves the formation of carbonium ions. The methyl carbonium ion, formed by β-fission of the secondary butyl carbonium ion, was not hydrogenated to methane, but appeared to undergo degradation to carbon. Carbon could be removed from well-used catalysts as the dioxide by heating in air at an elevated temperature.

The rearrangement of the secondary carbonium ion to the tertiary ion, and subsequent conversion to isobutene and isobutane did not occur.

The products of the hydrodesulfurization of 2-methylthiophene are in accordance with expectations based on the above mechanism. Of the two possible secondary pentyl carbonium ions, one would give equal quantities of C_2- and C_3-products as a result of β-fission, whereas the other would give C_4- and C_1-products. The C_4-olefins so formed could then undergo further cracking to C_3- and C_1-products. The results contained in Table 2 suggest that both pentyl carbonium ions are formed in approximately equal proportions over fresh catalysts derived from blue ultramarine, but that over well-used catalysts the symmetrical ion is the reactive intermediate.

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