CATALYTIC HYDROCRACKING OF TAR VAPOURS IN HYDROPYROLYSIS

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ABSTRACT

Tar vapours have been hydrotreated in the second stage of a fixed-bed two-stage hydropyrolysis reactor using hydrous titanium oxide catalysts exchanged with Ni, Co, Mo and Pd and a commercially available Ni/Mo on alumina catalyst. The primary tar, which accounted for 25-30% daf coal (UK bituminous, 82% dmmf C) was converted at 400°C and 150 bar to a colourless liquid low in heteroatoms of which up to 40% boiled below 150°C. The gas yield was only slightly higher than that obtained in corresponding single-stage tests. A lower boiling product was obtained with Ni/Co/Mo hydrous titanium oxide than with the commercial Ni/Mo catalyst. The most extensively hydrogenated product was obtained with Pd which was still effective at 300°C and 50 bar. The initial effects of carbon build-up on product composition are similar for the alumina- and hydrous titanium oxide-Ni/Mo catalysts tested.

INTRODUCTION

Thermal decomposition of coal under hydrogen pressure (hydropyrolysis) (1-3) is a possible route to chemical feedstocks and synthetic fuels. Tar yields are significantly higher than those obtained by conventional carbonisation. Above about 750°C, primary tars hydrocrack to give appreciable yields of benzene and ethane (3,4). Unfortunately, methane yields and, consequently, hydrogen consumptions are also high. However, tar vapours can be catalytically hydrotreated at about 400°C to give distillable liquids although, in early studies (5-7), the yields were low (<10% daf coal) principally because the reactors were operated at relatively low pressure (<50 bar). Recently, much higher yields of low boiling products (20-25% daf coal) with little methane have been obtained in a two-stage fixed-bed reactor operated at 150 bar (8) and using a commercial Ni/Mo catalyst.

Previous work by one of the authors has demonstrated that hydrous titanium oxide (HTO) exchanged with Pd can hydrogenate polynuclear aromatic compounds at much lower temperatures and pressures than conventional Ni/Mo and Co/Mo on alumina catalysts (9,10). In the present study, HTO formulations containing Ni, Co, Mo and Pd have been used to hydrotreat tar vapours in two-stage hydropyrolysis. The results are compared with those obtained previously using a commercial Ni/Mo catalyst (8).

EXPERIMENTAL

Coal

The proximate and ultimate analyses of the high volatile UK bituminous coal used are listed in Table 1.

Catalysts

The HTO catalysts belong to a group of alkoxide-derived amorphous ion-exchange compounds represented by the empirical formula ($C_x M_y O_z H_z$), where C is an exchangeable cation and M is either Ti, Zr, Nb or Ta. Six catalysts containing Ni, Co, Mo and Pd and combinations of these were prepared by the method

described previously (11,12) The compositions and some properties of these formulations, together with those of the commercial Ni/Mo catalyst used for comparison, are given in Table 2.
Powdered catalyst was made into discs (35 mm dia. by 3 mm thick) in a press operated at 690 bar. The discs were crushed and sieved to obtain the 0.5-1.7 mm fraction. All but the Pd catalyst were pre-sulphided with 10% H_2S in hydrogen at 400°C and atmospheric pressure. Most of the tests were performed with catalyst pre-sulphided prior to loading into the reactor. However, the Ni/Co/Mo HTO and the commercial Ni/Mo catalysts were also pre-sulphided in-situ.

Apparatus and procedure

The apparatus shown schematically in Figure 1 is similar to that described previously (8). Hydrogen under pressure flows downwards through the reactor tube. Coal in the upper section is heated resistively, the temperature of the hydropyrolysis zone being monitored by a thermocouple in the coal bed. The lower section heated by a muffle furnace is used for hydrotreating of tar vapours. Liquid products, including water, condense in the dry ice trap.
Two-stage hydropyrolysis was normally carried out at 150 bar pressure with pyrolysis and hydrotreating temperatures of 500° and 400°C respectively. However, the more promising catalyst formulations were also tested under less severe conditions, namely at 300°C and 50 bar, the hydropyrolysis temperature being raised to 575°C to maintain the same tar yield. 10 g of vacuum dried coal (250-500 μm) mixed with 20 g of sand and 8 g of catalyst were placed in their respective zones in the reactor. The hydropyrolysis zone was heated at a rate of 5°C/s from ambient and held at the desired temperature for 10 minutes. A hydrogen flow equivalent to 5°C/min. at normal temperature and pressure was used giving an estimated residence time of 10 s for tar vapours in the catalyst bed. Deactivation experiments were carried out by using the Ni/Mo HTO and alumina catalysts in six consecutive passes. To accelerate carbon build up, the ratio of coal to catalyst was increased to 3:1 (15 g of coal).

Product recovery and analysis

Gas, liquid and char, as well as the catalyst, were recovered for analysis. Much of the liquid product that collected in the cold trap could be drained out, the remainder being recovered with ether. Water was removed from the liquid products using phase separating paper. Some of the used catalysts were Soxhlet extracted with dichloromethane (DCM) to remove any trapped product.

^1H NMR and elemental analyses and enthalpimetric titrations (13) to determine acidic OH concentrations were carried out on the liquid products. Concentrations of low boiling constituents were determined by GC using a squalane capillary column and iso-butylbenzene as internal standard. Carbon and, in some cases, sulphur contents of the recovered and DCM-extracted catalysts were determined. Concentrations of trapped product in the used catalysts from the deactivation experiments were estimated from the weight loss up to 500°C.

RESULTS AND DISCUSSION

Previous work (8) using a single-stage reactor at 500°C and 150 bar, showed that between 25 and 30% tar was obtained from Linby coal while the hydrocarbon gas yield was only 5%. This work also showed that, although the tar yield increased with temperature up to about 650°C, the gas yield increased much faster e.g. at 600°C, the tar yield had reached 35% but the hydrocarbon gas yield had risen to 18%, including 10% methane.

In the present work the fresh catalysts tested at 400°C and 150 bar yielded 20±3% colourless liquid product (Table 3), while gas yields were only slightly higher than those obtained in the equivalent single-stage hydropyrolysis tests (8). The liquids contain up to 40% boiling lower than about 150°C, the major

constituents being alkylcyclohexanes, alkylbenzenes and alkanes (Figure 2 and Table 4). ^{1}H NMR indicates that the concentrations of naphthalenes and other di-aromatic species are low (Figure 3 and Table 5). Nitrogen-containing compounds and phenols are only minor constituents (Table 5). (Reliable sulphur values could not be determined possibly due to the presence of elemental sulphur released from the fresh catalysts.)

The Pd HTO catalyst gave the most hydrogenated liquid product, the aromatic hydrogen content (Table 5) and ratios of benzene to cyclohexane and toluene to methylcyclohexane (Table 4) being the lowest achieved. The extent of hydrogenation was greater for the pre-sulphided Ni/Mo on alumina catalyst than for the other HTO catalysts tested. The Ni/Co/Mo formulation pre-sulphided in-situ gave the most aliphatic product.

The light naphtha yields given in Table 4 provide a convenient comparison of catalyst hydrocracking ability, the highest yield being obtained with the Ni/Co/Mo HTO catalyst pre-sulphided in-situ; it is uncertain why the method used to pre-sulphide this catalyst affects both the extent of hydrogenation and hydrocracking. Light naphtha yields for the Ni/Mo and Co/Mo HTO and Ni/Mo on alumina catalysts were similar. Interestingly, the Pd HTO catalyst gave a lower yield indicating that hydrocracking and hydrogenation abilities are not related.

The yields of liquid products obtained at 300°C and 50 bar pressure were lower (about 15%) than at 400°C (Table 3) because more tar remained on the catalysts (Table 6). The Ni/Co/Mo HTO catalyst was much less effective under the milder conditions giving a more aromatic and phenolic product (see Tables 4 and 5). In contrast, the product obtained with the Pd catalyst was similar to that obtained at 400°C, BTX concentrations being extremely low. The 300°C product contained more light naphtha probably because a greater proportion of the high MW constituents in the tar condensed on the catalyst bed. However, the initial build-up of carbon does not seem to impair the low temperature hydrogenating ability of the Pd catalyst (9,10).

All the catalysts gained carbon but the pre-sulphided catalysts also lost sulphur (Table 6). However, the recovered HTO catalysts contained less carbon than the corresponding commercial Ni/Mo catalyst. Soxhlet extraction with DCM removed between 2 and 3% material leaving as little as 1% carbon (equivalent to about 3% of the primary tar). Although the extracts were dark in colour, their acidic OH contents (1-2%) were significantly lower than that of the primary tar (about 5%, ref.8).

After a sharp initial rise during the first pass, there was a steady build-up of carbon on both the HTO and alumina Ni/Mo catalysts in the deactivation experiments (Table 6). However, the carbon content of the HTO catalyst was always lower. The amount of extractable material on the catalysts remained fairly constant after the first pass, about 3% DCM soluble material being recovered from both catalysts after the sixth and final pass.

Figure 4 summarises the changes in the composition of the liquid products as deactivation progressed. The products after the first pass had little colour but were more aromatic and contained less light naphtha than the corresponding products from the catalyst screening tests (Tables 4 and 5) because less catalyst and more coal was used. The products from the remaining passes were all dark in appearance and contained more nitrogen, acidic OH and aromatic hydrogen (Figure 4). The extent of hydrogenation remained fairly constant after the first pass (see aromatic hydrogen contents, Figure 4) but the heteroatom content continued to increase while the light naphtha yield decreased.

These results suggest that tar trapped on the catalysts is largely responsible for the initial deactivation but the slower build up of coke (non-extractable material) continues to reduce the extents of heteroatom removal and of hydrocracking. The level of deactivation appears to be fairly similar for the HTO and alumina catalysts tested (Figure 4) taking into account that the alumina catalyst initially gave the more hydrogenated product.

CONCLUSIONS

1. Hydrous titanium oxide catalysts are capable of upgrading tar vapours to give low boiling products.

2. Pd and Ni/Co/Mo hydrous titanium oxide catalysts are particularly promising. Pd gave a more extensively hydrogenated product and Ni, Co, Mo, a lower boiling product than the commercial Ni/Mo catalyst. The Pd catalyst was still effective at 300°C.

3. The effect of deactivation on product composition was similar for Ni/Mo hydrous titanium oxide and alumina catalysts.

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TABLE 1 - Analyses of Linby Coal

NCB CRC	ISO Class	Proximate analysis % ar H_2O	% db Ash	% daf V.M.	Ultimate analysis % dmmf C	H	O	N	% db S	Cl
802	811	9.8	6.9	37.9	83.0	5.5	8.7	1.9	1.5	0.45

TABLE 2 - Catalyst formulations and properties

Type	Active Metal Content (wt %)[a]	BET Surface Area (m^2/g)	Sulphur Content (wt %)[a.b]
HTO	10.1 % Mo	84	3.8
	10.0 % Ni	148	3.9
	2.0 % Ni 12.2 % Mo	174	5.4
	1.7 % Co 12.8 % Mo	135	6.1
	1.2 % Co 1.0 % Ni 12.3 % Mo	148	6.2
	15.7 % Pd	189	--
Alumina[c]	3.0 % Ni 15.0 % Mo	180	5.9

KEY
a = Volatile-free basis
b = Freshly presulphided catalyst
c = Akzo 153

TABLE 3 Product yields from two-stage catalytic hydropyrolysis tests

Hydrotreating T°C		400									300	
Catalyst type		HTO							Alumina		HTO	
Active Metals		Ni	Mo	Ni/Mo	Co/Mo	Ni/Co/Mo		Pd	Ni/Mo		Ni/Co/Mo	Pd
Pre-sulphiding		S	S	S	S	S	P	O	O	P	P	O
% daf coal	Char	63	63	62	63	63	64	63	62	63	61	61
	Liquid Product	21	23	21	23	19	20	22	20	18	15	15
	Total gas[a]	7	7	8	7	8	7	7	7	7	11	11
	Methane	3.0	3.0	3.6	2.7	4.3	3.4	3.7	3.5	3.6	6.1	7.0

KEY [a] = C_1-C_4 hydrocarbons, CO_2 and CO

S = beforehand
P = in-situ
O = not pre-sulphided

TABLE 4 GC analysis of light naphtha fractions

Hydrotreating T°C	400									300	
Catalyst type	HTO							Alumina		HTO	
Active metals	Ni	Mo	Ni/Mo	Co/Mo	Ni/Co/Mo		Pd	Ni/Mo		Ni/Co/Mo	Pd
Pre-sulphiding	S	S	S	S	S	P	O	O	P	P	O
% Light naphtha in liquid products (up to, and including, o-xylene)	18	22	31	30	20	40	27	33	32	17	42
Major constituents (% wt of liquid products)											
Cyclopentane	0.10	0.15	0.30	0.40	0.20	0.52	0.24	0.30	0.29	0.02	0.33
n-Hexane	0.40	0.82	0.70	0.75	0.54	1.08	0.64	0.87	0.77	0.21	0.90
Methylcyclopentane	0.76	0.72	1.33	1.78	1.13	1.88	0.55	0.78	0.70	0.18	0.68
Benzene	0.23	0.77	1.03	1.57	1.02	1.60	0.01	0.70	0.22	1.08	<0.01
Cyclohexane	0.78	1.03	1.94	1.06	1.24	2.30	3.44	2.72	3.67	0.07	6.41
n-Heptane	0.42	0.81	0.82	0.72	0.69	1.03	0.73	1.17	0.89	0.63	1.09
Methylcyclohexane	1.59	0.72	3.75	2.33	2.67	4.62	8.00	6.53	8.32	0.29	13.24
Ethylcyclopentane	0.17	0.52	1.34	0.99	1.01	1.44	0.38	0.44	0.38	0.24	0.38
Toluene	1.61	3.18	4.19	5.14	4.41	5.45	0.18	3.47	1.41	4.33	0.13
n-Octane	0.45	0.64	0.68	0.57	0.58	0.80	0.59	0.99	0.72	0.82	0.90
Ethylcyclohexane + ethylbenzene	1.60	1.86	2.26	2.08	2.82	2.76	2.65	2.79	3.12	1.33	3.59
Xylenes	2.45	3.03	4.15	4.51	4.48	4.10	0.10	3.41	1.70	4.07	0.28
Benzene/cyclohexane	0.29	0.75	0.53	1.48	0.82	0.70	<0.01	0.26	0.06	~15	<0.01
Toluene/methylcyclohexane	1.01	4.42	1.12	2.21	1.65	1.18	0.02	0.53	0.17	~15	0.01

KEY S = beforehand
P = in-situ
O = not pre-sulphided

TABLE 5 Analytical data for liquid products

Hydrotreating T°C		400									300	
Catalyst type		HTO							Alumina		HTO	
Active metals		Ni	Mo	Ni/Mo	Co/Mo	Ni/Co/Mo		Pd	Ni/Mo		Ni/Co/Mo	Pd
Pre-sulphiding		S	S	S	S	S	P	O	O	P	P	O
%	C	88.6	87.9	87.7	87.9	87.6	85.6	85.6	85.8	86.0	85.4	84.0
%	H	11.9	11.3	12.3	11.7	11.5	12.2	13.2	12.5	13.2	10.0	13.6
%	OH	<0.1	0.8	0.03	0.04	0.03	0.03	0.03	0.01	0.01	2.0	0.03
ppm	N	210	520	25	ND	50	10	15	10	7	1400	15
% of H (from ^{1}H NMR)	Aromatic	10	15	9	13	12	7	2	6	4	21	<0.5
	- 2 rings	1	6	1	1	1	<0.5	<0.2	<0.5	<0.5	5	
	α to an aromatic ring	15	24	14	17	18	12	4	12	6	26	<1
	Other aliphatic H	75	61	77	70	70	81	94	82	90	53	>99

KEY
S = beforehand
P = in-situ
O = non pre-sulphided
ND = not determined

TABLE 6 Carbon and sulphur contents of recovered catalysts

Hydrotreating T°C	400								300	
Catalyst type	HTO							Alumina	HTO	
Active metals	Ni	Mo	Ni/Mo	Co/Mo	Ni/Co/Mo		Pd	Ni/Mo	Ni/Co/Mo	Pd
Pre-sulphiding	S	S	S	S	S	P	O	P	P	O
% C	3.9	2.6	4.6 (2.2)	3.6 (2.9)	3.6	3.3	2.6	4.4 (1.5)	8.1 (5.0)	6.2 (3.5)
Δ % C (+)	3.3	1.3	3.4 (1.2)	1.9 (1.3)	2.0	1.9	ND	4.4 (1.5)	4.7 (1.6)	ND
% S	2.3	3.0	5.1	4.9	4.9	ND	ND	ND	ND	0.3
Δ % S (-)	1.6	0.2	0.3	1.3	1.3	ND	ND	ND	ND	ND

Deactivation experiments

Pass No.	1	2	3	4	5	6
Ni/Mo HTO catalyst % C	4.2	4.9	5.5	5.8	7.2	8.2
Δ % C	2.5	3.2	3.8	4.1	5.5	6.5
Ni/Mo on alumina % C[a]	6.3	8.3	7.7	7.7	9.0	11.6

KEY
S = beforehand
P = in-situ
O = not pre-sulphided
( ) = after extraction with dichloromethane
ND = not determined
[a] = Δ % C since initial catalyst contains no carbon

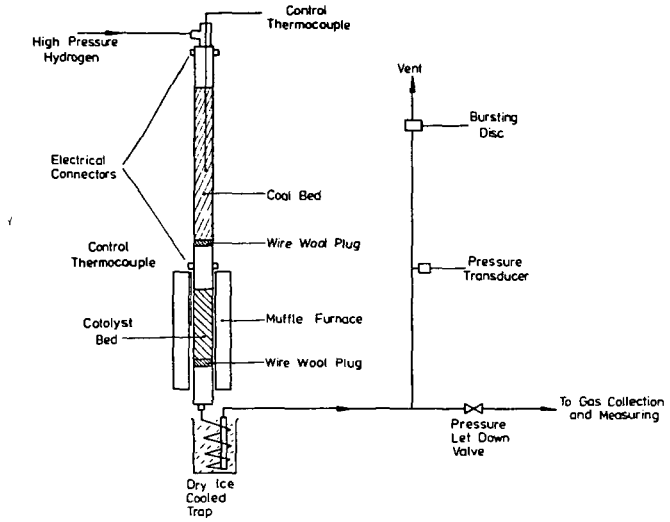

FIGURE 1. SCHEMATIC OF FIXED-BED TWO-STAGE HYDROPYROLYSIS REACTOR

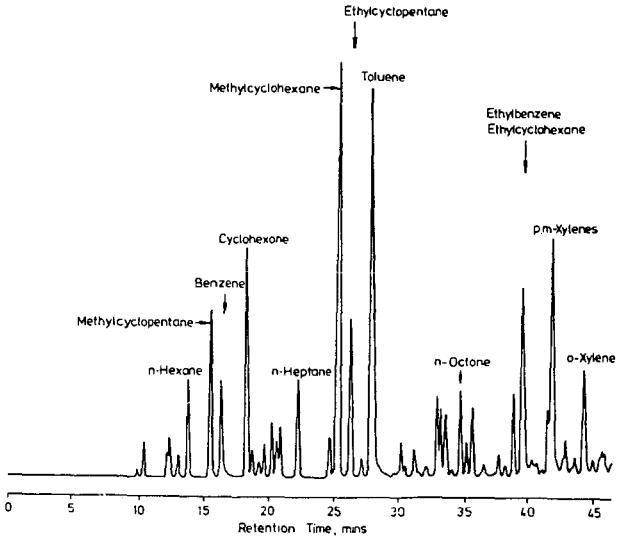

FIGURE 2 GAS CHROMATOGRAM OF LIGHT NAPHTHA FRACTION FROM THE PRODUCT OBTAINED WITH THE Ni/Mo HTO CATALYST

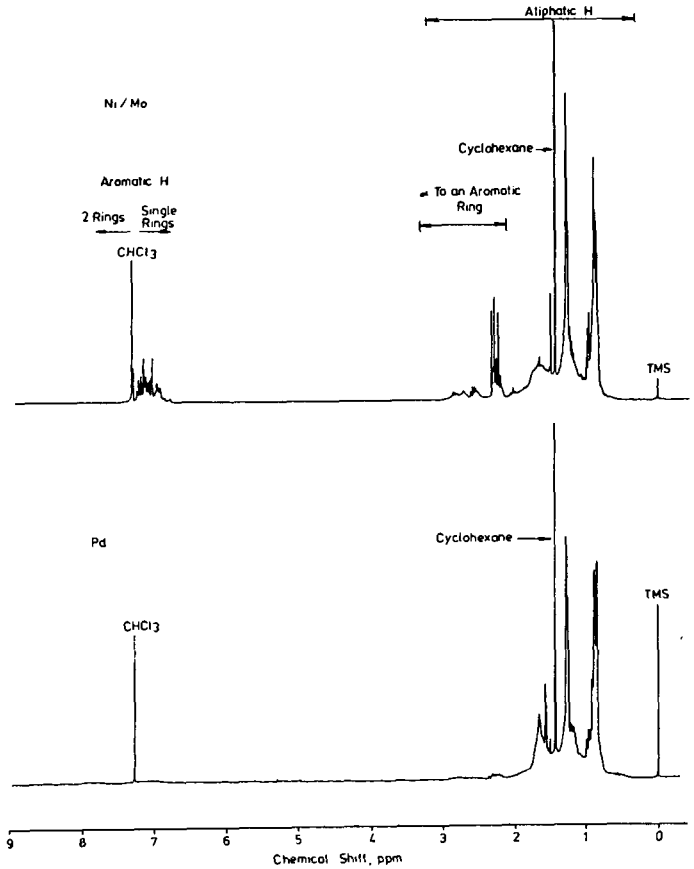

FIGURE 3. ^{1}H NMR SPECTRA OF LIQUID PRODUCTS OBTAINED WITH HTO CATALYSTS

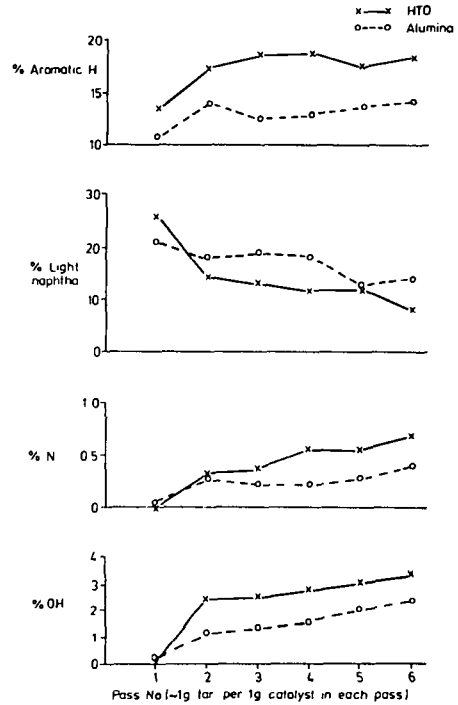

FIGURE 4. EFFECT OF DEACTIVATION ON PRODUCT COMPOSITION FOR THE Ni/Mo CATALYSTS