

CATALYTIC HYDROGENATION OF POLYAROMATIC COMPOUNDS USING COKE-OVEN GAS INSTEAD OF PURE HYDROGEN.

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ABSTRACT

In order to improve the economy of the conversion process of polyaromatic molecules to their hydroaromatics analogs, catalytic hydrogenation of phenanthrene has been carried out under pressure of different simulated coke-oven gases instead of pure hydrogen. The influence of reaction time, temperature and pressure on the hydrogenation yields and on the nature of the obtained products has been studied. Comparisons have been made with reaction with pure hydrogen in the same conditions. The influence of the different components of a real coke-oven gas has also been pointed out. The results indicate that coke-oven gas can be used if the goal is not to obtain perhydroaromatics compounds for a thermal cracking, but to give partly hydrogenated compounds to be used as hydrogen donor solvent in a coal liquefaction process. The results have been applied to coal-tar highly aromatic fractions.

INTRODUCTION

Coal derived heavy oils contain principally polyaromatics hydrocarbons (P.A.H.). Previously published studies^{1,2} showed that these molecules must be hydrogenated to their perhydrogenated analogs in order to obtain high yields of light aromatics (B.T.X.) and ethylene by thermal cracking. Moreover, these perhydrogenated molecules could provide one of the best solution to the requirement of modern jet plane fuels³⁻⁵. If the hydrogenation is not complete, the partly hydrogenated oils could also be used as hydrogen donor solvent in a coal liquefaction process.

An important economic factor in hydrogenation processes is the hydrogen cost. To reduce this cost will be beneficial. In this perspective, Doughty and al.^{6,7} studied the hydrocracking of coal derived liquids using bimetallic catalyst and a gas mixture of 90% H₂ / 10% CO instead of pure hydrogen. They showed that the conversion to low boiling point materials was lower in presence of 10% CO, probably because the CO molecules occupy the H₂ sites at the catalyst surface. Fu and al.⁸ performed the hydrogenation of model compounds in presence of petroleum solvent using syngas (H₂ : CO = 1:1). The experiments were carried out in a microreactor during 45 minutes. The results showed that the hydrogenation of anthracene at 350°C under H₂ pressure gave 90% conversion. The reaction with syngas at the same temperature gave only 65.9% anthracene conversion. The most important product was dihydroanthracene.

The use of H₂/CO mixtures may introduce other competing reactions which lead to undesirable products. For example, if the experimental conditions are similar to those used in the methanation reaction, hydrogen and carbon monoxide will be consumed, producing unwanted methane and water. Even with low levels of CO, catalyst poisoning may be increased. The loss in catalytic activity would lead to reduced conversions, which have to be compared to the gain in cost due to the use of a coke-oven gas. Moreover, industrial gases used directly may contain H₂S which could poison the catalyst.

The aim of this work is to hydrogenate polyaromatics hydrocarbons using the coke-oven gas instead of pure hydrogen. Coke oven-gas contains approximately 55% H₂, 30% CH₄, the balance being made by CO₂, CO, C_nH_m, N₂. Phenanthrene has been chosen as a model compound for the P.A.H. in the heavy oils. Many works over catalytic hydrogenation of P.A.H. were published, but anyone study the possibility of using coke-oven gas instead of pure hydrogen.

EXPERIMENTAL

Procedure

Experiments were performed in a 250 ml stainless steel PARR 4570 autoclave. 10 g of phenanthrene and 2 g of catalyst are introduced in the reactor, without solvent. The installation is purged with the reactive gas and pressurised at ambient temperature. Temperature is then raised as quickly as possible to the desired one. The reaction system is continuously stirred at 250 rpm. After reaction, the autoclave is cooled at ambient temperature and depressurised. The gases and the liquids are collected and analyzed.

Catalysts

A commercial nickel-molybdenum catalyst (3% NiO, 15% MoO₃ on alumina, surface area : 300 m²/g) was used in all experiments. For comparison, some experiments were carried out with a cobalt-molybdenum catalyst and also with a palladium catalyst.

Analyses

Gases and liquids products are analyzed by gas chromatography. The g.c. conditions are described elsewhere⁶. The products, first identified by gc/ms, are dihydrophenanthrene (DHP), tetrahydrophenanthrene (THP), sym-octahydrophenanthrene(sOHP), asym-octahydrophenanthrene (asOHP), and perhydrophenanthrene (PHP). Mass balances are controlled after each experiment. The compositions of the different simulated coke-oven gases used in this work are given in table 1.

RESULTS AND DISCUSSION

Hydrogenation of phenanthrene with pure hydrogen (gas 1)

The hydrogenation of phenanthrene under H₂ pressure was studied as a function of reaction time. Temperature and pressure were kept constant (370°C-21 MPa). The results are summarized in table 2 and confirms these of Colglough¹⁰ at the same temperature and pressure. It can be seen also that the yield of cracking products remains low. These results will be used for the comparison with the hydrogenation performed with the other gases mixtures.

Hydrogenation of phenanthrene with simulated coke-oven gases.

Influence of reaction time.

The hydrogenation of phenanthrene was studied as a function of time, at 370°C and under 21 MPa of a gas containing the two main components of a coke-oven gas, the balance being made by nitrogen (gas 3). The results are presented in table 2. As in pure hydrogen, the conversion of phenanthrene is high, more than 90% after 2 hours. The PHP yield increases regularly but cannot reach the value obtained under pure hydrogen, even after 16 hours of reaction.

Influence of temperature

The hydrogenation of phenanthrene with gas 3 was studied between 300 °C and 450°C. Pressure and reaction time were kept constant (21MPa-16 hours). The results are shown in table 2. It can be seen that a rise in temperature favour the hydrogenation reactions. The maximum yield of PHP is obtained at 370°C. At higher temperature, the yield of PHP decreases while the yields of cracking products and phenanthrene increase. Higher temperatures introduce ring opening reactions, leading to the formation of lower molecular weight products. The formation of aromatics compounds by deshydrogenation reactions is also favoured by increasing temperature and explain the high yield of phenanthrene.

Influence of pressure.

The hydrogenation of phenanthrene was studied between 11 and 25 MPa of gas 3. Temperature and reaction time were kept constant (370°C-16 hours). Table 2 gives the yield of the products as a function of pressure. At the lower pressure, the conversion of phenanthrene is low and the hydroaromatics species are the major products. The hydrogenation of phenanthrene is favoured at higher pressure. These results are also in agreement with these of previous works.

Influence of the components of the coke-oven gas.

In order to learn more about the influence of each components, catalytic hydrogenation of phenanthrene was studied under pressure of different simulated coke-oven gases. Temperature, pressure and reaction time were kept constant (370°C-21MPa-16 hours). Results are shown in table 2. The results are also compared to the one obtained under 11.5 MPa of hydrogen, this pressure corresponding to the H₂ partial pressure in the coke-oven gas.

- Hydrogen influence

Under pure H₂ pressure, the conversion of phenanthrene is 99%. The yield of PHP is more than 80% and the yield of cracking products is small. The conversion and the yield of PHP decrease in presence of nitrogen (gas 2). However, the yield of cracking products become important. The comparison between the results obtained under 11.5 MPa of hydrogen and under 21 MPa of gas 2 permitted to distinguish between the influence of total pressure and hydrogen partial pressure. It can be seen that for the same hydrogen pressure, the yield of cracking products is less important if the total pressure is higher.

- Methane influence

The comparison of the results of reaction with gas 2 and gas 3 showed that the yields of the different hydrogenated products are not significantly influenced by the presence of methane. In our experimental conditions, methane does not handicap the catalytic hydrogenation of phenanthrene.

- Influence of the other components

The presence of ethane, ethylene and carbon dioxide (gas 5) modifies slightly the composition of the hydrogenation products. On the other hand, the presence of CO lead to an important drop of the yields of hydrogenated compounds and specially the PHP. The cracking becomes also important; it raises from 10% to 30%.

The influence of the carbon monoxide can be explained by the following hypotheses:

- formation of alkanes by Fisher-Tropsch type reactions, consuming hydrogen, for example:



- partial deactivation of the catalysts, the carbon monoxide occupying preferentially some active sites^{6,7}.

In our experimental conditions, these reactions occur as shown by the following experiments. The composition of the hydrogenating gas (gas 4) has been compared before and after reaction in 3 cases: Exp1 : the autoclave contains coke-oven gas (gas 4) alone;

Exp2 : the autoclave contains coke-oven gas (gas 4) and the NiMo catalyst;

Exp3: the autoclave contains coke-oven gas (gas 4), the NiMo catalyst and the phenanthrene. The results are shown in table 3. The experiments 2 and 3 confirm the reactivity of carbon monoxide: the yield of methane increases while the yield of hydrogen decreases when coke-oven gas is treated in presence of the catalyst. The formation of propane could also be explained by Fischer-Tropsch reaction. Partial hydrogenation of ethylene occurs also, even in the absence of the catalyst.

Thermal cracking of the hydrogenated compounds.

In order to verify the thermal behaviour of the hydrogenated compounds, thermal cracking experiments have been performed on the mixtures obtained after hydrogenation of the phenanthrene with gas 4 and with pure hydrogen. The crackings are made at atmospheric pressure under nitrogen at 800°C and with a residence time of 1 s. As shown in table 4, the BTX yields obtained by thermal cracking are directly related to the amount of perhydrogenated compounds present in the hydrogenation products, as explained previously¹².

Hydrogenation of heavy oils.

Two different industrial oils have been hydrogenated : a heavy naphtha fraction of petroleum (HLN) and a chrysenic fraction of a coal tar (HC). The experimental conditions are: T°: 370°C, P : 21 MPa, t : 16 h, cat.: sulfided Ni-Mo. The hydrogenating gas used is gas 4 and the results are compared with hydrogenation under pure hydrogen. Due to the complexity of the oils, the thermal cracking of the mixtures obtained after hydrogenation has been directly performed, mainly to compare the BTX yields. It has to be pointed out that the untreated heavy oils do not contain BTX. The results, summarized in table 5, indicate clearly that the amounts of perhydrogenated compounds are lower when the simulated coke-oven gas is used for the hydrogenation, confirming the results obtained on the model substance.

CONCLUSIONS

The results obtained during this research have shown, the possibility to use a coke-oven gas to perform the hydrogenation of PAH with a commercial catalyst. But it was not possible, even by increasing the reaction time, to obtain with a gas containing 55% H₂ the same yield of PHP as the one obtained with pure hydrogen.

The influence of the various components of the coke-oven gas on the hydrogenation yields has been investigated: CH₄ does not handicap the catalytic hydrogenation of the phenanthrene; the presence of C₂H₄, C₂H₆, and CO₂ modifies slightly the composition of the hydrogenation products; the presence of CO leads to an important drop of the yields of hydrogenated compounds and specially the perhydrogenated.

It can be concluded that, if the goal of the hydrogenation is not to obtain perhydrogenated compounds for a chemical upgrading by thermal cracking, but to give partly hydrogenated compounds to be used as hydrogen donor solvent in coal liquefaction processes, then the hydrogen can be economically replaced by a coke-oven gas.

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Table 1. Composition (vol.%) of the gases used for hydrogenation.

Gas 1 : 100% H ₂
Gas 2 : 55% H ₂ , 45% N ₂ .
Gas 3 : 55% H ₂ , 15% N ₂ , 30% CH ₄
Gas 4 : 55% H ₂ , 1% N ₂ , 30% CH ₄ , 6% CO, 3% C ₂ H ₄ , 3% C ₂ H ₆ , 2% CO ₂
Gas 5 : 55% H ₂ , 7% N ₂ , 30% CH ₄ , 0% CO, 3% C ₂ H ₄ , 3% C ₂ H ₆ , 2% CO ₂

Table 2. Hydrogenation of phenanthrene (catalyst : sulfided Ni-Mo)

Gas	T° (°C)	t (h)	P (MPa)	Phen. (Wt%)	DHP (Wt%)	THP (Wt%)	OHP (Wt%)	PHP (Wt%)	Others (Wt%)	
1	370	1	21	5.8	8.3	5.9	26.8	48.0	0.9	
		2		1.2	7.3	1.9	24.8	60.2	1.2	
		4		0.7	4.9	1.6	23.6	67.9	1.1	
		16		0.7	1.9	0.6	20.7	81.2	1.1	
		16		11.5	3.9	5.8	6.0	16.5	55.6	2.4
3	370	2	21	6.8	11.1	13.1	33.7	26.6	0.5	
		4		6.2	10.0	10.5	25.9	38.9	1.3	
		8		5.4	7.5	8.2	18.7	47.9	2.3	
		12		5.2	6.0	6.8	17.9	54.3	7.1	
		16		2.8	5.4	5.2	14.6	61.0	8.9	
3	300	16	21	3.4	0.5	1.9	72.5	12.7	2.6	
		350		2.7	5.7	4.8	24.1	58.0	1.3	
		400		5.3	8.3	7.9	20.1	40.5	7.3	
		450		25.0	5.4	5.2	3.5	33.9	18.0	
3	370	16	11	25.3	7.3	13.6	13.5	21.4	3.5	
				15	12.2	6.1	11.4	19.1	37.8	5.3
				25	0.9	3.2	1.9	9.7	72.8	7.2
2 4 5	370	16	21	3.7	5.6	5.8	13.9	59.8	0.8	
				7.4	5.2	8.0	16.4	26.6	29.2	
				3.1	5.2	5.0	14.6	57.8	9.0	

Table 3. Behaviour of the hydrogenating gas (gas 4) during the reactions (vol.%)

	H ₂	CH ₄	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	N ₂
Gas 4	55.0	30.0	6.0	2.0	3.0	3.0	0.0	1.0
Exp.1	54.3	30.9	5.8	2.4	1.3	4.3	0.0	1.0
Exp.2	52.4	36.7	1.1	2.1	0.3	5.2	1.3	1.0
Exp.3	39.4	46.0	1.7	2.1	0.3	8.1	1.4	1.0

Table 4. Thermal cracking of the phenanthrene hydrogenation products.

Cracking conditions : T°: 800°C, residence time : 1 s, P : 0.1 MPa N₂.

Hydrogenation conditions : T° : 370°C, t : 16 h, P : 21 MPa.

Product 1 : hydrogenated with gas 1.

Product 2 : hydrogenated with gas 4.

Wt% of the main compounds.

	Product 1		Product 2	
	Before cracking	After cracking	Before cracking	After cracking
Benzene	-	10.6	-	2.6
Toluene	-	4.8	-	1.7
Xylenes	-	1.7	-	0.8
Total BTX	-	17.1	-	5.1
Phenanthrene	0.7	3.9	7.4	15.4
DHP	1.9	-	5.2	0.4
THP	0.6	-	8.0	0.8
OHP	20.7	0.8	16.4	1.2
PHP	81.2	1.9	26.6	0.5

Table 5. Thermal cracking of the heavy oils hydrogenation products.

Hydrogenation and thermal cracking conditions are the same as in table 4.

BTX yields (in wt%)

	HLN		HC	
	gas 1	gas 4	gas 1	gas 4
Benzene	6.7	3.6	5.1	2.1
Toluene	5.5	2.9	2.8	0.7
Xylenes	2.3	1.9	1.5	0.5
Total BTX	14.8	8.4	9.4	3.3