

EFFECT OF A SULFIDED, NON-POROUS AEROSOL Fe_2O_3 CATALYST ON THE
CHEMICAL STRUCTURE OF COAL LIQUIDS FROM THE
HYDROLIQUEFACTION OF A HIGHLY VOLATILE BITUMINOUS COAL

Vicente L. Cebolla¹, Moustapha Diack^{2*}, Michèle Oberson³, Robert Bacaud³, Dénise Cagniant² and Brigitte Nickel-Pépin-Donat³.

¹ Instituto de Carboquímica, CSIC. Plaza de Paraíso, 4. 50004 Zaragoza, Spain.

² Laboratoire de Chimie Organique, Université de Metz. Ile du Saulcy. 57045 Metz, France.

³ Institut de Recherches sur la Catalyse, CNRS. 2, Avenue Albert Einstein. 69626 Villeurbanne, France.

* Present address: Department of Chemistry, University of Tennessee. Knoxville, TE 37996-50.

INTRODUCTION

Previous studies related with coal liquefaction in a batch reactor demonstrated that the pertinent parameter for the activity of a dispersed catalyst is not its total surface but the accessible external surface [1]. Thus, non-porous ultrafine aerosol oxides were synthesized by combustion of the corresponding metal chlorides in a hydrogen-oxygen flame [2-4]. Iron oxide precursors obtained in this manner, and sulfided with elemental sulfur during heating, showed a high catalytic activity for a highly volatile bituminous coal even at temperatures lower than that of most bond breaking [3]. Furthermore, the sintering of the initially dispersed iron sulfide was prevented by the presence of carbonaceous solid substances [5,6].

This work was extended to other aerosol types (SnO_2 , MoO_3 , SiO_2 , Al_2O_3 , $\text{NiMo}/\text{Al}_2\text{O}_3$). Attempts were made to elucidate their active phases [7,8]. Their concentration, mode of sulfidation and introduction were also studied, as well as the effect of temperature and the solvent used [9]. Moreover, sulfided iron oxide aerosols also showed high yields in a multistage hydroliquefaction procedure [2, 10, 11].

In this paper, the effect of a sulfided aerosol Fe_2O_3 on the chemical structure of oils and asphaltenes coming from the hydroliquefaction of a highly volatile bituminous coal will be compared to the effect of the other above-mentioned aerosols. For this purpose, methods of evaluation of hydroliquefaction runs in batch reactor and analytical techniques which permit differentiation between the effects of the catalysts have been developed.

EXPERIMENTAL

Catalysts

Fe₂O₃, MoO₃ and SnO₂ aerosol precursors were obtained by combustion of the corresponding chloride vapors. They were non-porous, with particle size lower than 50 nm and with BET surfaces from 20 to 60 m²g⁻¹. SiO₂, Al₂O₃ and NiMo/Al₂O₃ were commercial aerosols from Degussa and Institut Français du Pétrole (200 m²g⁻¹ S_{BET}). More details are given in [1, 12].

Hydroliquefaction procedure

This was described elsewhere [9]. Briefly, 40 g of a high volatile bituminous coal (from Freyming, France) were suspended in tetralin (95 g) with (or without in the blank run) 2% of catalyst precursor. Elemental sulfur was added in order to obtain a partial pressure of 1% H₂S. The magnetically stirred reactor was pressurized (14 MPa) with H₂. After the heating period (3°Cm⁻¹), the nominal temperature (350, 400 or 430°C) was maintained for one hour before cooling.

Evaluation of catalytic activity in the hydroliquefaction runs

Conversions were evaluated by parallel solvent extraction with THF, toluene and n-hexane, using microfiltration under pressure as it has been described in detail [9, 13]. The results were expressed in terms of the percentage of conversion into soluble products, calculated by the difference in weight of the insoluble fractions.

The activity of catalysts in hydrogen transfer reactions was evaluated by the extent of dehydrogenation of the solvent (expressed as the ratio of naphthalene to naphthalene + tetralin, measured by gas chromatography) and by the total consumption of hydrogen gas determined by the variation of the total pressure during a run [8, 14].

The influence of the catalyst was also confirmed by measurements of Electron Spin Resonance of the stable radicals of the THF insoluble fractions. Spectra were performed in a Varian E 112 apparatus at 9 GHz. Freyming macerals had been previously isolated by Density Gradient Centrifugation [15], and ESR parameters, also obtained at 9 GHz. Assuming that inertinite is the least reactive maceral, the percentage of "destroyed" fossil radicals in inertinite after hydroliquefaction runs can be calculated. This technique has been described in depth [16].

Analytical characterization of coal liquids

Raw coal liquids were submitted to extrography [17]. A 2 g sample was dissolved in 15 ml of dichloromethane; then 16 g of activated (2 h at 120°C) silicagel were added to the solution and the mixture transferred to a column after elimination of the solvent. It was successively eluted with pentane/toluene (85/15), chloroform, chloroform/ethanol (97/3) and THF. The efficiency of extrography as a fractionation tool, advantages and structural attributions to the separated fractions have been described elsewhere [18, 19].

Derived oils and asphaltenes were separated by careful distillation of tetralin (controlled by GC/MS at 65°C under 0.27-0.4 kPa) and subsequent sequential ultrasonic extraction (Sonoclean B30 probe) in the conditions described in [20, 21].

Gas Chromatography (GC) of oils on a SE 30 glass capillary column were carried out in a Intersmat IGC 121C3 apparatus under the conditions described in [20, 21]. Identification of individual structures was out of the scope of our work. Results were summarized by retention index zones, which were calculated according to Lee et al. [22] with naphthalene,

phenanthrene and chrysene as standards. Literature reported that elution is made according to the number of total rings (aromatic or not) [23]. Index between 100-200 correspond to compounds with one ring, 200-300 to two rings, etc... This classification of ring size by retention indices can also be applied to phenolic and heterocyclic compounds, mainly nitrogen, neutral and basic compounds [23], and thiophenic structures [24].

The use of n-decane as internal standard allows a quantitative estimation (index zones) and the evaluation of non-dosed products.

Gel Permeation Chromatography (HPLC-GPC) on three μ -styragel columns in series (1 x 500 Å + 2 x 100 Å) was applied to the oils and asphaltenes in a M-600 Waters apparatus with refractive index detection using dichloromethane as eluent [20]. Qualitative interpretation of chromatograms according to the partition in four zones as a function of the retention factor (k) was carried out on the basis of 70 model compounds, as follows: $0.1 \leq k < 0.6$: "asphaltenic type" of unknown structure, $0.6 \leq k < 0.75$: alkylated aromatics, $0.75 \leq k < 0.85$: non-alkylated aromatics, and $0.85 \leq k < 1.1$: pericondensed aromatics.

RESULTS AND DISCUSSION

The evaluation of catalytic effect

At the first stage of hydroliquefaction (350°C), differentiation between the effects of the catalysts is net and related to the different conversions in preasphaltenes and asphaltenes, hydrogen consumption and percentages of stabilized fossil radicals of inertinite [3]. Fe₂O₃ and MoO₃ precursors were the most active catalysts (fig.1), also giving an enhancement of hydroaromatic structures (NMR ¹³C/CP/MAS data) and breaking of ether bridges (FTIR data) in Freyming coal [8].

Taking into account that tetralin is not dehydrogenated at this temperature, and that tetralyl radicals do not stabilize fossil radicals of inertinite, a mechanism of H₂ dissociation on catalyst surface and subsequent migration of activated hydrogen (H^{*}) to stabilize the fossil radicals of inertinite, was proposed [8]. The small size of H^{*} would allow its diffusion into the inertinite structure.

Our results show that the catalytic effect is reduced at higher temperatures and the differentiation of catalysts by the total conversion in soluble products at 400 and 430°C is somewhat indecisive, as already observed by Makabe et al. [25]. Our total conversions are comprised in all the cases between 83 and 90% [26].

The wt% of consumed H₂ is more dependent on the nature of the catalyst. Tetralin donates hydrogen in the absence of added catalyst at 400°C but when used with a catalyst, the result is an increase of the contribution of gaseous hydrogen consumption [14]. Makabe et al. [25] pointed out that thermally produced coal radicals are mainly stabilized by H^{*} when the catalyst is active. With less active catalysts, the stabilization is due to tetralin. Therefore, catalyst efficiency can be related to its ability to dissociate H₂ into H^{*} and the ratio of hydrogen transferred from gas phase to hydrogen transferred from the solvent (H_{gas}/H_{soln}) is a good test to evaluate it (table 1).

The efficiency of the catalysts (at 350 and 400°C) evaluated by H_{gas}/H_{soln} parameters, are well related to the wt% of fossil radicals stabilized in the inertinite during hydroliquefaction at the same temperatures. Table 1 shows that trends are similar for both parameters at 350°C. The order of wt% of fossil radicals stabilized at 400°C decreases in the following order: SnO₂,

~ Fe₂O₃ ~ NiMo/Al₂O₃ > MoO₃ > SiO₂ > no catalysts. Trends are also similar to H_{gas}/H_{solv}, although this last allows a clearer differentiation among catalysts. At 430°C these ratios decrease significantly as the amount of hydrogen transferred from the solvent increases because of the thermal bond cleavage.

The influence of Fe₂O₃ precursor on the structural composition of coal-derived liquids

According to the results of extrography of the raw liquids (fig.2) [13, 26], the formation of PAHs (main constituents of F1 and F2 fractions) increases significantly as the temperature increases, at the expense of polar compounds (F4) and residues. However the differentiation, for a given temperature, between runs with or without Fe₂O₃, is not decisive using this technique, except for a small increase of the lightest compounds (F1) for Fe₂O₃ runs (400 and 430°C).

More details about the structural analyses were found when characterization of oils and asphaltenes were performed by GC on capillary columns and HPLC-GPC.

GC data, using the classification according to ring size as previously described in Experimental, revealed the higher and significant proportion of two-nuclei aromatic compounds in the oils when the runs were performed with non-porous sulfided Fe₂O₃ or MoO₃ catalyst rather than with SiO₂, SnO₂ or NiMo/Al₂O₃. This effect was found at 400 and 430°C for the iron precursor (fig 3). This fact could be attributed to hydrogenolysis of ether oxide or alkyl linkages between doubled two-ringed structures rather than to hydrocracking PAHs, all structures known to exist in the products of coal liquefaction [27]. Hypothesis of hydrocracking can be eliminated because pyrrhotite Fe_{1-x}S formed from Fe₂O₃ aerosol does not meet the requirements of hydrogenative and acid functions, needed for a hydrocracking reaction [28, 29]. The hypothesis of hydrogenolysis is supported by literature data on model compound reactions using iron oxide catalyst [30-32] and pyrrhotite [33, 34]. The possibility of a hydrodesulfurization activity of some carbon-based iron catalysts has been also reported [35] and should also be considered.

GC and HPLC-GPC data showed the important effect of temperature for oils and asphaltenes, in general, and for a given catalyst run [26]. On one hand, the wt% of non-dosed GC compounds decrease as the temperature increases (from 400 to 430°C), the cases of SiO₂ and SnO₂ being the most significant (fig. 3). On the other hand, HPLC-GPC showed that the same increase of temperature involves degradation of the heaviest components of asphaltenes (0 < k < 0.6) (fig. 4). However, this technique did not permit the observation of differences among the catalysts for a given temperature neither for oils nor for asphaltenes.

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Table 1. Evaluation of catalytic activity in coal hydroliquefaction by ESR and hydrogen balance measurements

Catalyst	% of stabilized R.		H_{gas}/H_{soliv}	
	350°C	400°C	350°C	400°C
Without	0	60	0.83	0.33
Al ₂ O ₃	0	66	1.87	0.65
SnO ₂	19	77	6.29	7.74
Fe ₂ O ₃	52	74	8.75	8.53
MoO ₃	72	68	15.62	3.17
NiMo/Al ₂ O ₃	-	73	-	13.05

Figure 1. % of conversions (THF) of hydroliquefaction runs at 350°C.

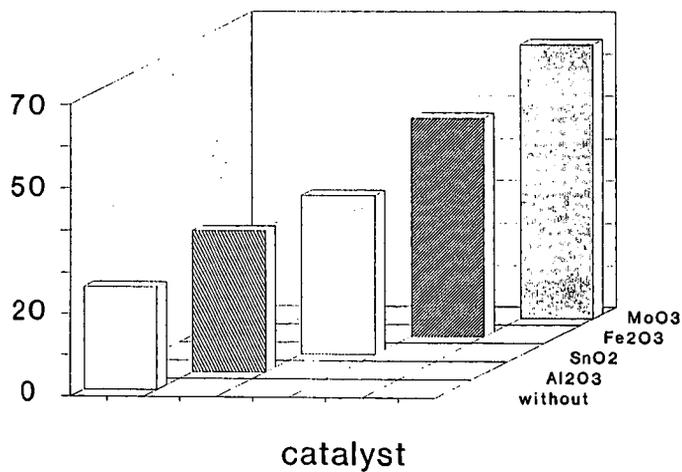


Figure 2. Iron oxide runs. Fractionation by Extrography.

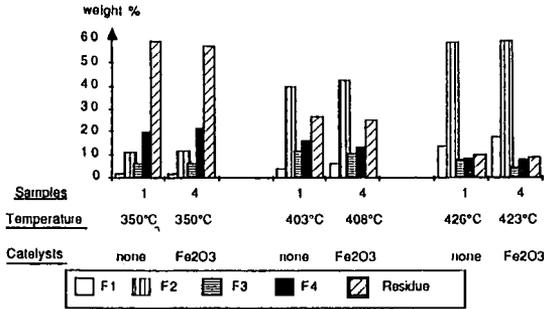


Figure 3. GC/CC analysis of oils. Classification by retention index zones.

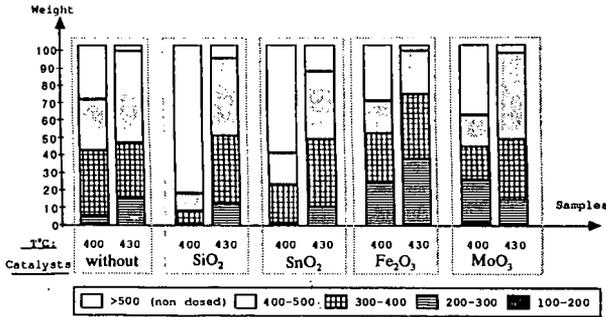


Figure 4. HPLC-GPC of oils (A) and asphaltenes (B) of iron oxide runs. (- - : 400°C; - : 430°C).

