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Carbon versus alumina as a support for Co–Mo catalysts reactivity towards HDS of dibenzothiophenes and diesel fuel

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Abstract

A series of cobalt–molybdenum catalysts supported on two different carbons has been prepared by conventional successive impregnation and/or successive impregnation with sulfiding between impregnation. Commercial Co–Mo/Al_2O_3 catalyst and the synthesized Co–Mo supported carbon catalysts have been compared for activity in the hydrodesulfurization (HDS) of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and hydrotreated diesel fuel. HDS experiments were carried out in a batch magnetically stirred micro autoclave reactor at 2.9 MPa hydrogen pressure and temperature range from 300°C to 380°C. The Co–Mo/carbon catalysts exhibited higher HDS activity for DBT and diesel fuel than the commercial Co–Mo/Al_2O_3 catalyst. However, large differences in catalytic behavior were observed for Co–Mo/carbon catalysts dependent on the preparation method and the nature of carbon support. The highest activity was observed for catalysts prepared by successive impregnation with sulfiding between impregnations. The HDS selectivity of DBT was found to be almost independent of the temperature. In contrast, a dramatic change in HDS selectivity for 4,6-DMDBT with temperature was observed. The kinetic behavior of HDS for both DBT and 4,6-DMDBT was verified to be pseudo-first order. Activation energies of each reaction step in the mechanism of HDS of DBT and 4,6-DMDBT were determined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: 4,6-Dimethyldibenzothiophene; Cobalt–molybdenum catalysts; Alumina

1. Introduction

Sulfided transition metal catalysts are of great industrial importance because they are widely used in petroleum refining hydroprocessing applications such as hydrodesulfurization and hydrodenitrogenation. Generally, industrial catalysts are derived from sulfided oxides of an element of Group VIB (Mo or W) and Group VIII (Co or Ni). Alumina is the most widely used support material for commercial Co or Ni promoted molybdenum hydrotreating catalysts. Notable features of alumina supports are their ability to provide high dispersion of the active metal phase [1] and good mechanical properties. However, the results of intensive research [2–7] have shown that in the final oxidic or precursor state numerous chemical interactions exist between the amorphous alumina and the transition metal oxides. Some of the species formed are very stable and resist complete sulfidation. In recent years, carbon has received much attention as a support for hydrodesulfurization catalysts as high HDS activities have been reported [8], which may be due to more favorable support/catalytic species inter-

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actions. In addition, carbons have many other interesting features such as high surface areas with controlled pore volume and pore size, reduced coking activity and controllable surface functionality.

The present paper examines the potential of carbon as a support for Co–Mo catalysts in hydrodesulfurization of dibenzothiophene (DBT), dimethyldibenzothiophene (4,6-DMDBT) and hydrotreated diesel fuel. Such model compounds represent the most refractory sulfur compounds found in petroleum products. The catalysts prepared were investigated in terms of their activity and selectivity and the results were compared with those of a conventional Co–Mo/Al_2O_3 commercial catalyst.

2. Experimental

In the present study, two kinds of activated carbon supports were used, i.e. carbons A and B. Table 1 shows the elemental analysis and physical characterization of these carbons. Both carbons were used as-received. Cobalt and molybdenum acetylacetonates and methanol were used as the catalyst precursors and impregnation solvent, respectively. Carbon supported Co–Mo catalysts (Co 2 wt%; Mo 10 wt%) were prepared by two methods. In the first method I, Mo was incorporated by impregnation first, followed by drying at 110°C, Co was then incorporated by impregnation, followed by drying at 110°C. In the second method II, Mo was incorporated as in method I, but the catalyst was sulfided with 5% H_2S in H_2 at 360°C prior to Co incorporation. All the catalysts were presulfided with 5 wt% H_2S/H_2 mixture at 360°C and 1 atm for 3 h prior to the reaction. A commercial Co–Mo/Al_2O_3 catalyst containing 3.2 wt% Co and 13.7 wt% Mo provided a base case for comparison of hydrodesulfurization performance. In the text, the catalysts are referred to as MC-(method of preparation)-(kind of Carbon). For example, MC-I-A means Co–Mo supported carbon catalyst that prepared by method I and the carbon support was A.

Hydrodesulfurization activity for model compounds was measured with DBT (obtained from Wako Chemical) and/or 4,6-DMDBT (synthesized according to [9]) in decane at 2.9 MPa hydrogen pressure in a magnetically stirred autoclave reactor of 100 ml capacity. DBT studies utilized 0.1 g DBT, 0.1 g catalyst and 10 cc decane. 4,6-DMDBT studies utilized 0.010 g 4,6-DMDBT, 0.2 g catalyst and 10 cc decane. The reactor was purged four times with hydrogen and then pressurized to 2.9 MPa H_2 at ambient temperature. After reaction, the hot reactor was quenched in cold water. The liquid contents were washed out with toluene and the catalyst was removed by filtration through fine filter paper. A known concentration of a reference material (4,4′-diethylbiphenyl) was added to the collected sample after filtration to facilitate quantitative analysis of product yields and mass balances. Analysis of this sample was accomplished with a Yanaco (G-3800) gas chromatograph equipped with a differential flame ionization detector and linear temperature programming. A capillary column (OV-101; 0.25 mm×50 m) was used and permitted good separation. Quantitative analysis of the chromatograms was obtained with the aid of an electronic integrator. The response factors for all reaction products were determined and related to the reference material. Qualitative analysis of the sample was obtained from retention time of standard sample and GC-Mass Spectra. The mass balance of each experiment has been calculated according to the same equation used in [10].

Deep desulfurization was simulated as a second stage reaction in which a diesel fuel meeting today's specification of 0.25 wt% S was further treated to lower the sulfur content. The diesel fuel was provided by Japan Energy Corporation and contained about 20% aromatics. The desulfurization reactions were conducted, using procedures similar to those

Table 1
Elemental analysis and physical characteristics of carbons

Carbon	Elemental Analysis					Pore volume ($cm^3 g^{-1}$)	Pore size (Å)	Surface area ($m^2 g^{-1}$)
	C	H	N	(O+S)	Ash			
A	94.9	0.5	0.1	4.5	2.4	0.52	12.5	907
B	89.9	0.6	0.2	9.3	0	1.76	9.9	3213

described above, with 0.5 g catalyst and 10 cc diesel fuel at 340°C, and 2.9 MPa hydrogen pressure. Short reaction times of 10–30 min were employed to facilitate rate comparisons. Analyses were conducted as before but utilized GC equipped with FPD detector to determine the percent of sulfur compounds.

3. Results and discussion

3.1. HDS of DBT

DBT and its derivatives were selected as model compounds for HDS to evaluate the activity of the novel carbon supported catalysts relative to the commercial catalyst. All the catalysts were tested under identical experimental conditions. The HDS products detected from DBT were H_2S, phenylcyclohexane, biphenyl, and tetrahydrodibenzothiophene (H4-DBT). Fig. 1 shows the pseudo-first order plot of HDS of DBT over various catalysts at 340°C and 2.9 MPa H_2. Table 2 summarizes the pseudo-first order rate constants for the catalysts. Hydrogen consumptions during the reactions were negligible in these experiments. Carbon supported Co–Mo catalysts exhibited much higher HDS activity than the commercial one, especially when method II was employed in the preparation. Even though different carbon supports were used for catalysts preparations, Co–Mo supported carbon catalysts prepared by method II showed very high activity, nearly twice those observed for catalysts prepared by method I. Accordingly, the advantage of method II appears to be general for

Table 2
Rate constant for HDS of DBT and 4,6-DMDBT over carbon based catalysts and Co–Mo/Al_2O_3 commercial catalysts

Catalyst	k_{DBT} $\times 10^4$ s^{-1} g cat^{-1}	$k_{\mathrm{4,6\text{-}DMDBT}}$ $\times 10^4$ s^{-1} g cat^{-1}
MC-I-A	104.7	19
MC-II-A	214.5	36.0
MC-I-B	124.1	12.2
MC-II-B	193.1	17.5
Co–Mo/Al_2O_3	60.0	18.6

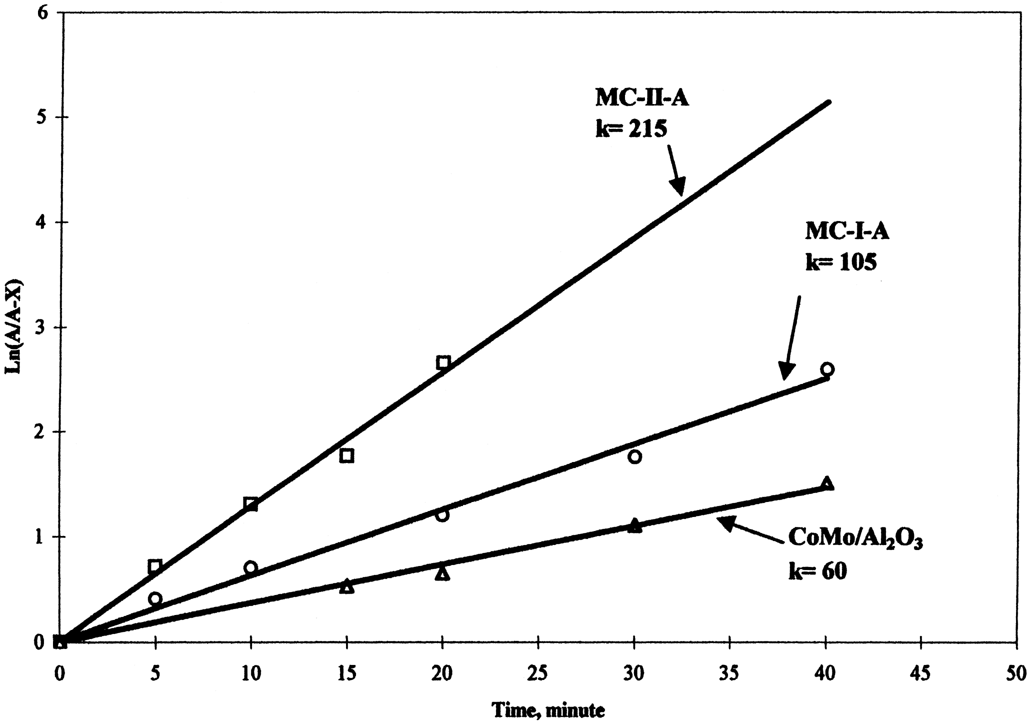

Fig. 1. Pseudo-first order kinetics of HDS of DBT (340°C and 2.9 MPa H_2). *Note*: k, 10^4 s^{-1} g cat^{-1}.

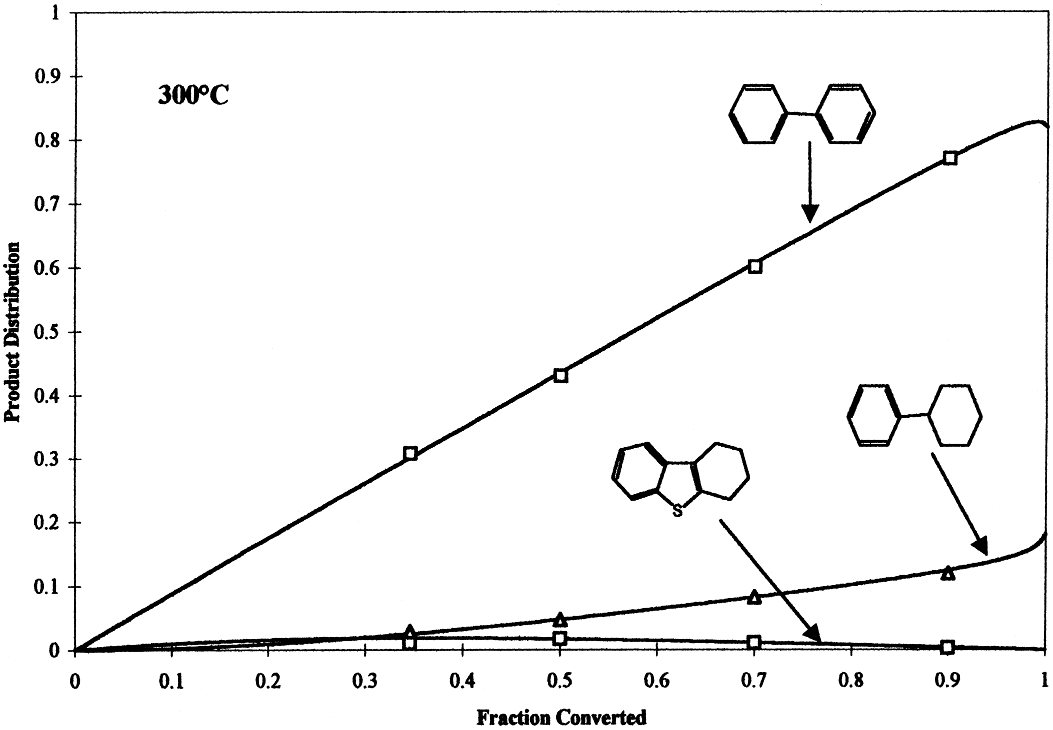

Fig. 2. HDS selectivity of DBT over MC-II-A catalyst at 300°C under 2.9 MPa H_2.

different carbons. In spite of the much larger surface area of carbon B, MC-I-B and/or MC-II-B catalysts had almost the same relative activity as carbon A catalysts for DBT.

It is interesting that the HDS products of DBT over all the catalysts were qualitatively similar. This strongly indicates that the mechanism for the conversion of DBT over the various catalysts was the same. However, some subtle differences in product selectivities for the different catalysts were noted. Fig. 2 shows the theoretical selectivity curves for the HDS of DBT and the experimental points that match them considering the boundaries we have set in a previous study [11]. As shown in Fig. 2, biphenyl was the major HDS product of DBT but a significant amount of phenylcyclohexane was also observed to form in a parallel fashion. Independent studies showed that the hydrogenation of biphenyl was very slow for these catalysts. This indicates that both direct desulfurization and hydrogenative desulfurization occurred.

3.2. *HDS of 4,6-DMDBT*

4,6-Dimethyldibenzothiophene was also studied as a representative model of refractory sulfur compounds for hydrodesulfurization. HDS rate constants of 4,6-DMDBT over the various catalysts at 340°C and 2.9 MPa hydrogen pressure are shown in Table 2. The rate constant values were derived from pseudo-first order expression as mentioned previously. Under these reaction conditions, H_2S, 3,3′-dimethylbiphenyl (3,3′-DMBP), *cis* and *trans* dimethylphenylcyclohexanes (3,3′-DMPC), and 4,6-dimethyltetrahydrodibenzothiophene (H4-4,6-DMDBT) were the only products observed. The HDS of 4,6-DMDBT proceeded on all catalysts through two independent reaction pathways, direct desulfurization route (DDR) (producing 3,3-DMBP) and hydrogenative desulfurization (HYD) (producing H4-4,6-DMDBT and 3,3′-DMPC). At 340 °C, the two routes provided about equal contributions. HDS activity of 4,6-DMDBT over all catalysts was 3–11 times lower than that for DBT, showing the magnitude of the difficulty in desulfurizing certain alkyl substituted dibenzothiophenes. The commercial catalyst was again observed to have a lower HDS activity with about similar selectivity when compared with the carbon supported catalysts. For all catalysts, the hydrogenated compounds (H4-DBT and H4-4,6-DMDBT) were observed to be present in lower amounts than in the case of HDS of DBT. This observation may be related to a thermodynamic limitation [11]. Surprisingly, while the HDS activities for DBT over MC-II-A and MC-II-B were almost the same, they varied by a factor of two in the HDS of 4,6-DMDBT. The carbon with the highest surface area but smaller average pore size (B) had a lower activity. This is most likely due to a diffusional restriction of the larger 4,6-DMDBT molecule within the small pores of carbon B (the molecular volume of 4,6-DMDBT is 226.3 Å^3 while it is 189.06 Å^3 for DBT, calculated

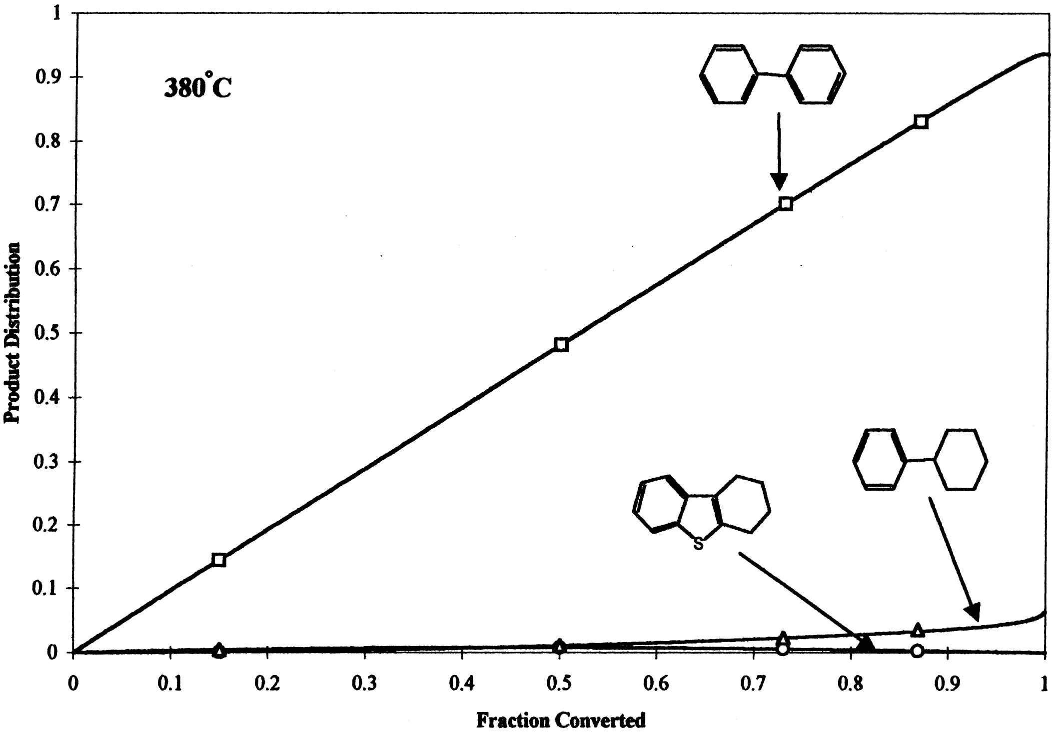

Fig. 3. HDS selectivity of DBT over MC-II-A catalyst at 380°C under 2.9 MPa H_2.

Table 3
Pseudo-first order rate constants for HDS of dibenzothiophene and 4,6-dimethyldibenzothiophene over Co–Mo supported carbon and Co–Mo/Al_2O_3 catalysts at various temperatures under 2.9 MPa H_2

Catalyst	Temperature (°C)	$k_{DBT} \times 10^4$ s^{-1} g cat^{-1}	$k_{4,6\text{-DMDBT}} \times 10^4$ s^{-1} g cat^{-1}
MC-II-A	300	32.1	12.5
	340	215	36.0
	380	1129	151.3
Co–Mo/Al_2O_3[a]	300	12.1	6.0
	340	60.0	19.0
	380	435	80.1

[a] Commercial catalyst.

from MOPAC 93). As in the case of DBT, catalysts prepared by method II showed higher activities for HDS of 4,6-DMDBT.

3.3. *Effect of temperature on HDS of DBT*

The HDS activity of DBT over Co–Mo/C catalyst versus temperature is presented in Table 3 and compared with that over the reference commercial Co–Mo/Al_2O_3 catalyst. It can be seen that, as the temperature was increased, the overall HDS activity increased exponentially. Figs. 2 and 3 show the DDS and HYD selectivities of DBT reaction at low and high temperature level, respectively. The predominance of hydrogenolysis over hydrogenation is still apparent even at low temperature. In addition, it can also be noted that at high temperature the direct desulfurization route which produces biphenyl becomes even more preferable. However, the temperature effect on the selectivity was found to be almost identical for all catalysts.

Arrhenius plots of the appearance rates of direct desulfurization and hydrogenation routes of DBT reaction over Co–Mo/C and Co–Mo/Al_2O_3 commercial catalysts are shown in Fig. 4. It can be observed that the rate of direct desulfurization and hydrogenation are both Arrhenius type temperature dependencies. In the temperature range of 300–340°C the activation energy of direct desulfurization and hydrogenation reactions over Co–Mo/Al_2O_3 are 35.28 and 23.6 kcal mol^{-1}, respectively, while it was 34.2 and 34.8 kcal mol^{-1}, respectively, over Co–Mo/C catalyst. Above this temperature, the response of the hydrogenation rate to increasing temperature declines.

3.4. *Effect of temperature on HDS of 4,6-DMDBT*

The effect of temperature on the selectivity of HDS of 4,6-DMDBT is quite different from that of DBT HDS. The HDS activity of 4,6-DMDBT also increased exponentially with temperature (Table 3). Figs. 5 and

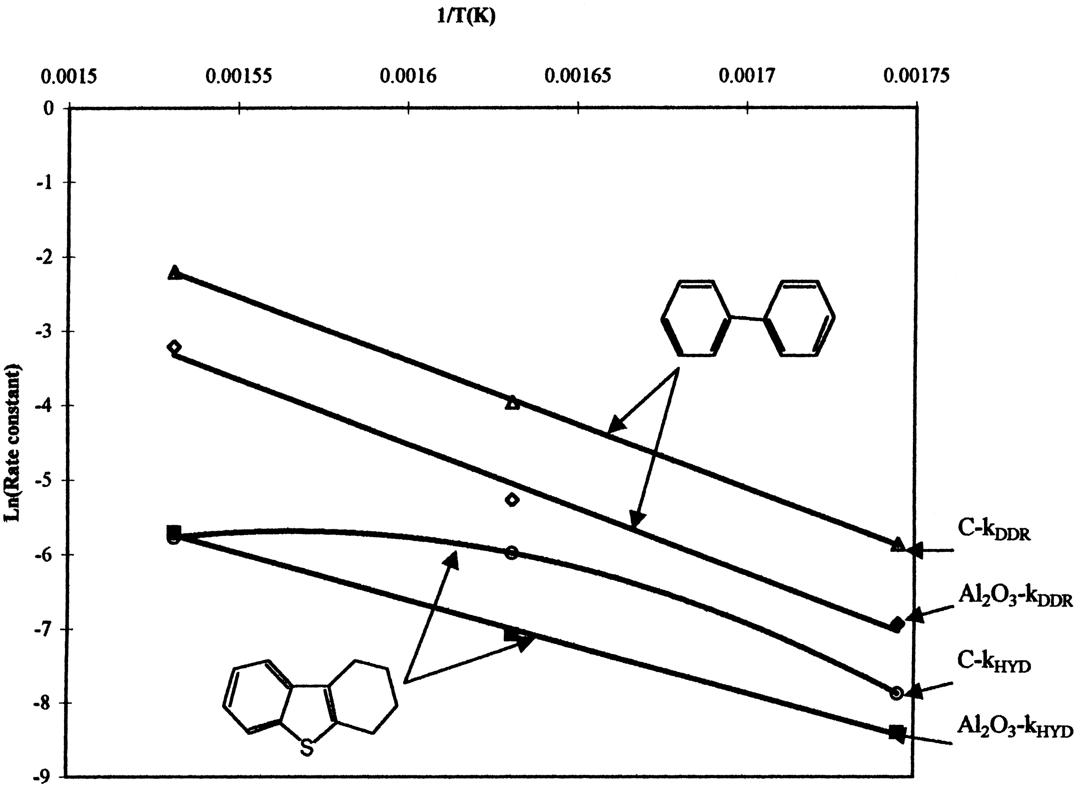

Fig. 4. Arrhenius plot of individual steps in HDS of DBT (Co–Mo/Al_2O_3 and Co–Mo/C, 2.9 MPa H_2).

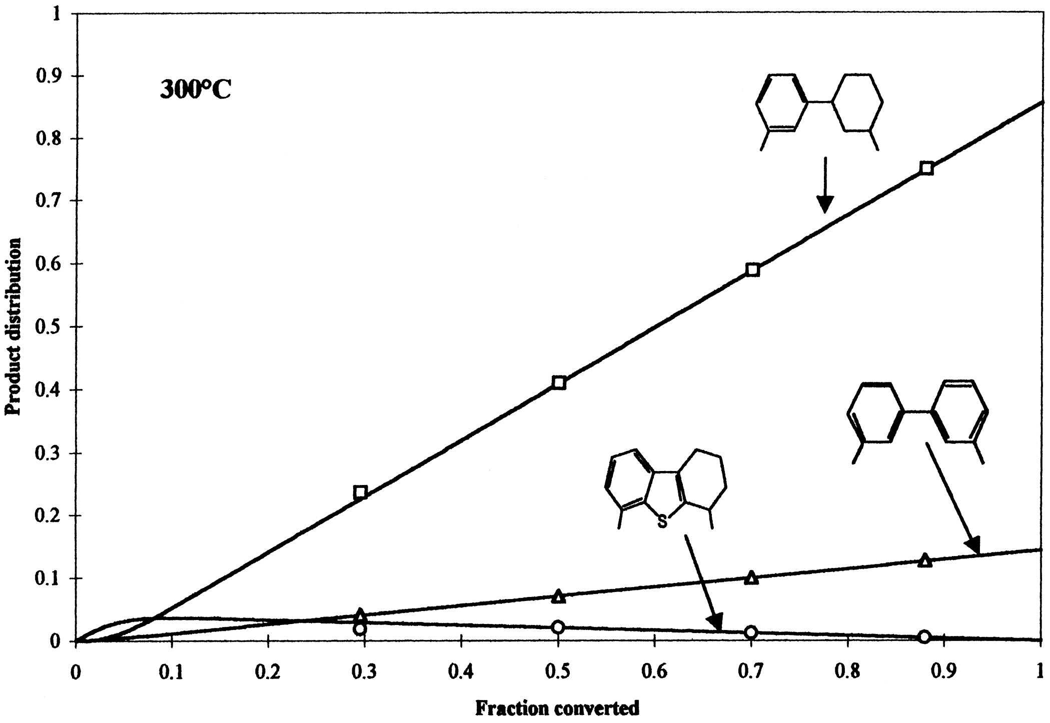

Fig. 5. HDS selectivity of 4,6-DMDBT over MC-II-A catalyst at 300°C under 2.9 MPa H_2.

6 illustrate the dependence of the product distribution on the conversion level at low and high temperatures and computer simulated curves that fit the experimental points. From inspection of these graphs it is evident that the product selectivity strongly depends on the temperature. The preferred mechanistic pathway for 4,6-DMDBT HDS changed dramatically with temperature. At low temperature (300°C), ring hydrogenation prior to desulfurization was preferred, but at high temperature (380°C) direct desulfurization became the dominant mode. Thus, the product selectivity for 3,3′-DMPC compounds over MC-II-A catalyst decreased from 81.9% at 300°C to 8% at 380°C. The explanation for this dramatic change in selectivity is believed to be the result of thermodynamic limitations on the concentration of the tetrahydro intermediate.

Fig. 7 shows the Arrhenius plots of direct desulfurization and hydrogenation reactions of 4,6-DMDBT over Co–Mo/C and Co–Mo/Al_2O_3 catalysts. A significant change in the selectivity has been found at 380°C suggesting that the hydrogenation route becomes unimportant. However, the maximum that can be observed for hydrogenation route in Fig. 7

Table 4
Deep hydrodesulfurization of diesel fuel feedstocks over Co–Mo/C and Co–Mo/Al_2O_3 catalysts

Catalyst	Reaction Time (min)	Conversion DBT (%)	Conversion 4-MDBT (%)	Conversion 4,6-DMDBT (%)	Sulfur remaining (%)
MC-I-A	10	100	65.4	48.3	0.094
	30	100	68.7	50.2	0.080
Co–Mo/Al_2O_3	10	100	41.8	29.7	0.197

Reaction conditions: 340°C and 2.9 Mpa H_2. Sulfur content in diesel fuel: 0.25 wt%.

(reverse temperature dependence) can be very probably attributed to either two factors: first the stronger thermodynamic limitation of the hydrogenation of 4,6-DMDBT to 4,6-dimethyltetrahydrodibenzothiophene [11]; second a depletion of the surface coverage of the reactant species with increasing temperature. So far the second explanation would be questionable as the reactant still shows much higher activity for the direct desulfurization route. Therefore, the most reasonable one is the thermodynamic limitations of such reactions. The apparent activation energy of direct desulfurization and hydrogenation (for the Arrhenius dependent part) reactions of 4,6-DMDBT over Co–Mo/Al_2O_3 catalyst were 50.76 and 13.36 kcal mol^{-1}, respectively, while 42.09 and 15.37 kcal mol^{-1} over Co-Mo/C catalyst, respectively.

3.5. Deep HDS of commercial diesel fuel

Table 4 shows a comparison of the performance of the novel carbon supported catalyst with the commercial catalyst in the deep desulfurization of commercial diesel fuel. As can be seen, the carbon supported catalyst was again more active than the commercial catalyst with this commercial feedstock. The specification of 0.05% S was not met under these conditions; however, the reaction times were very short in order to facilitate the rate comparisons. It should be noted that the experimental conditions used represent the equivalent of about 40LHSV (cat/oil=20 and 30 min contact time). It should also be noted that the carbon supported catalyst used in these preliminary experiments (MC-I-A) was not the most active catalyst in the present series. Thus, there is the potential that these new carbons supported catalysts can achieve the 0.05% S specification at low pressure (2.5 MPa) under the typical commercial conditions of 2LHSV. Work in this area is continuing.

4. Conclusions

Carbon supported catalysts were found to be more active than analogous alumina supported

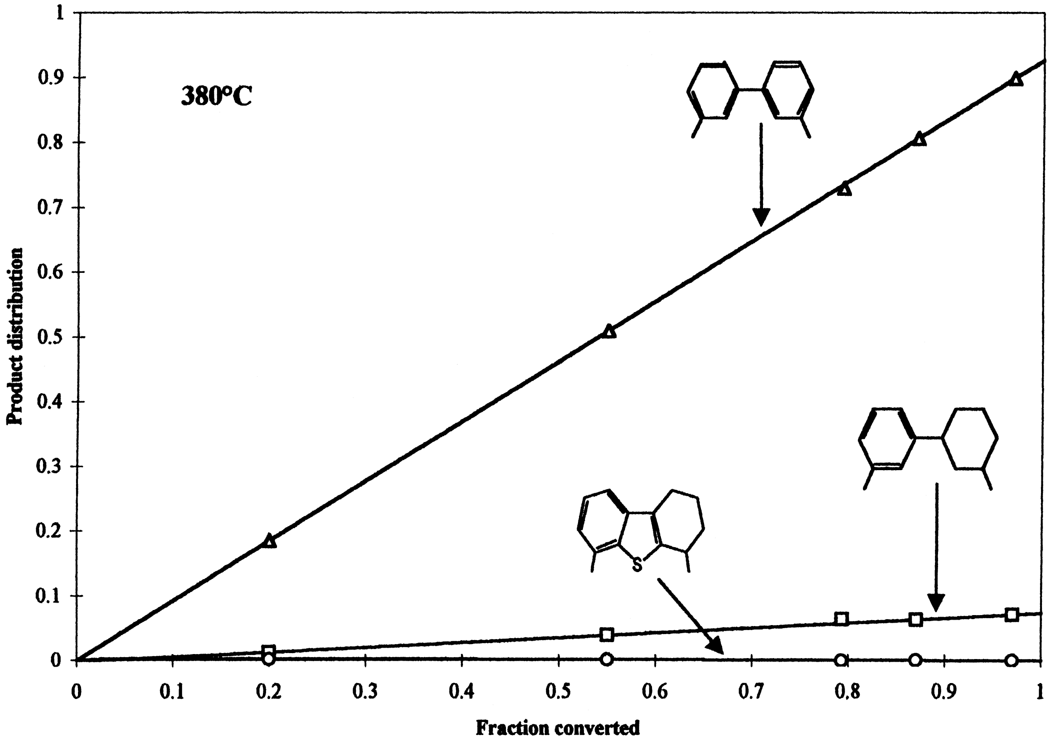

Fig. 6. HDS selectivity of 4,6-DMDBT over MC-II-A catalyst at 380°C under 2.9 MPa H_2.

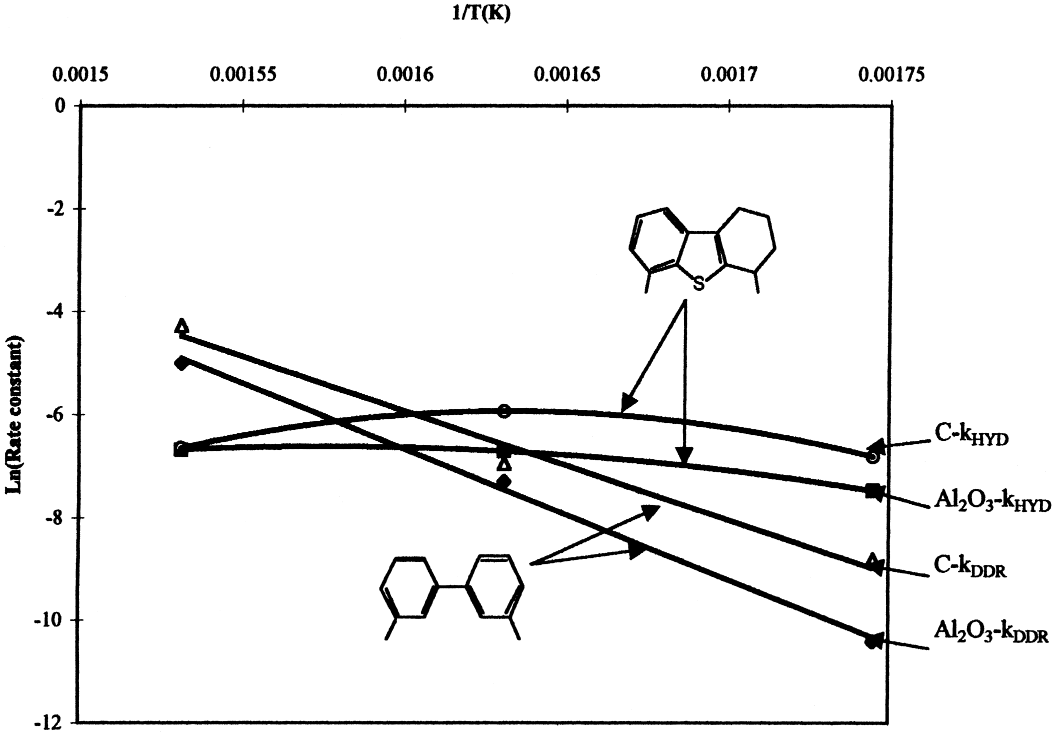

Fig. 7. Arrhenius plot of individual steps in HDS of 4,6-DMDBT (Co–Mo/Al_2O_3 and Co–Mo/C, 2.9 MPa H_2).

catalysts for both model compounds and commercial diesel fuel. The most active preparation was over three times more active for DBT HDS than a comparable commercial HDS catalyst. For all catalysts studied, the selectivities were close at the same temperature, however it was observed that there was a dramatic change in the preferred mechanistic pathway for desulfurization of 4,6-DMDBT. At low temperature, the hydrogenative route is preferred but at high temperature, direct desulfurization predominates.

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