Catalysis Letters 13 (1992) 131–136

Effect of temperature on activity and selectivity of carbon supported Mo sulfide in simultaneous hydrodenitrogenation of pyridine and hydrodesulfurization of thiophene

Z. Vít

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6, Czechoslovakia

Received 9 September 1991; accepted 18 December 1991

Activity and selectivity of carbon supported Mo catalyst was tested in parallel hydrodenitrogenation (HDN) of pyridine and hydrodesulfurization (HDS) of thiophene in the temperature range 260–350°C at 2 MPa of hydrogen pressure and compared with that of commercial NiMo-alumina catalyst Shell 324. The main advantages of carbon supported Mo sulfide over commercial NiMo catalyst can be summarized as follows: the markedly higher HDN and better HDS activities normalized to moles of active metals, the lower content of piperidine in the reaction products and the distinctly better selectivity towards HDN reaction.

Keywords: Hydrodenitrogenation; sulfide Mo catalyst; carbon supported sulfides

1. Introduction

Promising results have recently been obtained in improvement of hydrorefining catalysts for HDS and HDN with substitution of alumina support by more inert material, e.g. active carbon [1–3]. Carbon support is less expensive, possesses higher surface area and, due to lower polarity, is less sensitive to coke formation.

This work is a continuation of our project dealing with carbon supported catalysts [4–7]. In the previous study [7] we have found that in parallel HDN of pyridine and HDS of thiophene, the carbon supported Mo, CoMo and NiMo catalysts were more active than catalysts on alumina support. At the same time, the selectivities of alumina and carbon supported Mo catalysts toward HDN were considerably higher than those of CoMo and NiMo catalysts. As a result, the carbon supported Mo catalyst seems to be the most convenient for HDN.

Literature data comparing HDN activity of carbon supported catalysts with conventional alumina supported CoMo or NiMo systems are scarce [2,3,5–7,9] and moreover, they have been compared only at one reaction temperature. We assumed that in our test procedure consisting of parallel HDN and HDS reactions, the extent of competitive adsorption of pyridine and thiophene on alumina and carbon supports shall depend differently on reaction temperature and that large effects of it on the rates of individual reactions and consequently on the HDN/HDS selectivity could be expected. For this purpose, the catalytic properties of carbon supported molybdenum sulfide were compared with classical NiMo-alumina catalyst at different temperatures in the range of 260–350°C.

2. Experimental

The Mo/C catalyst (0.8 mmol of Mo per gram) was prepared by impregnation of active carbon GA-1 (1070 m^2/g) by ammonium heptamolybdate as was described previously [7]. The NiMo-alumina catalyst was Shell 324. It contained 0.46 mmol of Ni, 1.23 mmol of Mo and 0.45 mmol of P per gram. The activity of catalysts in parallel HDN/HDS reaction was tested at temperatures 260–350°C and 2 MPa of hydrogen pressure with the feed containing 220 ppm of pyridine and 240 ppm of thiophene in hydrogen. Sulfidation of catalysts, test procedure and apparatus were described in details earlier [5].

The products of thiophene HDS were C_4 hydrocarbons and H_2S. The activity of the catalysts was described by pseudo-first order rate constants $k(\mathrm{TH})$. The products of pyridine HDN were piperidine, C_5 hydrocarbons and NH_3. First-order rate constants for pyridine hydrogenation $k(\mathrm{PY})$ and for consecutive piperidine hydrogenolysis $k(C_5)$ were used for characterization of the catalysts.

As in our earlier studies [5,7], the following definitions of activity and selectivity have been used. The overall HDN activity, $A(\mathrm{HDN})$, was defined as the space velocity needed for 50% conversion of pyridine to C_5 hydrocarbons. The selectivity of individual HDN reaction, $S(\mathrm{SA})$, expressing the extent of piperidine formation, was calculated as $\int_0^1 x_{\mathrm{PI}} \mathrm{d} x_{\mathrm{PY}}$, where x_{PI} and x_{PY} are the fractional conversions of pyridine to piperidine and overall conversion of pyridine, respectively. The selectivity between competitive HDN and HDS reactions, $S(\mathrm{HDN/HDS})$, was defined as the conversion of pyridine to C_5 hydrocarbons at 50% conversion of thiophene.

3. Results and discussion

The rate constants for both reactions together with HDN activities were evaluated from kinetic data and are summarized in table 1. Unfortunately, due to very poor activity they could not be determined for the NiMo-alumina

Table 1
Effect of temperature on the rate constants k(TH), k(PY), $k(C_5)$ and HDN activity A(HDN); all values are in (mol/h mol_{Me}).

T (°C)	Mo/C				$NiMo/Al_2O_3$			
	k(TH)	k(PY)	$k(C_5)$	A(HDN)	k(TY)	k(PY)	$k(C_5)$	A(HDN)
260	0.3	0.7	0.2	0.2	–	–	–	–
280	0.4	1.0	0.8	0.5	0.2	0.2	0.2	0.1
320	1.9	1.3	7.8	1.5	2.0	0.8	2.0	0.8
350	6.4	2.1	26.8	2.7	6.2	2.2	7.1	2.1

catalyst at 260°C. Nevertheless, it is seen from table 1 that at lower temperature the rate constants k(TH) and k(PY) for the Mo/C catalyst were significantly higher than those for the conventional NiMo system and by increasing the reaction temperature, the differences between the catalysts practically disappeared.

On the other hand, the rate constants for piperidine hydrogenolysis $k(C_5)$ increased almost parallel for both catalysts with increasing reaction temperature; the ratio between them was near to 4 in favour of carbon supported Mo catalyst. These findings suggest that the consecutive reaction steps in HDN proceed on different types of sites and moreover, that the sites responsible for pyridine hydrogenation are very probably the same as for thiophene HDS. This idea was stated for the NiMo-alumina catalyst by Satterfield et al. already in 1975 [8] but the present results suggest that the acceptance of it can be very probably extended to carbon supported catalysts too.

The values of A(HDN) confirm considerably less activity of the conventional NiMo catalyst in overall HDN reaction in the whole temperature range studied. The differences in HDN activity between Mo sulfide deposited on carbon of Czechoslovak production and NiMo catalyst Shell 324 are in range of that found between Mo sulfide supported on carbon Fluka and NiMo catalyst HR 346 [9] confirming generally the suitable properties of active carbons for preparation of catalysts with enhanced HDN efficiency.

Apparent activation energies of thiophene HDS and of both consecutive reaction steps in pyridine HDN were estimated from Arrhenius plots and are summarized in table 2. On both catalysts, piperidine hydrogenolysis was more temperature dependent than thiophene HDS and pyridine hydrogenation. The

Table 2
Apparent activation energies (kJ/mol) for HDS of thiophene, E(TH), hydrogenation of pyridine, E(PY), and hydrogenolysis of piperidine, $E(C_5)$, over Mo/C and NiMo/alumina catalysts.

Catalyst	E(TH)	E(PY)	$E(C_5)$
Mo/C	100	35	150
NiMo/alumina	140	95	150

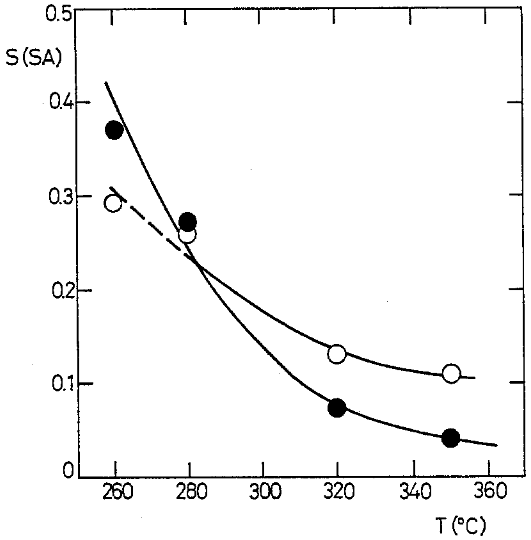

Fig. 1. Effect of temperature on the selectivity of piperidine formation, S(SA), of the Mo/C (●) and NiMo-alumina (o) catalysts. The value for the NiMo catalyst at 260°C was calculated using rate constants obtained by extrapolation of Arrhenius plot.

activation energy for pyridine hydrogenation on NiMo catalyst was close to that found by Köhler in the absence of thiophene in the feed (90 kJ/mol) [10] showing that competitive adsorption of thiophene on catalyst with alumina support does not influence significantly the reaction of more strongly adsorbed pyridine. On the other hand, much lower activation energy of pyridine hydrogenation on carbon supported Mo sulfide in comparison to the NiMo catalyst is probably caused by different temperature dependence of sorption capacities of carbon and alumina for pyridine and thiophene in the mixed feed.

The content of piperidine in the reaction mixture over NiMo alumina catalyst decreases with increasing reaction temperature in accordance with refs. [10,11] and the value of selectivity S(SA) decreases from 0.30 to 0.10 (fig. 1). The similar decrease in selectivity was observed for carbon supported Mo catalyst too, but as a result of larger variations between k(PY) and $k(C_5)$ this selectivity drops more steeply. At higher temperatures about 350°C the rate constant $k(C_5)$ is more than ten times higher than k(PY) and the Mo catalyst produces much smaller amount of piperidine than can be achieved with classical alumina supported NiMo catalysts. Similar difference in amount of piperidine and C_5 hydrocarbons was observed on NiMo catalysts HR 346 and Mo/C (Fluka) catalyst at 340°C and 6 MPa of hydrogen pressure in the presence of 5000 ppm of H_2S in the feed [9].

Generally, it is known that on conventional CoMo or NiMo catalysts the HDN reaction proceeds more difficultly than HDS [12]. In agreement with it, the selectivity of conventional catalytic systems between HDN of pyridine and

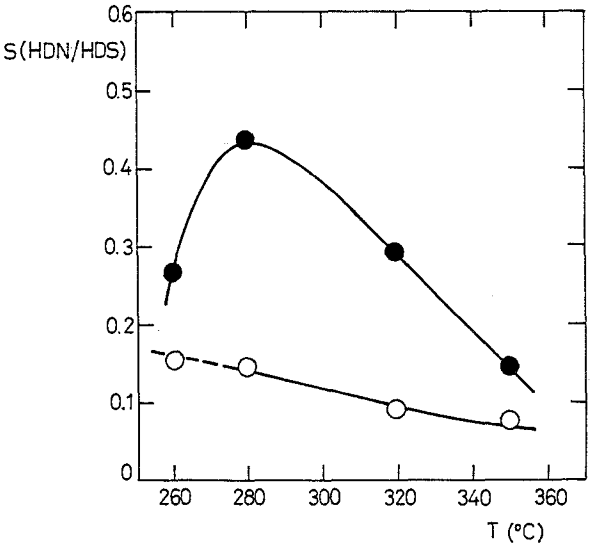

Fig. 2. Effect of temperature on HDN/HDS selectivity of the Mo/C (•) and NiMo-alumina (o) catalysts. The value for NiMo catalyst at 260°C was calculated using rate constants obtained by extrapolation of Arrhenius plot.

HDS of thiophene observed by us earlier was rather low [5]. In the present study, the much higher selectivity S(HDN/HDS) of carbon supported Mo catalyst over conventional NiMo system was confirmed in the whole temperature range studied (fig. 2). Moreover, the selectivity of the Mo/C sample was strongly temperature dependent possessing distinct maximum at about 280°C. At this temperature, the selectivity S(HDN/HDS), that is the conversion of pyridine to C_5 hydrocarbons, was 44% at 50% conversion of thiophene which is a great difference in comparison to classical NiMo or CoMo catalysts.

From this study together with earlier observations it follows that carbon supported Mo catalyst offers promising results regarding HDN activity and selectivity exceeding markedly those achievable with alumina supported NiMo combination even in a broad range of reaction temperatures.

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