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Hydrogenation of tetralin on a sulfided ruthenium on KY zeolite catalyst. Effect of the sulfidation method

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Abstract

Hydrogenation of tetralin was used to modelize the hydrogenation of aromatic compounds in gasoils. This reaction was carried out under a 5 MPa hydrogen pressure, at 300°C, in the presence of hydrogen sulfide. Before reaction, the Ru on KY zeolite catalyst was presulfided in situ at 400°C either by a H_2S/H_2 mixture, or by dimethyl disulfide in n-heptane. The catalyst sulfided by dimethyl disulfide was 3 times less active than that sulfided by H_2S, due to coking during sulfidation. Another type of carbonaceous deposit was formed during the tetralin reaction, the nature and the amount of this deposit was not depending on the sulfidation method.

Keywords: Tetralin hydrogenation of; KY zeolite; Ru catalysts

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1. Introduction

The hydrogenation of aromatic compounds in gasoils is necessary both to improve the cetane number and for environmental reasons. The feeds to be treated are generally mixtures of straight run gasoils and light cycle oils, containing ca. 1.5 wt.-% sulfur and 200 ppm nitrogen. This imposes the use of sulfide catalysts, such as the sulfided NiMo on alumina catalysts widely used in hydrotreating. However, these catalysts are not very active for the hydrogenation of aromatics, in particular in the presence of nitrogen. Consequently, new types of catalysts must be considered, e.g., the ruthenium sulfide on zeolite which we use in this work.

It is well known that the sulfidation process strongly influences the activity and the selectivity of classical sulfide catalysts for hydrogenation [1,2], hydrodesulfurization [1-3] or hydrodenitrogenation [3]. The aim of the present work was to check whether the hydrogenating activity of the ruthenium on zeolite catalyst depended on the sulfidation method.

2. Experimental

The hydrogenation of tetralin was carried out in a flow reactor at 300°C under a total pressure of 7 MPa (tetralin pressure = 0.010 MPa, hydrogen pressure = 5.19 MPa). n-Heptane (1.57 MPa) was used as a solvent, to which dimethyl disulfide (DMDS) was added in order to generate H_2S (0.113 MPa) during the reaction. First, the catalyst was sulfided for 12 h at 400°C

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either by DMDS (5 wt.-% in n-heptane) or by H_2S (10 wt.-% in H_2). In the first case, the total pressure was 3.5 MPa, with $p_{H_2S} = 0.24$ MPa, $p_{n\text{-}C_7} = 1.48$ MPa and $p_{H_2} = 1.54$ MPa. In the second, the sulfidation was carried out at atmospheric pressure, with a 5 ml min^{-1} H_2S/H_2 flow rate.

o-Xylene transformation was used to estimate the hydrogenating activity and the acid activity of the catalyst. This reaction occurred under the same conditions as above, except that tetralin was replaced by *o*-xylene. The reaction was carried out on freshly sulfided catalysts, or after tetralin hydrogenation.

The products of tetralin hydrogenation were analyzed every 30 minutes by gas–liquid chromatography (Varian 3400) on a 25 m CPSil5 capillary column (Chrompack), with a 75 to 120°C temperature programme (4°C min^{-1}). In the case of *o*-xylene transformation, a 50 m column was used, with a 40 to 70°C temperature programme (5°C min^{-1}).

After the tetralin hydrogenation experiment (6 h), half of the spent catalyst was sent to the 'Service Central d'Analyse CNRS' to have the carbon content measured. The coke was extracted from the other half according to the method developed in our laboratory [4]: dissolution of the catalyst in hydrofluoric acid, extraction of the soluble components by CH_2Cl_2 and analysis by GC–MS. The same analyses were carried out on freshly sulfided catalysts, which had not been used for tetralin conversion.

The RuKY catalyst was prepared [5] at the 'Institut de Recherches sur la Catalyse' in Villeurbanne, from a commercial dealuminated HY zeolite (Conteka CBV 712, Si/Al = 6). It was exchanged first with KNO_3, then with $Ru(NH_3)_6Cl_3$ and finally dried at 120°C. It contained 0.4 wt.-% K and 1.8 wt.-% Ru.

3. Results

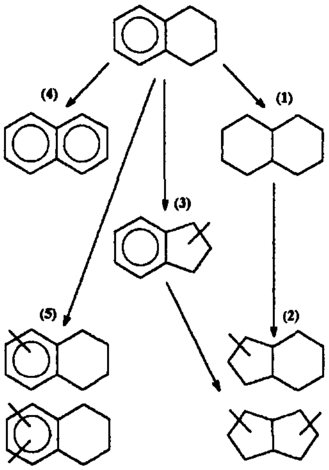

Fig. 1. Reaction scheme for the transformation of tetralin on the RuKY catalyst.

Fig. 1 gives the complete reaction scheme for the transformation of tetralin. Whatever the sulfidation method, the main reaction products were decalins ((1) in Fig. 1) and several products (2) with the same formula $C_{10}H_{18}$, determined by GC–MS. These products result from the isomerization into methyl cyclopentanes of one or two of the cycles of decalins, or from the hydrogenation of methyl indans. Indeed, these latter (3) were observed in small amounts, together with naphthalene (4), and methyl or dimethyl tetralins (5). Decalins and naphthalene were formed on the hydro–dehydrogenating sites (ruthenium sulfide), whereas the formation of the methyl indans and of the decalin isomers was linked to the acid sites of the catalyst (zeolite), in association with the hydrogenating sites (bifunctional isomerization). Methyl and dimethyl tetralins have the methyl groups on the aromatic ring and result most likely from a reaction between tetralin and the methyl fragments produced by dimethyl disulfide decomposition [6].

Fig. 2 shows the changes in tetralin conversion with time as a function of the sulfidation method (methyl and dimethyl tetralins were not taken into account). It can be seen that the catalyst sulfided by H_2S (method S_2) has the most stable activity, whereas the activity of the catalyst sulfided using dimethyl disulfide (method S_1) increases during the first 3 h of

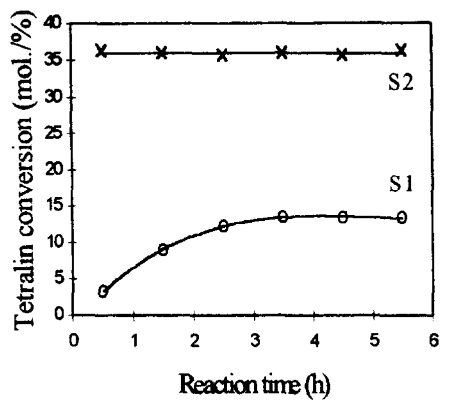

Fig. 2. Effect of the sulfidation method on the activity of the RuKY catalyst for tetralin conversion.

reaction. After stabilization, the conversion of tetralin is about 3 times greater after sulfidation S_2 than after sulfidation S_1.

Table 1 indicates that with sulfidation S_1 a very significant amount of carbon remains on the catalyst (5.4 wt.-%), which, of course, is not the case with sulfidation S_2. However, only traces of carbonaceous molecules can be extracted from the S_1 sulfided catalyst. This shows that the carbon deposited on the catalyst is not soluble in CH_2Cl_2. This type of 'insoluble coke' is often observed with zeolite catalysts, and is composed of highly condensed polyaromatics [7]. After the tetralin reaction, the carbon content of the catalyst increases by ca. 5 wt.-% whatever the sulfidation method, to reach 11.5 wt.-% for sulfidation S_1 and 5.2 wt.-% for sulfidation S_2 (Table 1). In both cases, this coke is now soluble in CH_2Cl_2 and composed of saturated cyclic compounds with 14 to 16 carbon atoms.

Table 1
Effect of the sulfidation method on the carbon content (wt.-%) and on the hydrogenating activity (H) and the acid activity (A) of the RuKY catalyst (10^{-7} mol h^{-1} g^{-1})

Sulfidation	S_1 (DMDS)		S_2 (H_2S)	
	Before test	After test	Before test	After test
Carbon	5.4	11.5	< 0.1	5.2
H	1.4	2.8	9.4	4.2
A	4.0	4.2	8.0	4.6

Table 1 also gives the results obtained in the o-xylene reaction. It has been previously demonstrated [8] that the rate of formation of the m- and p-isomers of o-xylene allowed to estimate the acid activity of a bifunctional catalyst; the hydrogenating activity could be defined as the rate of formation of all the C_8 naphtenic compounds. It can be seen that the hydrogenating activity (H) and the acid activity (A) measured before the tetralin test are much lower after sulfidation S_1 than after sulfidation S_2. On the other hand, the tetralin reaction provokes a strong decrease in both H and A activities in the case of sulfidation S_2, but an increase in the hydrogenating activity alone in the case of sulfidation S_1.

4. Discussion

The catalyst sulfided by dimethyl disulfide in n-heptane is less active for the hydrogenation of tetralin than the catalyst sulfided by H_2S. This lower activity is due to the formation of insoluble coke during sulfidation. Such an effect of the sulfidation method was not observed with alumina-supported sulfide catalysts [9], which indicates that the coke formed during the sulfidation by dimethyl disulfide in n-heptane is related to the presence of the zeolite. This coke is most likely formed inside the zeolite pores, preventing the reactant molecules from reaching the hydrogenating and acid sites. The activation period observed during the first hours of the reaction (Fig. 2), as well as the increase in the hydrogenating activity of the catalyst (Table 1), show that this coke is partially eliminated by tetralin. However, the unmodified acid activity implies that the acid sites must be irreversibly poisoned. This is in accordance with the fact that the coking of bifunctional catalysts occurs mainly on the acid sites [10]. On the other hand, during the reaction a much lighter coke is formed, the amount and the nature of this coke being independent of the sulfidation method.

The light molecules composing this coke probably condensate in the zeolite pores and again partly block the access to the active sites. This poisoning is not detected in the case of the catalyst sulfided by dimethyl disulfide in n-heptane, since the resulting deactivation is compensated to a large extent by the activation due to the elimination of part of the coke which was formed during the sulfidation. In contrast, the deactivation by tetralin is very apparent if the catalyst is sulfided with H_2S (Table 1). Moreover, the absence of any visible initial deactivation during tetralin reaction (Fig. 2) indicates that the poisoning of the catalyst is very rapid, thus occurring during the first minutes of the reaction.

5. Conclusions

Heavy molecules ('coke') are formed during the sulfidation of the RuKY catalyst by dimethyl disulfide in n-heptane, which block the access to the active sites. Some of these molecules can be eliminated by tetralin during the first hours of the reaction, but it is clear that the existence of this type of coke, which is the consequence of a particular sulfidation method, is responsible for the difference in activity of the catalyst for tetralin hydrogenation according to the sulfidation method. On the other hand, whatever the sulfidation method, other molecules are formed during the tetralin hydrogenation reaction, which block in turn part of the active sites.

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References

[1] R. Prada Silvy, P. Grange, F. Delannay and B. Delmon, Appl. Catal., 46 (1989) 113.
[2] J. van Gestel, J. Leglise and J.C. Duchet, J. Catal., 145 (1994) 429.
[3] C. Gueguen, P. Guesnet, H. Jacquez and G. Savin, F. Patent 8700585, 1987.
[4] P. Magnoux, P. Roger, C. Canaff, V. Fouché, N.S. Gnep and M. Guisnet, Stud. Surf. Sci. Catal., 34 (1987) 317.
[5] S. Göbölös, M. Breysse, M. Cattenot, T. Decamp, M. Lacroix, J.L. Portefaix and M. Vrinat, in M.L. Ocelli and R.G. Anthony (Editors), Advances in Hydrotreating Catalysts, Elsevier, Amsterdam, 1989, pp. 243.
[6] J. Léglise, A. Janin, J.C. Lavalley and D. Cornet, J. Catal., 114 (1988) 388.
[7] P. Gallezot, C. Leclercq, M. Guisnet and P. Magnoux, J. Catal., 114 (1988) 100.
[8] M. Guisnet, C. Thomazeau, J.L. Lemberton and S. Mignard, J. Catal., 151 (1995) 102.
[9] M. Mhaouer, J.L. Lemberton and G. Pérot, unpublished results.
[10] G. Pérot, P. Hilaireau and M. Guisnet, Proc. 6th Int. Zeolite Conf., (1984) 427.