

Hydrodesulfurization activity of zeolite-supported nickel and cobalt sulfide catalysts

Citation for published version (APA):

Welters, W. J. J., Koranyi, T. I., de Beer, V. H. J., & van Santen, R. A. (1993). Hydrodesulfurization activity of zeolite-supported nickel and cobalt sulfide catalysts. In L. Gucci, F. Solymosi, & P. Tétényi (Eds.), *New Frontiers in Catalysis : Proceedings of the 10th International Congress on Catalysis, Budapest, July 19 - 24, 1992. Part C* (pp. 1931-1934). (Studies in Surface Science and Catalysis; Vol. 75, No. Part C). Elsevier.
[https://doi.org/10.1016/S0167-2991\(08\)64193-2](https://doi.org/10.1016/S0167-2991(08)64193-2)

DOI:

[10.1016/S0167-2991\(08\)64193-2](https://doi.org/10.1016/S0167-2991(08)64193-2)

Document status and date:

Published: 01/01/1993

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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HYDRODESULFURIZATION ACTIVITY OF ZEOLITE SUPPORTED NICKEL- AND COBALT SULFIDE CATALYSTS

W. J. J. Welters, T. I. Korányi,¹ V. H. J. de Beer and R. A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O.Box 513, 5600 MB Eindhoven, The Netherlands

Abstract

Various zeolite (NaY or CaY) supported metal sulfide (Ni or Co) catalysts were prepared (impregnation or ion exchange) and characterized by means of thiophene HDS, ¹²⁹Xe NMR and TPS. Especially the acidic zeolites showed a very high initial activity. The observed activity differences are discussed in terms of sulfidation, dispersion, position of the metalsulfide relative to the zeolite pore system and acidity, the latter two being the most important. It is concluded that small Ni and Co sulfide clusters are very efficient thiophene desulfurization catalysts.

1. INTRODUCTION

Zeolites activated by transition metal sulfides are currently widely applied in hydrocracking. The aim of our study is to provide more insight in the significance of parameters such as the position of the metal sulfide relative to the pore system (in- or outside) and the metal sulfide - zeolite interaction strength on the initial properties of these catalysts.

Here we report thiophene hydrodesulfurization activities determined as a catalytic characterization of the metal sulfide function in the zeolite.

2. EXPERIMENTAL

NaY (Ketjen LZY-52), NaY derived CaY, γ -Al₂O₃ (Ketjen 001-1.5E) and carbon (Norit RX3-extra) supported oxidic Ni or Co catalysts were prepared via pore volume impregnation (with Ni (Co) chloride solutions), drying (393 K, 16 h, in air) and (except for the carbon supported catalysts) calcination (648 K, 24 h, in air). Ni or Co containing catalyst precursors were also prepared via ionexchange of NaY with aqueous solutions of NiCl₂ or CoCl₂, washing to remove Cl⁻ and drying (393 K, 16 h, in air). The initial activity and deactivation were measured using thiophene hydrodesulfurization (microflow reactor, 673 K, 1 bar, 2 h runtime).

¹On leave from Institute of Isotopes of the Hungarian Academy of Sciences, Budapest, Hungary.

Prior to the activity test the catalysts were sulfided (1 bar, 10 % H₂S in H₂, in 1 h from 293 K to 673 K and 2 h at 673 K).

The sulfidation of an ion exchanged NiNaY and impregnated NiNaY and NiCaY was studied by means of temperature programmed sulfidation (TPS) [1]. In addition the pore system of the sulfided ion exchanged and impregnated NiNaY was characterized by ¹²⁹Xe NMR according to a method described by Fraissard and Ito [2].

3. RESULTS AND DISCUSSION

The supports showed only very low thiophene HDS activity. However, when combined with Co or Ni sulfide, catalysts with a very high initial activity could be prepared. As shown in Table 1 both metal sulfides had similar activities, considerably higher than those of their Al₂O₃ supported counterparts and comparable to that of carbon supported catalysts. As in the case of carbon supported catalysts the presence of Mo or W is not required to obtain high activities. This finding supports models for HDS that propose a high intrinsic activity also for the so called 'promoter ions', viz. Co²⁺ and Ni²⁺ [3]. Whereas for Co this was illustrated on carbon [4] the zeolite catalysts also show the same for Ni. A striking difference between the zeolite and the carbon supported catalysts is the low stability of the former. It is found that the presence of acidic zeolite sites causes high initial activity as well as strong deactivation (NaY (ion ex.) and CaY (impreg.)) due to coke formation. In the absence of these sites the catalysts are more stable, however their initial activity is considerably lower.

Table 1
Quasi Turn Over Frequency (mol thiophene converted per mol metal per second) for Al₂O₃, carbon and zeolite supported metal sulfide catalysts. The metal loading is 4 wt% metal for each catalysts.

runtime (min.)	Ni		Co	
	5	120	5	120
NaY (impreg.)	3.0	2.2	3.0	2.4
CaY (impreg.)	5.5	2.5	4.4	2.0
NaY (ion ex.)	9.1	3.3	6.6	3.0
C	3.1	2.2	4.0	3.3
Al ₂ O ₃	0.9	0.8	1.4	1.4

The difference in initial activity may be due to differences in the metal sulfide dispersion. The ion exchanged catalysts showed linear activity increase with increasing metal loading (Fig. 1). The fact that this does not apply to the impregnated NaY catalysts indicates a decrease in dispersion with increasing Ni loading.

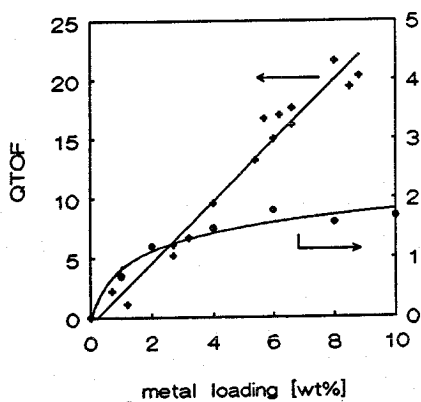


Figure 1. Quasi Turn Over Frequency (mol thiophene per mol metal per second) as function of the metal loading for ion exchanged(+) and impregnated (o) zeolites.

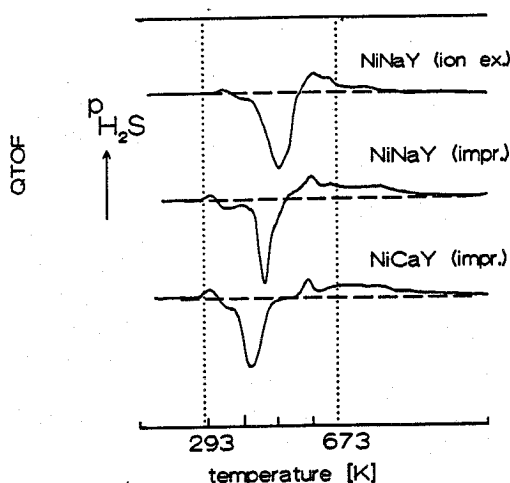


Figure 2. TPS patterns of zeolite supported Ni catalyst (metal loading is 4 wt%).

In order to verify this we examined the dispersion and the location of the nickel sulfide phase relative to the pore system by means of EXAFS, TPS and ^{129}Xe NMR measurements.

From preliminary EXAFS data obtained for 4 wt% Ni containing impregnated NiNaY and NiCaY as well as ion exchanged NiNaY catalysts we can conclude that the nickel is fully sulfided, with by far the main sulfide species being Ni_3S_2 . In all three catalysts the nickel sulfide dispersion appears to be comparable.

The TPS results of the same catalysts showed that although for the impregnated samples the H_2S uptake at room temperature was relatively high, the total H_2S consumption at 673 K was the same for all three catalysts (Fig. 2). In accordance with the EXAFS results the S/Ni ratio was almost equal to that for Ni_3S_2 which is the most stable compound under HDS reaction conditions in the presence of an inert support [5]. In the case of the ion exchanged sample the maximum H_2S uptake occurs at a somewhat higher temperature indicating a more difficult sulfidation.

Various nickel containing ion exchanged NiNaY zeolites and a 4 wt% impregnated NiNaY sample were examined by Xe NMR in their sulfided state. The results show a linearly increasing NMR shift with increasing density of adsorbed Xe which is to be expected if the Ni is fully sulfided. The diameters of the supercage spheres were calculated by the formula given by Derouane and Nagy [6] from the NMR shifts extrapolated to zero Xe pressure. These diameters decrease with increasing Ni loading as shown in Figure 3. This strongly suggests that nickel sulfide is at least partially present in the supercages and that its amount increases with increasing metal loading. The impregnated sample exhibited two kinds of supercage diameters, both of which were

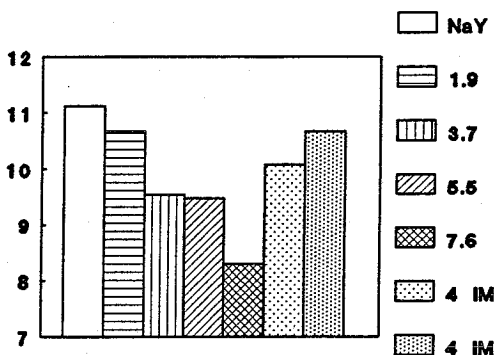


Figure 3: Calculated supercage sphere diameters (Å) of NaY and sulfided ion exchanged (x wt% Ni) and impregnated (IM) NiNaY zeolites.

larger than the comparable (3.7 wt%) ion exchanged zeolite. So, in this case less nickel sulfide is present inside the zeolite pore system compared to the ion exchanged sample, and the catalyst is less homogeneous.

From the above findings one can conclude that the difference in thiophene HDS activity is not primarily caused by variations in degree of sulfidation or nickel sulfide dispersion. It is more likely that this phenomenon is caused by differences in the position of the nickel sulfide relative to the pore system in combination with differences in acidity. The latter might influence the thiophene HDS directly or indirectly by enhancing the adsorption of thiophene in the zeolite.

Acknowledgement: These investigations are supported by the Netherlands' Foundation for Chemical Research (SON) with financial aid from the Netherlands' Technology Foundation (STW).

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