

## Decomposition of Dimethyldisulfide on Various W-Ni catalysts

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### Introduction

Presulfiding is one of the prominent steps to give the intrinsic activity of catalysts full play. Previous studies on DMDS decomposition are mainly focused on the comparison with other sulfiding agents, and the studies were conducted only with  $\text{Al}_2\text{O}_3$  supported catalysts. In refineries, another kind of important hydroprocessing catalyst, hydrocracking catalyst, adopts zeolites as cracking components. DMDS decomposition on such zeolite containing catalysts is also of great importance. The main purpose of this study is to investigate the decomposition of DMDS, for the first time, on zeolite Y and beta containing catalysts. An attempt is made to correlate the compositions of decomposed DMDS with the sulfiding of hydrogenation metals.

### Materials and Methods

The supports were prepared by mixing the modified zeolites Y or beta and alumina, extruded and calcined. The NiW catalysts were prepared by co-impregnation methods. The catalysts were characterized by  $\text{NH}_3$ -TPD, TEM. The catalyst sulfidation was carried out in a 1L autoclave.

### Results and Discussion

With or without the presence of the catalysts, methanethiol (MT) was always firstly formed via hydrogenolysis of the S-S bond of DMDS, indicating that DMDS is decomposed readily and completely to MT. Subsequently, the MT is transformed to methane and  $\text{H}_2\text{S}$ , and DMS and  $\text{H}_2\text{S}$ . The DMS may be further partly or completely converted.

On  $\text{WNi}/\text{Al}_2\text{O}_3$ , methane,  $\text{H}_2\text{S}$ , and DMS were formed at the same slow rate in the early stage of the decomposition of DMDS as that in absence of catalyst. However, after a short period of time, the concentrations of MT drastically decreased, accompanying a fast increase of methane,  $\text{H}_2\text{S}$ , and DMS concentrations. MT and DMS could only be partly transformed.

The decomposition of DMDS on the three zeolite containing catalysts proceeded in a very different way from that on  $\text{WNi}/\text{Al}_2\text{O}_3$ , and the decomposition patterns and composition changing trend were quite similar for all zeolite containing catalysts (Figure 1). Compared with  $\text{WNi}/\text{Al}_2\text{O}_3$ , the distinguished differences of DMDS decomposition on the three zeolite containing catalysts were: (1) MT was detected in the reaction system at a lower temperature (about  $260^\circ\text{C}$ ) on the zeolite containing catalysts than on  $\text{WNi}/\text{Al}_2\text{O}_3$  (about  $315^\circ\text{C}$ ); (2) MT was rapidly converted to methane,  $\text{H}_2\text{S}$ , and DMS, and then DMS was quickly and completely transformed on the zeolite containing catalysts, while MT and DMS were partially converted on  $\text{WNi}/\text{Al}_2\text{O}_3$ ; (3) a consider amount of C4-C5 alkanes were formed on the zeolite containing catalysts, while only a trace amount of the alkanes were produced at high temperatures and after a longer contact time on  $\text{WNi}/\text{Al}_2\text{O}_3$ .

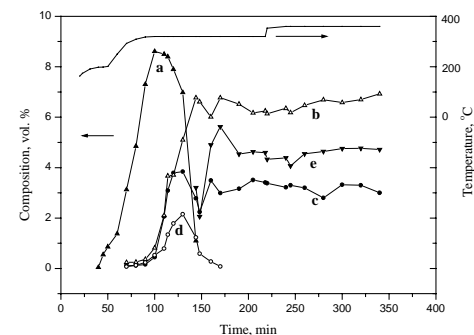


Figure 1 Decomposition of DMDS on WNi/Beta  
a: MT ( $\text{CH}_3\text{SH}$ ); b:  $\text{H}_2\text{S}$ ; c: methane; d: DMS ( $\text{CH}_3\text{SCH}_3$ ); e C4-C5 alkanes

On the zeolite containing catalysts, when MT and DMS were spent in the sulfidation of hydrogenation metals W and Ni, a considerable amount of C4-C5 alkanes were produced during the sulfidation process. DMS and/or MT molecules undergo S-H or S-C bond dissociation to form methyl thiolate, which has been demonstrated on most transition metal surfaces [1-3]. A correlation between the C4-C5 alkane concentrations and the reaction pressure changes with the reaction time indicates that the formation of C4-C5 alkane formation accompanied with hydrogen consumption. More C4-C5 alkanes were formed, more hydrogen was consumed.

### Conclusion

With the presence of  $\text{WNi}/\text{Al}_2\text{O}_3$ , methanethiol (MT) and dimethylsulfide (DMS) were partly converted and consumed in sulfidation, while over the zeolite containing catalysts, MT and DMS were completely and quickly transformed into sulfided species. MT was formed at a lower temperature over the zeolite containing catalysts than over  $\text{WNi}/\text{Al}_2\text{O}_3$ . A consider amount of C4-C5 alkanes were formed over the zeolite containing catalysts. The formation of the C4-C5 alkanes accompanied with hydrogen consumption.

### Significance

This work helps to understand sulfiding agent decomposition behavior. Subsequently it will be very helpful in studying optimum sulfiding conditions and how to improve the sulfiding extent of hydroprocessing catalysts.

### References

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