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DEHYDROGENATIVE OLIGOMERIZATION REACTIVITY OF TRANSITION METAL SULFIDES DERIVED FROM THEIR TRIS OR BIS(*o*-AMINOBENZENETHIOLATO)METAL COMPLEXES

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Several tris or bis(*o*-aminobenzenethiolato)metal complexes, where metals include ruthenium, rhodium, rhenium, molybdenum, platinum, and palladium, were synthesized. They were used as precursors to active metal sulfide catalysts for dehydrogenative oligomerization of 1,2,3,4-tetrahydroquinoline (THQ). The conversion of metal complex precursors to the corresponding metal sulfides was carried out *in situ* in the THQ solution at 210–270 ° C. These metal sulfides polymerized THQ to quinoline oligomers in 71–95% yield. We also observed a periodic trend on the activity of these catalysts showing a maximum oligomer yield with ruthenium sulfide.

Amorphous and poorly crystalline binary transition metal chalcogenides of groups VIB, VIIB and VIII are very interesting class of materials owing to their catalytic properties on the dehydrogenation reaction and the removal of sulfur (hydrodesulfurization treating) and nitrogen (hydrodenitrogenation treating) from petroleum feedstocks prior to refining [1,2]. In the case of the dehydrogenation and reforming reaction, they are very valuable industrial catalysts for the conversion of cyclohexane to benzene [3], the dehydrocyclisation of paraffins to aromatic hydrocarbons [4], and the dehydroisomerisation of alkylcyclopentane to cyclohexane [5]. It is interesting to note that these metal sulfides actually behave as either dehydrogenation catalysts in the absence of hydrogen or hydrogenation catalysts in a reverse manner in the presence of a high hydrogen pressure.

The recent discovery of catalytic dehydrogenative polymerization [6,7] (CDHP) of 1,2,3,4-tetrahydroquinoline (THQ) to quinoline oligomers (**1**) using rhenium sulfide as a catalyst, as shown in scheme 1, extended the understanding of the catalytic capability of this type of sulfides beyond the use of them in the production of small hydrocarbons [3–5]. The results from the concurrence of dehydrogenation and oligomerization of THQ molecules on the surface of rhenium sulfides could provide basic informations on the mechanism of molecular chemisorption and physisorption and reactivity of organics on the surface. This CDHP reaction was also found to undergo better results in terms of reproducibility using conveniently prepared soluble catalyst precursors of tris(*o*-aminobenzenethiolato)rhenium complexes, $Re(C_6H_4NHS)_3$ and $Re(C_6H_4NHS)_2(C_6H_4NS)$, to generate the finely divided active rhenium sulfide catalysts *in situ* in the reaction medium [8,9]. The improved method eliminates the confusion and difficulties to reproduce transition metal sulfides with the same morphology, chemical composition and surface area, which apparently significantly affect their CDHP activity. From the light of these developments, we further investigated the dehydrogenative polymerization behavior of THQ molecules with other transition metal sulfides using tris(*o*-aminobenzenethiolate) complexes of groups VIB, VIIB and VIII transition metals as catalyst precursors.

It is known that transition metal sulfides exhibited an interesting periodic trend on their catalytic activity toward the hydrodesulfurization (HDS) of dibenzothiophene [10]. This trend yielded typical "volcano" plots [11] across the periodic table with a maximum HDS activity on Ru metal sulfide. It was interpreted as an electronic effect related to the position the metal occupies in the periodic table. Several electronic factors including the orbital occupation of the HOMO, the degree of covalency of the metal-sulfur bond, and the metal-sulfur covalent bond strength have been identified to be related to catalytic activity [12]. In this paper we describe for the first instance a similar observation of a periodic trend on the CDHP activities of transition metal sulfides, showing a maximum oligomer yield with a ruthenium sulfide catalyst. This result substantiated the high efficiency of ruthenium sulfides on the catalytic hydrogenation-dehydrogenation reversibility.

Several transition metal complexes used in this study as catalyst precursors were prepared as follows. The *o*-aminobenzenethiolate complexes of Ru, Rh, and Pt were synthesized by a reaction of the *o*-aminobenzenethiol (3 equivalent) with $(NH_4)_2RuCl_6$, $RhCl_3 \cdot 2H_2O$, and $H_2PtCl_6 \cdot 6H_2O$, respectively, in an aqueous NaOH (60 equivalent) solution (0.5N). The *o*-aminobenzenethiolate complex of Pd was prepared by a reaction of the *o*-aminobenzenethiol (2 equivalent) with K_2PdCl_4 in a minimum amount of water, followed by the treatment of the resulting precipitates with an aqueous NaOH solution (3N) and peroxide (30%). The tris(*o*-aminobenzenethiolato)molybdenum complex $Mo(abt)_3$ (**3**) and tris(*o*-aminobenzenethiolato)rhenium complex $Re(abt)_3$ (**4**) were synthesized according to the literature procedure [13]. Elemental analysis of these new *o*-aminobenzenethiol complexes of Ru, Rh, Pt, and Pd fits best with the chemical composition of $Ru(abt)_3$ (**5**), $Rh(abt)_3$ (**6**), $Pt(abt)_2$ (**7**), and $Pd(abt)_2$ (**8**), respectively. The thermal conversion of complex precursors **3** to **8** to the active CDHP catalyst was carried out *in situ* in the 1,2,3,4-tetrahydroquinoline solution at 210 °C for 2 hrs and at 270 °C for 30 min. Under this reaction condition, the final metal and sulfur stoichiometric composition of the resulting metal sulfides was found to approach MoS_2, ReS_2, RuS, RhS_2, PtS, and PdS, respectively. Further reaction of the same mixture at 270 °C polymerized THQ molecules to quinoline oligomers. The product was separated into fractions differing in solubil-

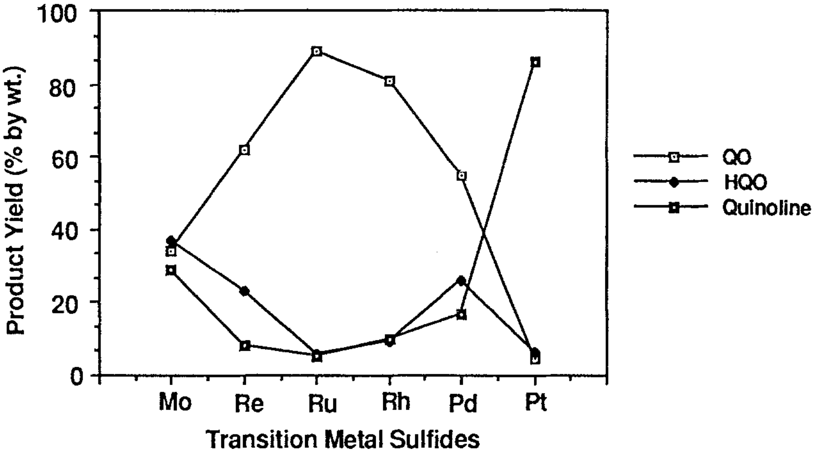
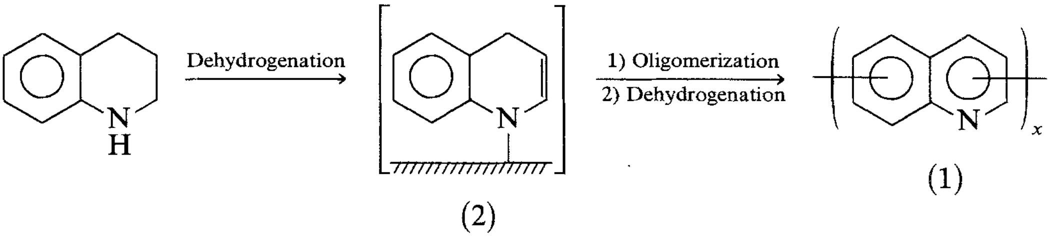


Fig. 1.



(2)

(1)

Scheme 1.

ity in solvents as quinoline oligomers (QO), partially hydrogenated quinoline oligomers (HQO), and quinoline. The results were summarized in fig. 1 and table 1, where the yield (% by wt.) of the chloroform insoluble fraction of quinoline oligomers was indicated in the parenthesis. From fig. 1 we observed a systematic increase in the CDHP activity of these *o*-aminobenzenethiolate metal complex derived catalysts from molybdenum sulfide to rethenium sulfide at a maximum and then decrease to a minimum with platinum sulfide. The change represents a similar periodic trend as that observed for the hydrodesulfurization (HDS)

Table 1

Catalyst precursor	QO (%)	HQO (%)	Quinoline (%)
$Mo(abt)_3$	34 (18) *	37	29
$Re(abt)_3$	62 (5)	23	8
$Ru(abt)_3$	89 (50)	6	5
$Rh(abt)_3$	81 (28)	9	10
$Pd(abt)_2$	55 (28)	26	17
$Pt(abt)_2$	4.5 (0.5)	6.5	86

* In the parenthesis indicates the yield (% by wt.) of the chloroform insoluble fraction of quinoline oligomers.

activity of metal sulfides on dibenzothiophene molecules, even though the CDHP reaction is a dehydrogenation process and the HDS reaction is a hydrogenation process.

All of the catalysts, which were prepared from their *o*-aminobenzenethiolate complex precursors, used in this study showed a high dehydrogenation reactivity that was demonstrated by a nearly quantitative conversion of 1,2,3,4-tetrahydroquinoline to either oligomeric products or quinoline. The difference in the yield of oligomer products as shown in table 1 can be correlated to the relative oligomerization reactivity of the catalyst. A high oligomerization reactivity of ruthenium sulfide results in a low yield (5%) of quinoline. In other words, the low oligomerization activity of platinum sulfide is accompanied with a high yield (86%) of quinoline. The degree of polymerization was found to decrease in the order of $Ru > Rh > Pd > Mo > Re > Pt$ with the highest yield of chloroform insolubles (the higher molecular weight oligomer) from the reaction using ruthenium sulfide as catalyst. From the difference in the yield of HQO, it indicates that the relative dehydrogenation reactivity of these metal sulfides to complete the aromatization of partially hydrogenated quinoline oligomers to quinoline oligomers follows the order of $Ru > Rh > Re \approx Pd > Mo$.

The origin of this dehydrogenative oligomerization reaction is currently under investigation. The understanding of the reaction mechanism on the rhenium sulfide surface is a complex issue. It involves several key parameters on the catalyst alone, such as crystallinity, surface area, chemical composition, and surface structure of reaction site. From the preliminary kinetic study, we believe that the initial dehydrogenation of THQ affords a reactive intermediate of 3,4-dihydroquinoline. This intermediate can be further dehydrogenated to quinoline or isomerized to 1,2-dihydroquinoline as well as 1,4-dihydroquinoline. A slow surface hydrogenation of quinoline to dihydroquinolines equilibrated with the dehydrogenation reaction depending upon the hydrogen concentration on the surface. However, we are not able to isolate and identify these three dihydroquinolines from the reaction, indicating their high reactivity at the reaction temperature. The subsequent thermal oligomerization or condensation reaction between dihydroquinolines initiated by the surface absorbed 1,4-dihydroquinoline (**2**), as shown in scheme 1, gives partially hydrogenated quinoline oligomers (HQO), which are the precursors to the product of quinoline oligomers (**1**) [14]. The dehydrogenation of HQO to the product of quinoline oligomers is apparent a slow process that requires a reaction period of more than 24 h to complete the conversion.

In conclusion, we studied the dehydrogenative polymerization activity of transition metal sulfides derived from the *in situ* reductive thermal conversion of tris or bis(*o*-aminobenzenethiolato)metal complexes $M(abt)_n$. These metal sulfides polymerized THQ to quinoline oligomers in 71–95% yield. We found that ruthenium sulfide gave the highest oligomerization and dehydrogenation/aromatization activity among group VIB, VIIB, and VIII metal sulfides. Interestingly, we observed a periodic trend on the activity of these catalysts showing a maximum oligomer yield with ruthenium sulfide.

References

[1] O. Weiser and S. Landa, eds., *Sulfide Catalysts: Their Properties and Applications* (Pergamon, Oxford, 1973).
[2] R.R. Chianelli, Int. Rev. in Phys. Chem. 2 (1982) 127.
[3] Kh.M. Minachev and M.A. Ryashentseva, Izv. AN SSSR, Otd. Khim. Nauk (1961) 103; C.H. Kline and V. Kollonitsch, Ind. Eng. Chem. 57 (1965) 53.
[4] B.L. Moldavskii and H.D. Kamusher, Doklady AN SSSR 10 (1936) 355.
[5] W. Schneider, J. Teubel and R. Mahrwald, Chem. Technik 13 (1961) 139.
[6] L.Y. Chiang and R.R. Chianelli, J. Chem. Soc., Chem. Commun. (1986) 1461.
[7] L.Y. Chiang and R.R. Chianelli, U.S. Patent 4,727,135, February 23, 1988.
[8] L.Y. Chiang, J.W. Swirczewski, R.R. Chianelli and E.I. Stiefel, Catal. Lett. 1 (1988) 177.
[9] L.Y. Chiang, J.W. Swirczewski and R.R. Chianelli, Polym. Prep., Am. Chem. Soc. Div. of Polym. Chem. 29 (1988) 210.
[10] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.
[11] J.H. Sinfelt, Progr. Solid State Chem. 10 (1975) 55.
[12] S. Harris and R.R. Chianelli, J. Catal. 86 (1984) 400.
[13] J.K. Gardner, N. Pariyadath, J.L. Corbin and E.I. Stiefel, Inorg. Chem. 17 (1978) 897.
[14] From the structural elucidation of oligomers **1** based on the study of X-ray diffractions and 2D COSY ^{1}H NMR spectra, we concluded that the major ring conjunctions between quinoline moieties occur at carbon positions of C_2 (the α carbon to the nitrogen atom) and C_6; L.Y. Chiang, R.V. Kastrup, C.S. Hsu and J.W. Swirczewski, Mat. Res. Soc. Symp. Proc. 134 (1989) 101.