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Advances in the study of hydrogen transfer to model compounds for coal liquefaction

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Abstract

The advances in the study of hydrogen transfer to model compounds for coal liquefaction are reviewed. The results from many model reactions indicate that molecular hydrogen promotes thermolysis, hydrogenation, and hydrocracking of model compounds, whereas hydrogen-donating solvents inhibit the reactions. Unlike metallic catalysts such as Fe, Pd, and Ni, their sulfides catalyze radical hydrogen transfer to model compounds. The reactivities of model compounds toward hydrocracking depend not only on their hydrogen-accepting abilities, but also on their adsorption strength on catalyst surface and the stabilities of the resulting leaving groups. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Coal liquefaction is a promising process for clean and effective utilization of coal. Although a large amount of work has been done, coal liquefaction is not yet competitive economically. To develop economically feasible processes for coal liquefaction, it is necessary to understand the mechanisms for coal liquefaction on the molecular level.

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Because coal structures are not clear, a study of the reactions of coal-related model compounds has become a powerful approach to coal liquefaction mechanisms.

This paper reviews the advances in the study of model reactions for coal liquefaction. The main concern is focused on resolving the following problems: what roles do molecular hydrogen, solvent and catalyst play in the model reactions and what relationship exists between the reactivity and molecular structure of various model compounds?

2. Roles of molecular hydrogen, solvent and catalyst in hydrogen transfer

According to conventional theory on coal liquefaction, hydrogen-donating solvents promote coal liquefaction by stabilizing thermally generated radical fragments from coal; thermolysis is the precondition for hydrogenation; catalysts promote hydrogen transfer from molecular hydrogen to solvent and then from solvent to coal, i.e., solvent acts as a shuttle for transferring hydrogen to coal.

McMillen et al. [1] proposed that hydrogen from hydrogen-donating solvents can cleave some strong C–C bonds. However, their kinetic study on diphenylmethane (DPM) decomposition [1] shows that DPM conversion in tetralin, a hydrogen donor solvent, is less than 0.1% even in 20 h reaction at 400°C. Even in the presence of a stronger hydrogen donor, such as 9,10-dihydrophenanthrene (DHP) or 9,10-dihydroanthracene (DHA), DPM conversion is negligible.

Many alternative propositions [2–5] have been put forward, suggesting that the main hydrogen transfer occurs directly from molecular hydrogen to coal rather than via the hydrogen-donating solvents, especially in the presence of active catalyst and pressurized hydrogen. Our previous investigations [6–12] show that in the absence of catalyst, hydrogen-donating solvents hardly cleave diarylmethanes, but inhibit 1,2-di(1-naphthyl)ethane and 1,3-diphenylpropane thermolyses; in the presence of FeS₂, hydrogen-donating solvents retard the hydrocracking of diarylmethanes by competitive adsorption on catalyst surface and by scavenging active hydrogen atoms generated from catalytic reactions. These investigations make a denial of conventional viewpoints on hydrogen transfer in coal liquefaction and are verified by the experimental results of Grigorieva et al. [13], Artok et al. [14] and Ikenaga et al. [15].

The inhibiting effects of the hydrogen donor solvents on model reactions are noteworthy. Hydrogen-donating solvents are considered to promote coal liquefaction, but their promotional roles in coal liquefaction may be predominantly attributed to the good solubility of coal in them rather than their roles as a “hydrogen shuttle”.

3. Catalyses of metal and their sulfides in hydrogen transfer

Iron-based catalysts are widely used for coal liquefaction process because of their easy availability. Correspondingly, the catalyses of iron-based catalysts, especially the iron–sulfur system, have been extensively investigated.

Conventional viewpoints [16–18] insist that the catalysis of the iron–sulfur system, especially of Fe_{1-x}S , for hydrocracking reaction is attributed to the resulting Fe_{1-x}S , which is the active site of the catalyst, and that H_2S itself also promotes hydrocracking. The well-known “evidence” supporting the viewpoint is that most of the recovered catalyst was detected to be Fe_{1-x}S rather than FeS_2 , although pyrite was used as the initial catalyst. However, this “evidence” ignores the possibility that the recovered catalyst may be different from the working catalyst.

In fact, our investigations [7,8,19] show that Fe_{1-x}S alone is less active. The catalysis of FeS_2 for cleaving C–C bonds is caused by H_2 produced by the reaction with H_2S . At temperatures below 400°C , H_2S itself does not promote hydrogenation and hydrocracking, while hydrocracking of diarylmethanes occurs at 300°C or even at lower temperatures in the presence of FeS_2 and H_2 . Fe selectively catalyzes the hydrogenation of aromatic rings. Adding sulfur to an Fe-catalyzed system significantly inhibits hydrogenation, but promotes hydrocracking. Similar differences in catalysis for model reactions between other metals (such as Ni and Pd) and their sulfides were also observed [12].

Recently, we examined the effects of Fe, Ni and their sulfides on the hydrogenation of 9,10-diphenylanthracene (9,10-DPA). The results show that the main products were tetrahydro- and octahydro-derivatives of 9,10-DPA in the presence of metallic Fe and Ni whereas *trans*-9,10-dihydro-9,10-diphenylanthracene was mainly produced by the reactions catalyzed by the sulfides of the metals [20]. According to the results, it is evident that unlike metallic Fe and Ni, their sulfides catalyzed radical hydrogen transfer to 9,10-DPA.

4. Relationship between reactivities of model compounds and their structures

Futamura et al. [21] examined the hydrogenolysis of some diarylmethanes. They found that the reactivities of the diarylmethanes toward hydrogenolysis are closely related to the hydrogen-accepting abilities of aromatic ring in the compounds. We [22,23] compared FeS_2 -catalyzed reactions of various α,ω -diarylalkanes at 300°C and found that the reactivities of the compounds toward hydrocracking depend not only on their hydrogen-accepting abilities, but also on their adsorption strength on catalyst surface and the stabilities of the resulting leaving groups. Autrey et al. [24] also suggested that the stability of the resulting leaving group derived from a model compound is an important factor that affects C–C bond cleavage.

5. Summary

In recent years, great progress has been made in the studies of hydrogen transfer to model compounds for coal liquefaction. The understanding of the different roles between molecular hydrogen and hydrogen-donating solvents, between metallic catalysts and their sulfides in hydrogen transfer, and of the relationship between the reactivities of model compounds and their structures is useful for the development of mild and directional coal liquefaction process.

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