



Research article

Hydrogenation of polycyclic aromatic hydrocarbons over a solid superacid



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ABSTRACT

Hydrogenation reactions of some polycyclic aromatic hydrocarbons (PAHs), including anthracene, 9-phenylanthracene (9-PA) and 9,10-diphenylanthracene (9,10-DPA), were carried out under moderate reaction conditions (with the initial hydrogen pressure of 5 MPa at room temperature, reaction temperature was 300 °C) over a solid superacid (SSA). The results showed that the reactivity of the PAHs decreased in the order of anthracene > 9-PA > 9,10-DPA. It was found that not only the hydrogenation and the reversible dehydrogenation through hydrogen atom transfer, but also disproportionation reaction by intermolecular hydrogen transfer took place in the process of PAHs reactions. The catalyst proved to be versatile for the hydrogenation of anthracene and 9-PA through biatomic hydrogen transfer (BAHT) and for the hydrocracking of 9,10-DPA by monatomic hydrogen transfer (MAHT). The SSA is able to catalyze the cleavage of the C_{ar}–C_{ar} bridge bond in 9,10-DPA to produce 9-PA and benzene, in which the key step is the generation of the mobile H⁺ as well as the H⁺ transferring to the ipso-position of anthracene ring in 9,10-DPA. The SSA has the selectivity to catalyze the hydrogenation or hydrocracking of different PAHs.

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1. Introduction

Aromatic hydrocarbons are widely present in heavy fossil resources such as petroleum and coal, for instance, >70% of oil reserves are composed of the heavy oil, tar sands and other unconventional resources of higher aromatics-containing composition [1], in which >60% of carbon atoms exits as 1–4 ring of polycyclic aromatic hydrocarbons (PAHs) [2,3]. The aromatics released by the incomplete combustion of these fuels on one hand are recognized as environmental pollutants and carcinogenic to human beings, on the other hand PAHs have side effects to the combustion such as impoverishing the cetane value in petroleum and reducing the quality of diesel. With the increasingly stringent environmental requirements, in addition to the sulfur content of fuel, aromatics have been limited strictly in each country and with gradually strengthened tendency especially diesel drop aromatics received special attention. Nowadays, catalytic hydrogenation is the primary method of reducing the aromatic content of diesel desulfurization as well as one of the key reaction of coal direct liquefaction. Therefore, hydroconversion of aromatics is becoming an important subject in deeply upgrading liquid fuels.

Hydrogenation and hydrocracking of aromatics can not only improve fuel quality and reduce environment pollution, but also produce lots of high value-added chemicals, such as toluene, xylene, tetralin and tetrahydro-anthracene which are important chemistry raw materials. Therefore, the researches on aromatic oriented transform into high value-added compounds are of great significance. Many scholars have made efforts to study the structure and composition of coal, but limited knowledge has been obtained due to the highly complex compositions of coal. Thus, studying the corresponding reaction mechanism regarding the coal structure and its reactivity have become one of the hotspots of fundamental research. The current researches of aromatics hydrogenation catalyst pay much more attention on metal (Pt, Pd, Ni, Fe) and metal sulfides (CoMoS, NiMoS, FeS). Pinilla investigated the hydrogenation of naphthalene over the catalysts of carbon-supported Pd nanoparticles and found that the production selectivity of hydrogenated species depended on the temperature [4]. Potapenko et al. [5] reported intermolecular hydrogen transferred from naphthene to hexane with zeolite catalysts. They suggested that the monomolecular cracking reaction proceeded mostly on HZSM-5 zeolite, while the bimolecular hydrogen transfer reactions were catalyzed by the wide-pore HREY zeolite. Wang et al. [6,7] researched the hydrocracking reactions of arenes over solid acid SO₄²⁻/ZrO₂ at temperatures up to 435 °C and they speculated the carbenium ions played dominant role in the hydrocracking process. According to the reports by Wei et al. [8–12], hydrogenation proceeded via biatomic hydrogen transfer (BAHT) when used metals

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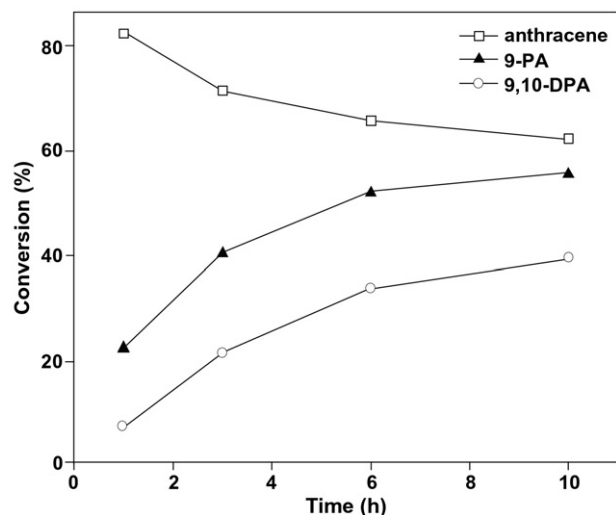


Fig. 1. Time profiles of the conversions of anthracene, 9-PA and 9,10-DPA.

as catalysts and via monatomic hydrogen transfer (MAHT) when used metal sulfides or activated carbon (AC) as catalysts. They advised the hydrogenation reactivity of PAHs depended on hydrogen accepting abilities and the stabilities of the resulting leaving groups [13,14].

A solid superacid (SSA) was prepared by impregnated AC with isometric trimethylsilyl trifluoromethanesulphonate (TMSTFMS) and antimony pentachloride (PCA) under microwave irradiation in our previous studies [15,16]. In our previous work [15], the effects of reaction time, temperature and initial hydrogen pressure on di(1-naphthyl)methane hydrocracking were examined over SSA. The hydrocracking reaction of di(1-naphthyl)methane in the presence of SSA started at a temperature of 200 °C. According to the previous results, 5 MPa initial hydrogen pressure, 300 °C for 3 h are the optimal conditions and the reaction extent attained during the heating procedure from 20 °C to 300 °C in the presence of SSA is negligible. In the present study, the reactivity of several PAHs over the SSA was examined in detail and the reaction mechanism of SSA-catalyzed hydrogenation was proposed. The PAHs investigated include anthracene, 9,10-dihydroanthracene (9,10-DHA), 9-phenylanthracene (9-PA), and 9,10-diphenylanthracene (9,10-DPA), which were functional molecules with fluorescence efficiency and the important coal-related model compounds.

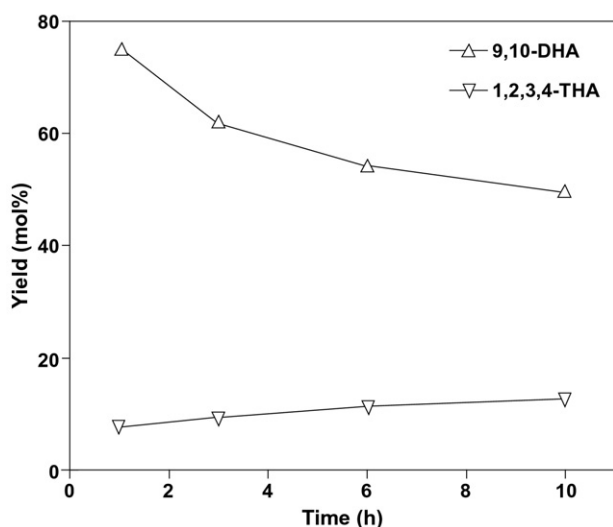


Fig. 2. Time profiles of the product distribution from anthracene hydrogenation.

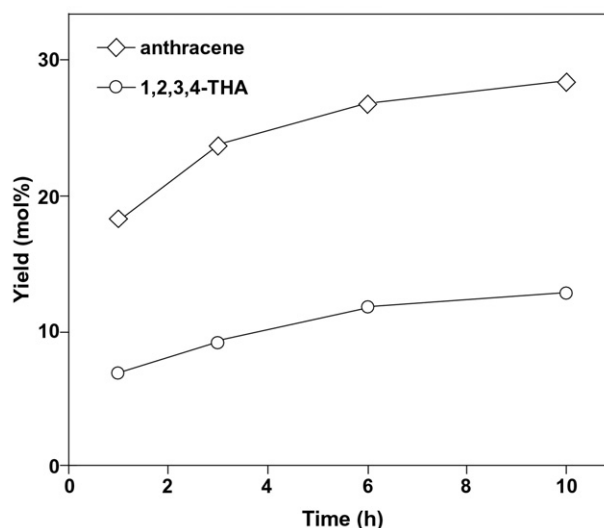


Fig. 3. Time profiles of the product distribution from 9,10-DHA hydrogenation.

2. Experimental

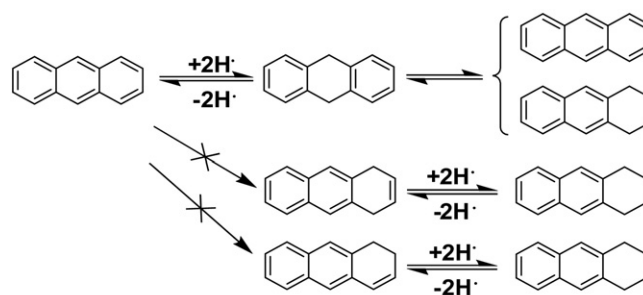
2.1. Materials

AC, TMSTFMS (99.5%), PCA (99.8%), benzene (99.5%), cyclohexane (99.5%), naphthalene (97%), anthracene (97%), 9,10-DHA (97%), 9-PA (98%) and 9,10-DPA (97%) were commercially purchased. AC was ground to <75 μm and dried under vacuum before use. In order to remove the impurities, benzene and cyclohexane were purified by distillation through rotary evaporator at 82 °C, and naphthalene, anthracene, 9,10-DHA, 9-PA and 9,10-DPA were purified by recrystallization before use. A small amount of n-hexane and the substance used in this work were added to a flask respectively and the contents of the flask were heated until the solid dissolves completely. Next, the solution was cooled slowly to room temperature overnight before setting the flask in an ice bath, and the purer solid precipitate was crystallized, leaving impurities dissolved in the solvent. Crystals of purified solid were isolated by vacuum filtration. After purified, the purity (quantified by GC) of benzene, cyclohexane naphthalene, anthracene, 9,10-DHA, 9-PA and 9,10-DPA are 99.9678%, 99.9527%, 99.9331%, 99.9129%, 99.8641%, 99.9002% and 99.8990%.

Catalyst SSA was prepared by the impregnation method under microwave irradiation with isometric TMSTFMS and PCA into AC. A full description of the SSA preparation can be found in our previous studies [15,16].

2.2. General procedure

A substrate (0.5 mmol), SSA (0 or 0.2 g), and cyclohexane (30 mL) were put into a 60 mL stainless, magnetically stirred autoclave. After



Scheme 1. Proposed pathway of anthracene hydrogenation over the SSA.

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