



Full Length Article

Temperature-controlled hydrogenation of anthracene over nickel nanoparticles supported on attapulgite powder



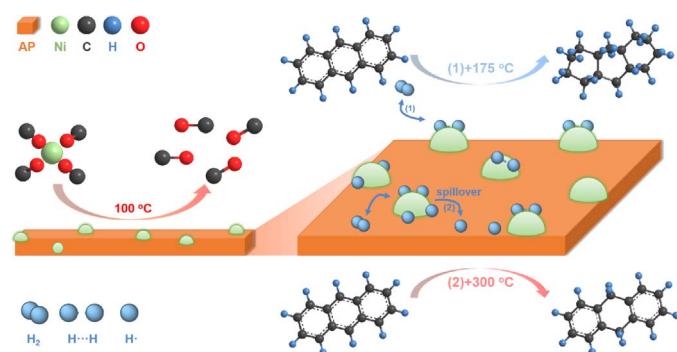
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GRAPHICAL ABSTRACT



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ABSTRACT

Catalyst Ni/attapulgite powder (AP) was facilely prepared by thermally decomposing nickel tetracarbonyl onto AP. Anthracene was used as a condensed arenes (CAs)-related model compound to evaluate the catalytic activity and selectivity of Ni/AP for hydrogenating CAs. The results show that anthracene can be completely converted to perhydroanthracenes (PHAs) at 175 °C and selectively converted to 9,10-dihydroanthracene (DHA, ca. 86.4%) at 300 °C by catalytic hydrogenation over Ni/AP. Ni/AP effectively promotes the formation and transfer (F & T) of biatomic active hydrogen (H...H) at 175 °C, resulting in the complete hydrogenation of anthracene to PHAs. The mechanism for the F & T of H...H is consistent with the observation from the higher selectivities of *cis*-PHAs than that of *trans*-PHAs. At 300 °C, the catalytically produced H...H over Ni/AP tends to be homolytically spilted to hydrogen radical (H[·]), inducing the partial hydrogenation of anthracene to DHA. Quantum chemical calculations based on density functional theory further confirmed the temperature-controlled hydrogenation of anthracene over Ni/AP. This finding is a conclusive proof that the active hydrogen species is crucially important for affecting the product selectivities from the catalytic hydrogenation of anthracene over Ni/AP. Our research also offers a novel strategy for highly selective conversion of CAs to polycyclic alkanes or hydroarenes.

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Nomenclature

AP	attapulgit powder	H ₂ -TPR	H ₂ -temperature programmed reduction
AR	anthracene ring	IHP	initial hydrogen pressure
CAs	condensed arenes	MPs	metal particles
CMs	carbaceous materials	MSs	metal sulfides
DFT	density functional theory	NBCs	nickel-based catalysts
DHA	9,10-dihydroanthracene	NNPs	nickel nanoparticles
EDS	energy dispersive spectrometer	NPs	nickel particles
F & T	formation and transfer	NTC	nickel tetracarbonyl
FTIR	Fourier transform infrared	OHA	1,2,3,4,5,6,7,8-octahydroanthracene
ΔG	Gibbs free energy change	PHA	perhydroanthracene
$\overline{\Delta G}$	average value of Gibbs free energy change	RBRs	related benzylic radicals
GC/MS	gas chromatograph/mass spectrometer	RE	resonance energy
H [•]	hydrogen radical	S _r	superdelocalizability
HFRs	heavy fossil resources	TEMI	Transmission electron microscopic image
H···H	biatomic active hydrogen	THA	1,2,3,4-tetrahydroanthracene
HP	heavy petroleum	XRPEs	X-ray photoelectron spectrum
		XRD	X-ray diffraction

1. Introduction

The hydrogenation reaction of unsaturated organic molecules is a textbook reaction in heterogeneous catalysis [1]. Such a reaction is widely used for the production of specialty and fine chemicals [2], coal conversion [3,4], and crude oil upgrading [5]. In addition, the hydrogenated products may also act as hydrogen storage media for proton exchange membrane fuel cell systems [6]. Therefore, more and more attentions have been attracted to the catalytic hydrogenation reactions in the past few years.

Condensed arenes (CAs), which extensively exist in heavy fossil resources (HFRs), such as heavy petroleum (HP) and coals, are a complex class of organic compounds containing several fused benzene rings [7]. Nevertheless, CAs not only reduce the cetane number and diminish the overall quality of diesel fuel derived from the HFRs, but also pollute the environment from the incomplete combustion of the HFRs [8–11]. Recently, various methods, such as chemical oxidation, photo-degradation, and thermal treatment, have been proposed for eliminating CAs, but these processes often need long processing time and high energy consumption [12–15]. Hence, there is an urgent need to develop efficient processes for upgrading CAs.

The catalytic hydrogenations have become a powerful tool for upgrading CAs recently. It is commonly known that transition metals, especially precious metals, were used for catalyzing aromatic ring hydrogenation at relatively low temperatures [16,17]. Moreover, a number of studies have demonstrated that transition metal catalysts could effectively catalyze the formation of biatomic active hydrogen (H···H) and subsequent hydrogenation of unsaturated species [18–20]. Nevertheless, the practical use of such precious metal catalysts faces serious difficulties in strong tendency to be poisoned by heteroatoms existing in industrial materials and their high price [21,22]. Metal sulfides (MSs) (or metal-sulfur system) have been successfully tested in the hydrotreating processes of CAs [23,24]. Furthermore, carbaceous materials (CMs) [25], such as carbon black and activated carbon, have also been successfully applied as catalysts for the catalytic hydrogenations of CAs. More interestingly, the MSs and CMs can also offer several amazing advantages, including relatively low cost, availability, chemical stability, and considerable mechanical strength, for the catalytic hydrogenations of CAs. MSs [26] and CMs [27,28] were found to be effective for facilitating the formation of hydrogen radical (H[•]) and for subsequently hydrogenating aromatic rings. Unfortunately, the MSs for the catalytic hydrogenations of CAs might lead to product contamination and fouling in equipment surface. The deep hydrogenations of CAs

over CMs were only achieved after long residence time. Thus, it remains challenging to develop efficient and robust catalysts for upgrading CAs.

As we know, nickel-based catalysts (NBCs), which have several compelling advantages such as low cost, relatively easy availability, and high activity [29,30], were widely used for hydrogenating unsaturated compounds. It is important to highlight that the activity of NBCs for hydrogenating unsaturated compounds is higher than that of either MSs or CMs, but their selectivities still remain at a lower level. Moreover, such catalysts were usually prepared from different nickel precursor salts with low nickel dispersion on the support and agglomeration of nickel particles (NPs) during subsequent reduction of the supported nickel nitrate precursor. Metal carbonyls as ideal precursors of highly active metal particles (MPs) could be decomposed to fine MPs at elevated temperatures [19,20]. Due to its microfibrillar morphology, high specific surface area, silanol-based chemistry of surface, and excellent thermal/mechanical stability, attapulgit powder (AP) is a remarkable metallic catalyst support [31–33]. On the basis of a variety of CA structures in HFRs, the investigation on the catalytic hydrogenations of HFR-related model compounds, especially anthracene [28,34], proved to be a valuable tool for revealing the catalytic hydrogenations for CA upgrading at molecular level.

In the present work, we describe a high performance of Ni/AP, which was prepared by thermally decomposing nickel tetracarbonyl (NTC) onto AP, for the selective hydrogenation of anthracene. We found that the product selectivities were greatly affected by the reaction temperature.

2. Experimental**2.1. Materials**

Anthracene is analytical reagent purchased from Energy Chemical Industrial Inc., Shanghai, China. AP and NPs were purchased from Huahong Mining Chemical Co., Ltd., Jiangsu, China and Jien Nickel Co., Ltd., Jilin, China, respectively. AP was pulverized to pass through a 200-mesh sieve. The commercially available cyclohexane was purified by distillation prior to use.

2.2. Catalyst preparation

NTC was produced by the reaction of 5.0 g NPs with 6.0 MPa CO in a 100 mL stainless steel and magnetically stirred autoclave at 100 °C for 2 h. AP was treated in 0.5 M HCl aqueous solution at 60 °C for 4 h,

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