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Coke formation on the surface of Ni/HZSM-5 and Ni-Cu/HZSM-5 catalysts during bio-oil hydrodeoxygenation

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HIGHLIGHTS

- Coke formation is the main cause of catalyst deactivation in bio-oil hydrodeoxygenation.
- Quantity and species of coke on spent catalysts determine possibility of catalyst regeneration.
- Oxygenated compounds and graphitic carbon contained in coke deactivate catalysts.
- Cu reduces coke formation for Ni/HZSM-5 catalyst.

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ABSTRACT

Deactivation of zeolite catalysts due to coke deposition is a pronounced challenge in the hydrodeoxygenation (HDO) of bio-oil. This paper reports on the mechanism of coke formation and catalyst regeneration for two catalysts (Ni/HZSM-5, Ni-Cu/HZSM-5). FT-IR, XPS and Raman spectroscopy characterizations indicate that catalyst deactivation can be divided into three main stages: (1) Lewis acid sites in HZSM-5 support are rapidly covered by oxygenated hydrocarbons. The Brønsted acid sites of HZSM-5 donate protons to oxygenates, leading to the formation of carbocations - precursors of soluble coke on the catalyst surfaces. (2) Soluble coke is then stacked to form disordered filament-like carbon strands that are similar to carbon nanotubes or graphite-like structures. (3) Filament-like carbon evolves into graphite carbon. At the same HDO temperature, more graphite particles are found on the Ni/HZSM-5 catalyst than on the Ni-Cu/HZSM-5 catalyst, indicating higher resistance for the coke formation for Ni-Cu/HZSM-5 catalyst.

1. Introduction

Hydrodeoxygenation (HDO) is an effective process for upgrading a bio-oil [1]. Noble metal catalysts, such as Pd/C and Ru/C, have been shown to reduce coke formation and to achieve a high hydrogen to carbon ratio (H/C) for a bio-oil [2]. However, the high cost of noble metals makes these catalysts infeasible for large-scale applications. Although traditional sulfide Co-MoS_2 and Ni-MoS_2 catalysts can be used for bio-oil HDO [3], their activity declines quickly due to the transformation of metal sulfide to metal oxide [4]. Additionally, the regeneration of Co-MoS_2 and Ni-MoS_2 requires hydrogen sulfide. Thiols formation resulting from H_2S can contaminate the environment.

Zeolite based catalysts are known for their shape selectivity, remarkable adsorption and solid acidic sites. All of these make them applicable to petrochemical refinery processes. Protonated HZSM-5 zeolites are effective and stable for the conversion of methanol into light olefins (MTO) and for the methanol to gasoline process [5]. However, catalyst deactivation problem is very outstanding. Catalyst deactivation is a very complicated process. For the Zeolite catalysts, deactivation is strongly dependent on the zeolite pore structure, the acidic properties, the reaction temperature and the nature of the reactant [2,6]. The deactivation could occur by nitrogen or sulfur poisoning, catalyst sintering, metal deposition or carbon deposition. In the case of hydroprocessing, nitrogen/sulfur compounds are the most common poisons by virtue of their strong adsorption on catalyst sites. Because of their

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basic nature, they adsorb on catalyst acidic sites, viz. Lewis and Brùnsted sites, and may adsorb reversibly or irreversibly, depending on reaction conditions. This results in either incapacitating the site or competition with the reactants of a given reaction [5,6]. During hydroprocessing, part of the metals present in the feed will deposit on the catalyst surface and cause deactivation, which is irreversible [6]. Fortunately, Biofeeds, usually prepared by a thermal treatment of biomass, are the least contaminated by nitrogen, sulfur and metals. So, these are not the primary cause for catalyst deactivation. However, an acidic zeolite catalyst can be deactivated rapidly in a bio-oil HDO process due to coke formation in the channels or cages of the HZSM-5 [5]. As is known that the principle function of Lewis acid sites is to bind species to the catalyst surface. Brønsted sites function by donating protons is to the compounds of relevance, forming carbocations which are believed to be responsible for coking. The effect of acid on deactivation pathways has been analyzed and discussed (see the related Ref. [2]). It is found about the effect of acidity on the reaction and deactivation pathways that: (1) if the acidic sites are stronger, the chemical steps become faster, and hence, the retention of coke precursors and coke molecules adsorbed on Lewis acid sites become more obviously, i.e., the coking rate becomes faster. (2) if the density of the acid sites is higher, these sites are close to each other, more many species of containing oxygen are adsorbed, which are coke of precursor, hence, coking becomes faster [2,7]. During HDO of bio-oil, the oxygenated hydrocarbons adsorbed on Lewis acid sites obtain protons to form water. The other still stay there changes into the form of carbocations on the catalyst. With increasing reaction temperature, its concentration is accelerated and finally graphitic carbon is hence deposited on the catalyst.

Transition metals Ni and Co, loaded onto zeolite can form bifunctional acidic catalysts for HDO of bio-oil [8]. Ni metal catalyst alone can activate hydrogen and significantly inhibit the unsaturated hydrocarbon polymerizations by reducing their concentrations during bio-oil HDO. However, the formation of coke on the surface of Ni catalysts cannot be resolved.

Cu can improve the dispersion of nickel and reduce Ni particle sizes. The retention time of oxygenated hydrocarbons passing through the Ni becomes shorten. This weakens the dehydrogenation of Ni and slows down the conversion of oxygenated hydrocarbons to graphitic carbon. A bimetallic catalyst consisting of Ni and Cu can activate hydrogen at the lower reaction temperature, which is in favor of promoting hydrogenation and restraining polycondensation reaction at the same time [9]. As is known that hydrogen molecules are easily dissociated on Ni, then the dissociated hydrogen move to Cu site, leading to Ni site evacuated, hence, it can adsorb other hydrogen [10]. Again, the moved hydrogen on Cu is easily desorbed due to the lower dissociation barrier than Ni. This manifests that adding Cu is beneficial to HDO of bio-oil.

Most research in Ni-Cu catalysts were focused on the investigation of the effect of the Ni to Cu ratio [11]. Few paper were regarded on the deactivation of bimetallic Ni-Cu catalysts due to coke formation for the HDO of a bio-oil.

In this paper, Ni/HZSM-5 and Ni-Cu/HZSM-5 were chosen for investigating coke formation and catalyst deactivation behaviors. The quantitative analyses of coke formation during bio-oil HDO and the related mechanisms are reported in this paper.

2. Experimental

2.1. Materials

All reagents used were analytical grade. Toluene, copper nitrite, nickel nitrite, dichloromethane, hydrogen fluoride and *n*-butyl alcohol were obtained from Sinopharm Chemical Reagent Co., Ltd. HZSM-5 (Si/Al = 50, specific BET surface area, S_{BET} = 299.2 m^2/g, total specific pore volume, V_{total} = 0.192 cm^3/g) was purchased from Nankai University Catalyst Factory. Bio-oil sample was obtained from the fast pyrolysis of rice husk at 500 °C in a bench-scale fluidized-bed reactor at Zhengzhou University.

2.2. Catalyst preparation

Before loading metal particles HZSM-5 support was calcinated in air at 500 °C for 4 h [12,13]. Metal particle loading onto HZSM-5 was carried out by impregnating the support in an aqueous metal salt $Ni(NO_3)_2{\cdot}6H_2O$ solution or $Ni(NO_3)_2$ and $Cu(NO_3)_2{\cdot}3H_2O$ solution. The mass ratio of Ni to Cu was eight (8) and the mass percent of metal to the total mass of metal + HZSM-5 was 15 wt.%. During impregnation ethylene glycol (EG) was added to the metal nitrate aqueous solution at a 1:1 molar ratio of (Ni + Cu) to EG [12]. The aqueous solution was then evaporated at 60 °C in a water bath and the residues were dried at 110 °C in an oven for 12 h. The prepared catalysts were finally calcinated in air at 400 °C and reduced in 50 vol.% H_2 in N_2 gas at 460 °C for 4 h [13].

2.3. Catalytic bio-oil HDO

Bio-oil catalytic hydrogenation was carried out in a 500 mL stainless-steel autoclave (Weihai Automatic Control Inc.) equipped with an electromagnetic-driven stirrer. The autoclave temperature was controlled using an electric jacket thermocouple. A back pressure valve was used to regulate the reactor pressure. For each run the reactor was filled with 60.0 g bio-oil, 40.0 g organic solvent (20.0 g toluene + 20.0 g *n*-butyl alcohol) and 5.0 g catalyst. Subsequently, the reactor was purged three times with 3 MPa H_2 to replace the existing air in the autoclave. Then the reactor was pressurized with H_2 to 2.0 MPa at room temperature. The reactor was then heated to a target reaction temperature at a heating rate of 3.0 °C/min. The temperature was maintained for 1 h at a stirring rate of 650 rpm. Finally, the reactor was cooled to ambient temperature. The catalysts were separated from the liquid phase by filtration and washed three times with alcohol. The as-prepared catalyst powder was dried overnight at 110 °C. The liquid phase was then separated via a separator funnel into 2 or 3 phases (i.e., light/heavy oils and a water phase).

2.4. Analytical methods

The elemental compositions of bio-oil and the coke formed on spent catalysts were determined using a ThermoScientific Corporation Flash EA 1112 elemental analyzer (Delft, the Netherlands). All analyses were carried out at least two times and the values reported are the average of at least of two measurements.

Thermogravimetric (TG) studies on used catalysts were performed using an STA 409 PC Thermal Analyzer (NETZSCH). The TC analyses were under 60 mL/min of air flow rate with the sample mass of about 5.0 mg and 10 °C/min of heating rate.

Transmission Electron Microscopy (TEM) images were recorded on a Tecnai G2 20 S-TWIN transmission electron microscope (FEI, The Netherlands) at an accelerating voltage of 200 kV.

Fourier Transform Infrared (FT-IR) spectra of the oil phase and catalysts were recorded using a Bruker Alpha Class 1 instrument. The spent catalyst samples (1.0–1.2 mg) were pelletized with KBr (100 mg, purity > 99%) and the applied pressures were equivalent to 10 ton cm^{-2} for 10 min. The operation strictly followed typical quality analysis procedures to ensure the accuracy of results.

Raman spectra were obtained by using a Horiba HR800 spectrometer. Approximately 50 mg of samples were used with an argon laser of 514 nm and 2 mW power.