Journal of Catalysis 363 (2018) 26–33

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Robust nickel cluster@Mes-HZSM-5 composite nanostructure with enhanced catalytic activity in the DTG reaction

Zhiyong Wen [a,c,1], Zhimin Li [b,c,1], Qingjie Ge [a,*], Yang Zhou [b,c], Jian Sun [a], Hadi Abroshan [d], Gao Li [b,*]

[a] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China
[d] SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, 443 Via Ortega, Stanford, CA 94305, United States

ARTICLE INFO

Article history:
Received 21 November 2017
Revised 30 March 2018
Accepted 8 April 2018

Keywords:
Ni cluster
Mesoporous zeolite
HZMS-5
DME to gasoline
Isoparaffin

ABSTRACT

Isoparaffin-rich gasoline plays an essential role in the global energy consumption. In this regard, there have been extensive studies to prepare catalysts for efficient synthesis of isoparaffin-rich gasoline. In this paper, we report a protocol to incorporate Ni nanoclusters (NiNC) into mesoporous Mes-HZSM-5 zeolite for the synthesis of NiNC@Mes-HZ catalysts. The catalysts are prepared *via* impregnation of $Ni_6(PET)_{12}$ clusters into Mes-HZSM-5 zeolite, followed by annealing at 550 °C in air. The NiNC@Mes-HZ catalysts are characterized by TEM, XRD, H_2-TPR, NH_3-TPD, ICP-MS, as well as N_2-physical adsorption method. The Ni clusters (average diameter: ca. 1.2–2.7 nm) are found to locate at mesoporous area of the zeolite and interact with Brønsted acid sites of the HZSM-5 zeolite, evidenced by the pyridine adsorption Fourier-transform infrared spectrum analysis. The NiNC@Mes-HZ catalysts (Ni cluster loading = 0.11 wt%) exhibit 100% conversion of dimethyl ether (DME) with 66.4C% selectivity towards C5-11. Results show 53.5C% of C5-11 product contains isoparaffin. This is considerably higher than that for Mes-HZSM-5 zeolite (27.5C% isoparaffin selectivity) and xNiNP@Mes-HZ (73.4% DME conversion) catalysts in the DTG process at 350 °C. The higher selectivity of the 0.11NiNC@Mes-HZ catalysts towards isoparaffin production is deemed to associate with the ease of DTG reaction to take place at the interface of the Ni nanoclusters and acidic sites of the zeolite. Further, it is shown that the nickel nanoclusters largely improve the durability of Mes-HZSM-5 zeolite (over 205 h), which is mainly due to the inhibition of carbon deposition production during the DTG process, evidenced by TPO-MS analysis of the used NiNC@Mes-HZ. The Ni nanoclusters in the zeolite show good hydrogenation capacity and cracking performance, enhancing the olefin methylation pathway on the acidic sites of Mes-HZSM-5 and attenuating the aromatic methylation cycle during the DTG reaction.

1. Introduction

Isoparaffin-rich gasoline, as a great potential clean transportation fuel, attracts much attention in recent years, especially when it is obtained through non-petroleum resources (e.g., coal, biomass, and natural gas) via syngas [1–4]. For the Fischer-Tropsch synthesis (FTS) of gasoline, the hydrocarbon products are composed of a wide range of linear paraffinic hydrocarbons and a considerable amount of methane, which is due to limitations of the Anderson-Schulz-Flory (ASF) polymerization kinetics and a secondary cracking reaction [5]. The syngas to gasoline via a methanol or dimethylether (DME) process is potentially an efficient pathway to obtain isoparaffin-rich gasoline [6–9]. Nevertheless, tailoring the hydrocarbon products containing isoparaffin-rich gasoline remains as a serious challenge. For example, hydrocarbon products generally comprise of rich aromatics (>60C% selectivity) in the methanol/DME to gasoline (M/DTG) process over zeolite (e.g., HZSM-5). The aromatics need to be converted to isoparaffin-rich gasoline using secondary hydrogenation and isomerization [10–13]. Additionally, the carbon deposition is easily formed which can block the active sites or the zeolite channels, as large amount of C12+ hydrocarbon is quickly yielded during the M/DTG process. Of note, C12+ hydrocarbons are the precursor of carbon deposition [2,4], leading to a rapid deactivation of the zeolite catalysts. Therefore, enhancement of the isoparaffin content of the gasoline product as well as durability improvement of the catalyst become serious challenges for the process of methanol or DME to isoparaffin-rich gasoline.

* Corresponding authors.
E-mail addresses: geqj@dicp.ac.cn (Q. Ge), gaoli@dicp.ac.cn (G. Li).
[1] Z.W. and Z.L. contributed equally to this work.

https://doi.org/10.1016/j.jcat.2018.04.010
0021-9517/

Dual olefin and aromatic methylation catalytic cycles are observed in the M/DTG process over HZSM-5 zeolite [14–17]. The catalytic behavior of HZSM-5 (including the activity and product selectivity) can be modified by inducing metal nanoparticles [18,19]. For example, nickel species exhibit strong hydrogenation/dehydrogenation ability and cracking performance [20–23], thus they can improve the activity of olefin methylation pathway and suppress the aromatic methylation cycle in the DTG process. Qi et al. demonstrated that the nickel modified ZSM-5 can exhibit high activity for the hydrogenation of arenes in the MTG reaction [24]. Very recently, Wen et al. found that the metallic Ni species in the ZSM-5 zeolite can enhance the hydroisomerization of olefins (cracking reaction over metallic Ni^0 particles) [6]. The catalytic activity of HZSM-5 was significantly affected by the location of Ni species within the zeolite framework instead of the Ni chemical state [25]. However, the metallic Ni^0 nanoparticles inevitably remain in the channel of zeolite in the presence of hydrogen at high temperature (e.g., 350 °C), synthesized via traditional impregnation method. The metallic Ni^0 particles resulted in the formation of plenty of methane and the CO side-products [26]. The durability of the NiNP@ZSM-5 catalyst was shown to be somewhat low (<20 h). Higher dispersion of Ni clusters in the zeolite can provide more accessible Ni than nanoparticle and give higher hydrogenation rate, improving the durability of the nickel modified HZSM-5. Further, mesoporous ZSM-5 can effectively improve the catalyst's durability due to the improvement of mass transfer. Thus, to improve the catalyst's durability via incorporating ultrasmall nickel species (e.g., Ni cluster) within mesoporous of the zeolite is still a big challenge.

It is worthy to note that only Ni nanoparticles with big sizes (diameter > 10 nm) are produced if traditional impregnation protocol (zeolite with a nickel salt) is employed. Hence, one can include ulrasmall Ni nanoparticles by direct usage of well-defined Ni clusters as the precursor. Herein, we demonstrate a new protocol to induce Ni clusters encapsulated in the mesoporous of Mes-HZSM-5 zeolite *via* impregnation of $Ni_6(PET)_{12}$ (PET: 2-phenylethanethiolate) clusters with zeolite. The organic tailors ($-SC_2H_4Ph$) of the cluster are all removed after 550 °C annealing in air, and the clusters finally converted to $(NiO)_n$ species with average diameter of ca. 1.2–2.7 nm. To our best knowledge, it is the first time to report such small Ni clusters in the zeolite. For the DTG process in the presence of hydrogen gas, the 0.11NiNC@Mes-HZ catalysts show to prefer olefin methylation pathway instead of the aromatic methylation, which is proposed to react at the mesoporous of zeolite. It exhibits a decent 100% DME conversion with a high isoparaffin selectivity (53.5C%) in gasoline hydrocarbons, which is better than those catalyzed by xNiNP@Mes-HZ (73.4% DME conversion) and Mes-HZSM-5 (100% conversion and 27.5C% isoparaffin selectivity). Simultaneously, the 0.11NiNC@Mes-HZ catalysts exhibited an excellent durability over 205 h of operation, which is mainly due to the inhibition of carbon deposition production.

2. Experimental

2.1. Preparation of Mes-HZSM-5 zeolite

The Mes-HZSM-5 was synthesized by alkaline treatments of an HZSM-5 sample (the SiO_2/Al_2O_3 molar ratio is 300, purchased from Nankai University Catalyst Ltd.). Prior to the treatment, the as-received HZSM-5 zeolite was calcined at 550 °C for 4 h in air. And then, 10 g of parent zeolite was stirred in 300 mL mixed solution of 0.2 M NaOH and 0.2 M TBAOH at 65 °C for 30 min, followed by cooling in an ice-bath to suppresses desilication, and then washed with de-ionized water. The samples were ion exchanged with a 0.5 M NH_4NO_3 at 60 °C overnight. The samples were filtrated again, washed with water and then dried at room temperature. Finally, the Mes-HZSM-5 zeolite was obtained via a calcination process at 550 °C for 4 h with 2 °C/min step of heating.

2.2. Synthesis of $Ni_6(PET)_{12}$ clusters

The $Ni_6(PET)_{12}$ clusters were synthesized using modified literature method [27]. $NiCl_2{\cdot}6H_2O$ (20.3 mg, 0.09 mmol) were dissolved in 15 mL THF, and 37 μL phenylethanethiol (0.27 mmol) was added, and the reaction mixture was stirred for 10 min. This was followed by addition of 20 mg $NaBH_4$ (dissolved in 2 mL of cold water), yielding a dark-brown solution, indicating the formation of the nickel cluster. The reaction continued to stir for overnight. THF was removed by rotary evaporation. The product was washed with water and methanol to remove excess thiols and salts, followed by extraction with ethyl acetate. The obtained nickel cluster was dried under vacuum with ca. 80% yield based on the consumption of $NiCl_2$ salt.

2.3. Preparation of NiNC@Mes-HZ catalysts

Typically, 9 mg $Ni_6(SC_2H_4Ph)_{12}$ clusters were dissolved in 25 mL CH_2Cl_2, and 1.5 g Mes-HZSM-5 zeolite powder was added. After stirring for overnight at room temperature, the supernatant became colorless. The $Ni_6(SC_2H_4Ph)_{12}$@Mes-HZ catalysts were collected by centrifugation and was air-dried at 80 °C. NiNC@Mes-HZ was obtained via an annealing of the solid samples at 550 °C for 4 h in air. ICP-MS analysis shows that the Ni content is ca. 0.11 wt%, which is close to the expected Ni content (ca. 0.1 wt%).

2.4. Preparation of xNiNP@Mes-HZ catalysts

The xNiNP@ Mes-HZ catalyst was synthesized as follow. Typically, 0.15 g $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in 5 mL water, and 3 g Mes-HZSM-5 zeolite powder was added in the aqueous solution. After stirring for 24 h at room temperature, the solid was collected by centrifugation and then dried in air at 60 °C. Further, the sample was annealed at 550 °C for 4 h in air. ICP − MS analysis shows that the Ni content is ca. 0.87 wt%. 0.1NiNP@Mes-HZ was synthesized using the same method.

2.5. Characterization

The UV–vis spectra of the free nickel clusters (dissolved in CH_2Cl_2) were recorded on a Hewlett-Packard (HP) Agilent 8453 equipped with a diode array detector. Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was recorded with a PerSeptive-Biosystems Voyager DE super-STR time-of-flight mass spectrometer. Trans-2-[3-(4-*tert*-butylphenyl) -2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix in MALDI-MS analysis. Typically, 0.1 mg matrix and 0.01 mg analyte stock solution were mixed in 100 μL CH_2Cl_2. The solution was applied to the steel plate and then air-dried prior to MALDI-MS analysis. Temperature-programmed thermogravimetric analysis was performed on a TG/DAT 6300 analyzer (Seiko Instruments Inc.). Ca. 2 mg sample was used in the test, which was conducted in air with a 50 mL/min gas flow and a 10 °C/min heating rate. Inductively coupled plasma-mass spectrometry was recorded on PerkinElmer ICP-MS NexION 300D. The NiNC@Mes-HZ and NiNP@Mes-HZ samples were decomposed by aqua regia solution. Temperature-programmed oxidation mass spectrometry (TPO-MS) was performed using quadrupole mass spectrometer OmniStarTM GSD 301 (Pfeiffer Vacuum) to detect and analyze signal of H_2O and CO_2. After pretreated at 200 °C for 2 h in He flow, a 40 mg sample was heated from 30 °C to 900 °C with a heating rate 10 °C min^{-1}