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Catalytic performance of nickel immobilized on organically modified montmorillonite in the steam reforming of ethanol for hydrogen production

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Abstract: Nickel immobilized on organically modified montmorillonite (Ni/OMt) was prepared by impregnation method and used as the catalyst for hydrogen production from ethanol steam-reforming; the Ni/OMt catalyst was characterized by XRD, FT-IR, H_2-TPR, SEM, XPS and N_2 adsorption-desorption. The results indicate that in comparison with the catalyst of nickel supported on unmodified montmorillonite (Ni/MMT), the Ni/OMt catalyst exhibits higher surface area and pore volume as well as higher nickel dispersion with smaller metallic particle size. For the ethanol steam-reforming over Ni/OMt, the conversion of ethanol keeps at 100%, with a selectivity of 70% to hydrogen during the 30 h reaction test at 773 K; however, over the unmodified Ni/MMT catalyst, severe carbon deposition is observed after reaction for only 10 h, accompanying with catalyst deactivation and the formation of byproducts such as acetaldehyde and ethylene. The modification of MMT with cetyltrimethylammonium bromide (CTAB) can significantly improve the stability of the Ni/OMt catalyst in ethanol steam-reforming and reduce the carbon deposition rate by immobilizing highly dispersed nanoparticle Ni on the interlayers of OMt; the selectivity to ethylene and acetaldehyde is also greatly depressed.

Keywords: hydrogen production; nickel; ethanol steam reforming; intercalation with organic agents; cetyltrimethylammonium bromide

Hydrogen is known as a promising clean energy source[1]; at present, it can be produced from coal, methane, methanol, ethanol and other sources. Bio-ethanol, obtained from many renewable biomass resources such as sugar, cane, corn and agricultural wastes, can be used to produce clean hydrogen effectively through steam reforming via the stoichiometric equation[2]:

$$CH_3CH_2OH + 3H_2O = 2CO_2 + 6H_2 \qquad (1)$$
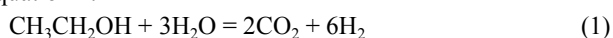
However, the steam reforming may be accompanied with some undesirable byproducts that affect the selectivity to hydrogen; the catalysts and reaction conditions should then be well determined to achieve high hydrogen yield[3].

Various catalysts have been used in hydrogen production from ethanol steam reforming. Noble metal catalysts, such as Ru, Pd, Pt and Rh[4,5], are highly active but quite expensive because of their scanty in nature. Non-noble metals like Ni, Co and Cu are also active for this reaction[6,7]; especially, the nickel catalyst with low cost has been widely used in various processes such as hydrogenation and dehydrogenation, owing to its high activity in breaking the C–C and O–H bonds[8].

However, the Ni-based catalysts often suffer from significant deactivation due to the metal sintering and carbon deposition. Previously, we found that alumina could improve the dispersion of Ni on NiAl-montmorillonite catalyst[9]; however, the selectivity to H_2 in ethanol steam reforming was still low due to the formation of acetaldehyde and ethylene, because of the acid sites of added Al_2O_3 and the formation of $NiAlO_3$ spinal between Ni and Al. As a result, it is interesting to find a way that can improve the dispersion of Ni without reinforcing the catalyst acidity.

Montmorillonite (MMT) is layered cationic aluminosilicate clay; its primary structure involves two tetrahedral sheets with Si in the cationic sites sandwiching an octahedral Al sheet. MMT is widely used as the supports for metal nanoparticles catalyst because of its high cation exchange capacity (CEC). The template has an effect on the morphology of nanoparticles. The intercalation of cationic surfactants is beneficial to expand the interlayer space of MMT and the surfactants exchanged into MMT can form micelles environment. The micelles can contribute to form metal nanoparticles. The

organophilic MMT supported metal catalyst exhibited high activity and selectivity. Zhou et al[10] found that organophilic MMT supported Ru catalyst could be well dispersed in organic solvents, which exhibited high activity and selectivity in the hydrogenation of quinoline[10]. Ren et al[11] proposed a mechanism for the promoting effect of organic modification during impregnation on the activity of Ni/MMT catalyst; the organic modification could improve the dispersion of Ni catalyst.

In this work, cetyltrimethylammonium bromide (CTAB) was used to exchange MMT to improve the dispersion of Ni on the Ni/MMT catalyst and to suppress the agglomeration and sintering of Ni particles, in order to enhance the catalytic performance of Ni/MMT in ethanol steam reforming.

1 Experimental

1.1 Catalyst preparation

Cetyltrimethylammonium bromide (CTAB) was used to prepare the organically modified montmorillonite (OMt). Montmorillonite (MMT, Zhejiang Sanding Group Co., Ltd.) with a cation-exchange-capacity (CEC) of 1.10 meq/g was used directly as a starting material without further purification. The molar ratio of CTAB to the CEC of MMT was 1.1:1.0. MMT (5.0 g) was dispersed in distilled water (100 mL) and CTAB (2.0 g) was then slowly added to the MMT suspension for ion-exchange at 353 K for 8 h. After cooling to room temperature, the mixture was filtered and the CTAB-exchanged MMT, viz., OMt, was thoroughly washed with ethanol and distilled water until no Br^- ions were detected with $AgNO_3$ solution, which was further dried at 353 K for 12 h.

The supported Ni/MMT and Ni/OMt catalysts were prepared by the impregnation method with nickel nitrate as the Ni precursor at 333 K; the Ni loading was kept at 10%. Water was then removed by evaporation. Then catalysts were dried at 373 K for 12 h and then calcined in air at 773 K for 3 h.

1.2 Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD 6000 diffractometer with Cu $K\alpha$ radiation (λ = 0.15418 nm) at 40 kV and 30 mA at a scanning rate of 8(°)/min from 3° to 80°.

FT-IR spectroscopic analysis was made on a Shimadzu FT-IR 8400 spectrometer. FT-IR spectra in the transmittance mode were recorded in the range of 400−4000 cm^{-1} at a resolution of 4 cm^{-1} using the KBr pelleting technique.

Nitrogen adsorption-desorption isotherms were measured with Micromeritics ASAP 2020 analyzer at 77 K. Prior to analysis, the sample (150 mg) was degassed at 573 K for 2 h. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The average pore diameters and cumulative volume of pores were obtained by the Barrett-Joyner-Halenda (BJH) method from the data of the adsorption branches of the isotherms.

Temperature programmed reduction with hydrogen (H_2-TPR) was carried out on a Micromeritics Autochem 2920 apparatus equipped with a TCD detector by passing a 5% H_2 in Ar stream (40 mL/min) through the catalysts (10 mg). The temperature is increased from 298 to 1023 K at a linear rate of 20 K/min.

Scanning electron microscope (SEM) images of MMT and OMt and the carbon deposition on the spent catalysts were examined with the SU-1500 (Hitachi, Tokyo, Japan) scanning electron microscope (SEM).

1.3 Catalyst activity measurements

The catalytic tests for ethanol steam reforming were performed in a stainless steel fixed bed reactor at atmospheric pressure at 773 K. Before reaction, the catalyst sample (0.375 g, 20–40 mesh) diluted with quartz sands were reduced at atmospheric pressure in a flow of pure H_2 (35 mL/min) at 823 K for 3 h. Ethanol steam was fed into the reactor as the liquid mixture with a water to ethanol molar ratio of 3 and at a flow rate of 0.075 mL/min; nitrogen with a flow rate of 35 mL/min was used as the carrier gas. Weight hourly space velocity (WHSV), defined as the ratio of inlet feed (water + ethanol) mass flow divided by the mass of catalyst, was fixed at 11.27 h^{-1}.

The gaseous products were detected by an on-line gas chromatography (GC-950), with a TDX-01 column and a TCD detector for H_2 and a FID detector for CO, CH_4, CO_2 and C_2H_4. After the reaction, the condensed liquid products were collected and analyzed by a gas chromatography (GC-9890B), with a Porapak-Q capillary column and a TCD detector. Ethanol conversion (x_{EtOH}) and product selectivity (s_i) are defined as:

$$x_{EtOH} (\%) = ((F_{EtOH,in} - F_{EtOH,out})/F_{EtOH,in}) \times 100\% \qquad (2)$$
$$s_i = n_i/\Sigma n_i \times 100\% \qquad (3)$$

Where F is the molar flow rate for the inlet (in) stream or outlet (out) stream; s_i represents the selectivity to the products i such as H_2, CO, CH_4, CO_2, C_2H_4 and CH_3CHO.

2 Results and discussion

2.1 XRD analysis

The XRD patterns of Na-MMT and OMt are shown in Figure 1.