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Effect of support in Ni-Bi-O/support catalyst on oxidative dehydrogenation of *n*-butane to butadiene

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ABSTRACT

NiO-Bi₂O₃/different support catalysts, 20 wt% Ni and 30 wt% Bi as metal weight to support weight (hereafter 20wt%Ni-30wt%Bi-O/support) have been studied for oxidative dehydrogenation of *n*-butane to butadiene. Al₂O₃, SiO₂, ZrO₂ and none (: without support) were served as gel and sol type supports. As the results, activity and selectivity of oxidative dehydrogenation of *n*-butane to butadiene over the Ni-Bi-O/support catalyst strongly depended on the supports. The order of the butadiene selectivity as gel-type support was Al₂O₃ > SiO₂ > ZrO₂ >> none, while SiO₂ showed the highest butadiene selectivity from 1-butene feedstock. The gel-type support effect as a hierarchical nano-particle cohabitation was also studied by using equilibrium adsorption method for the Ni-Bi-O impregnation. In the sol-type support case, the order is SiO₂ > Al₂O₃ > ZrO₂, where the SiO₂ sol shows not only superior to gel-type but also the best performance (*n*-butane conversion: 35.6%, selectivity: dehydrogenation 78.3%, butadiene 41.6%) among support types and species. The sol-type SiO₂ hold balanced acid and base sites cooperating to improve butadiene selectivity, with oxygenate suppressed by accelerating redox system with non-hierarchical nano-particle cohabitation of NiO, Bi₆O₇ and support SiO₂.

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1. Introduction

Butadiene is used mainly in the petrochemical and polymer industries as a raw material especially in the production of synthetic rubbers and automobile tires. It is mainly obtained as a byproduct from naphtha crackers (ethylene plants) with the main products being ethylene and propylene. The change of feedstocks from heavy into lighter (ethane and propane) has led to decrease in butadiene supply as against the ever increasing demand. This has led to worldwide search for an on-purpose butadiene production technology.

Direct dehydrogenation using mainly chromium oxide supported on alumina catalyst was first investigated for producing butadiene, but it requires very high temperature [1–3]. At such high temperature operation, frequent catalyst regeneration is required due to coke deposition. Though improved processes using butenes in the presence of steam to produce butadiene were reported, they are highly energy intensive [4,5]. On the other hand, oxidative dehydrogenation with oxygen is not limited by thermodynamic

equilibrium, it can be carried out at relatively lower reaction temperature and the catalyst deactivation is reduced due to the presence of oxygen [6–8]. However, controlling the product selectivity in ODH is a major challenge, considering the higher reactivity (than *n*-butane) of olefin products (i.e. butenes and butadiene) with oxidant forming unstable oxygenates and combustion products [9].

The performance of a catalyst in oxidative dehydrogenation is related to the acid-base surface character and its redox property. Many researchers have investigated different types of catalysts for the purpose of lower alkane oxidative dehydrogenation some of which include V₂O₅/supports (Al₂O₃, SiO₂, TiO₂, ZrO₂) [10], Cr₂O₃/SiO₂ [11], Zn-Cr-FeO [12], Fe-Zn-O [13], Mg₃(VO₄)₂/supports (Al₂O₃, ZrO₂, MgO, CeO₂) [14], Mg₃(VO₄)₂/MgO-ZrO₂ [15], V₂O₅/MO-Al₂O₃ (M=Mg, Ca, Ba, Sr) [16], V₂O₅/silica gel [17], VO_x/supports (USY, NaY, γ-Al₂O₃, α-Al₂O₃) [18], VO_x/Ti-HMS [19], VO_x/SBA-15 [20], MoO₃/MgO [21], V/supports (HMS, SBA-16, SBA-15, MCM-48) [22], V/TiO₂-SiO₂ [23]. Most of these catalysts have one problem or the other with either activity or selectivity to butadiene and in most cases the first step dehydrogenation products (1-butene and 2-butenes) dominate with little percentage of butadiene and some cracking products [8].

In our recent study, Ni-Bi-O/Al₂O₃ catalysts were shown to be effective for *n*-butane oxidative dehydrogenation. In particular, 20wt%Ni-30wt%Bi-O/Al₂O₃ catalyst subdued oxygenate

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production and showed high *n*-butane conversion and butadiene selectivity. The addition of Bi₂O₃ to NiO was found to incite moderate basicity and improve redox character [24]. We also reported that the catalyst calcination through two steps of appropriate temperatures positively result the highest dehydrogenation and butadiene selectivity. The cohabitation as ‘hierarchical nanoparticles’ consisting of NiO, Bi₂O₃ and Al₂O₃ obtained at the preferable calcination condition, was observed to create the redox and acid/base system of the combined oxides with porous structure that are found to be active and selective to the butadiene formation [25]. Furthermore, the composition effect of main metal species (Ni, Fe, Co) was also studied and improved catalyst performance was obtained on ternary main metal system (Ni-Fe-Co) due to double improvements by Fe and Co respectively [26]. In a parallel study, the effect of support was examined including support species and types in Ni-Bi-O/support catalysts.

The roles of supports in catalysis cannot be ignored as the support plays a significant role in metal oxide species dispersion and also contributes to the overall acidic/basic property of the catalysts. The oxidative dehydrogenation of propane using V₂O₅/supports (Al₂O₃, SiO₂, TiO₂, ZrO₂) was studied and it was found that V₂O₅ over SiO₂ support are more selective for propene formation mainly due to less subsequent reaction to CO and CO₂ compared to acidic supports such as Al₂O₃ and TiO₂ [10]. In our previous reports, the same Al₂O₃ support was used for the catalysts, hence there is need to investigate the effect of different support species on dispersing Ni-Bi-O. This manuscript tends to study the effect of support using Al₂O₃, SiO₂, ZrO₂ as shaped/calcined gel-type and un-calcined sol-type on the oxidative dehydrogenation of *n*-butane to butadiene. The important role of the supports was substantiated by testing the Ni-Bi-O metal oxide without support system. The states of nano-particle cohabitation with supports were examined by using equilibrium adsorption with or without enforced deposition by drying for the Ni-Bi-O impregnation. The catalytic performances with different supports were finally evaluated considering the textural characteristics with BET surface area, porosity, XRD, TEM, and TPR/TPD for redox and acid-base property.

2. Experimental

2.1. Catalyst synthesis

The nano-sized porous Al₂O₃ with pore diameter of 9.8 nm, pore volume of 0.83 ml/g was prepared using pH-controlled precipitation method [27–29]. For preparation, the boehmite precursors such as aluminum nitrate and sodium aluminate along with acid–base pair as precipitating reagents were used. The SiO₂ support was obtained from the market as CARIACT supplied by Fuji Silysia Chemical Ltd. The ZrO₂ support was prepared by calcination at 550 °C for 3 h from hydrated amorphous zirconia JRC-ZRO-2 with surface area of 254 m²/g as the Reference Catalyst supplied by Catalysis Society of Japan.

The Bi-Ni-O/support catalysts were prepared as standard (STD) samples by co-impregnation methods of equilibrium adsorption and enforced deposition. In order to clarify state of metal oxide species, stopping impregnation at equilibrium adsorption (EQA) step was applied to prepare EQA catalysts. Nickel nitrate hexahydrate Ni(NO₃)₂·6H₂O (99%, Fisher Scientific) was used as nickel source, while bismuth nitrate pentahydrate Bi(NO₃)₃·5H₂O (98%, Fluka-Garantie) was used as bismuth source. For the preparation of 20 wt% Ni–30 wt% Bi-O/Al₂O₃ catalyst, 0.99 g of Ni(NO₃)₂·6H₂O was added to 80 ml of distilled water. After complete dissolution, 0.70 g of Bi(NO₃)₃·5H₂O was added and stirred. Then 1.0 g of dried support was added for impregnation and left overnight for aging. Then the sample was dried at 120 °C for 3 h and termed as-prepared catalyst.

The EQA as-prepared catalysts were obtained by removal of the liquid part after aging before drying. The calcination of as-prepared catalyst was done in two steps. In the first step, the temperature was raised to 350 °C at the rate of 10 °C/min and kept for 1 h. In the second step, the temperature was raised again at the rate of 15 °C/min to 590 °C and kept for 2 h for complete activation and stabilization.

2.2. Catalyst characterization

The elemental analyses for equilibrium adsorption Ni-Bi-O/support catalysts were obtained using ICP instrument: ULTIMA 2 (HORIBA Scientific). The textural characteristics such as surface area and pore structure were analyzed on Micromeritics ASAP 2020 instrument (Norcross, GA), the pore surface area, pore volume and pore diameter were measured using BJH adsorption method. X-ray diffraction of calcined samples were analyzed from (2θ) range of 5° to 80° using Rigaku Miniflex II desktop X-ray diffractometer and using Cu Kα radiation (wavelength λ = 1.5406 Å) and 30 mA and 40 kV as operating parameters, a step size of 0.02° and a speed of 2°/min.

The catalyst morphologies were analyzed using high-resolution transmission electron microscope (HRTEM-model JEM-2100F) with an acceleration voltage of 200 kV. The redox character and acid-base property was analyzed using Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) using BEL-CAT-A-200 chemisorption instrument. It is made up of a quartz sample holder having a furnace (suitable for high temperature), a mass spectrometer and a thermal conductivity detector (TCD). Injection of gas pulses with standard volume in helium background flow establishes the linearity of the TCD response. The redox property measurement was done using a gas mixture of Ar/H₂ (95/5 vol%) having a total flow rate of 50 cm³/min. 0.1 g of the calcined catalyst was preheated for 3 h at 300 °C in inert He after which it is cooled to room temperature. It was then heated at the rate of 20 °C/min up to 900 °C. H₂ intake was recorded with a TCD and CuO was used as a reference for calibrating the consumption of H₂. Ammonia and carbon dioxide temperature programmed desorption (NH₃ and CO₂ TPD) were carried out using the same equipment (BELCAT system) for acidity and basicity measurements respectively. 0.1 g of the calcined catalyst sample was pretreated for 1 h at 500 °C using inert He (50 ml/min). It was then exposed to He/NH₃ mixture (He/CO₂ mixture for CO₂ TPD) in volume ratio of 95/5 vol% for 30 mins at 100 °C. Gaseous NH₃ (CO₂) was removed by purging using He for 1 h and then TPD was performed using the same flow of He at a rate of 10 °C/min up to 600 °C and the desorbed gas (NH₃ or CO₂) was monitored using mass spectroscopy or TCD detector.

2.3. Catalyst testing

The oxidative dehydrogenation reaction was carried out in an automated fixed bed reactor purchased from BELCAT, Japan. The as-synthesized catalyst (0.3 g) was loaded in to the reactor and calcined under air atmosphere. After calcination, the reaction started under nitrogen atmosphere. The feed *n*-butane contact time was maintained at 93 h g/mol. The total flow rate of reactants including *n*-butane, air and nitrogen was maintained at 31.2 ml/min. The effect of three different temperatures (400, 450 and 500 °C) and various oxygen to *n*-butane ratio (O₂/*n*-C₄H₁₀ = 1.0, 2.0 and 4.0 mol/mol) was tested. The products was analyzed through online GC system, (Agilent, 7890N). The hydrocarbons and oxygenates were analyzed using FID and GC-Gas Pro capillary column (L: 60 m and ID: 0.32 mm), while gases, N₂, O₂, CO and CO₂, and H₂, respectively were detected using TCD and Shin Carbon 80/100 mesh SS column (He carrier) and MS5A 60/80 mesh SS column (Ar carrier). The products were confirmed by comparing with standard samples.

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