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Oxidative dehydrogenation of n-butane to butadiene catalyzed by new mesoporous mixed oxides NiO-(beta-Bi₂O₃)-Bi₂SiO₅/SBA-15 system



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Keywords: n-Butane Dehydrogenation Butadiene SBA-15 Bi ₂ SiO ₅	NiO-beta-Bi ₂ O ₃ -Bi ₂ SiO ₅ /SBA-15 catalysts, containing $10 - 20$ wt% Ni and $10 - 30$ wt% Bi loaded as metal weight on mesoporous SiO ₂ support (SBA-15), were utilized for the oxidative dehydrogenation of n-butane to butadiene, comparing from the viewpoint of Bi oxide phase and combination balance with Ni oxide and the support. Bi ₂ SiO ₅ and beta-Bi ₂ O ₃ phases change depending on Ni/Bi ratio. "Reverse core-shell" structure with uniform meso- porosity catalytically active for the oxidative dehydrogenation of n-butane to butadiene was successfully syn- thesized with semi-dry conversion method. The shell was formed as Bi ₂ SiO ₅ /SBA-15 by partially dissolving an array of silanol inside SBA-15 mesopores with impregnated bismuth nitrate. The Bi ₂ SiO ₅ of the shell was in- creased by co-impregnated nickel nitrate. The layered core faced to mesopore was formed as catalytically activel NiO/beta-Bi ₂ O ₃ on the shell. The degrees of formation Bi ₂ SiO ₅ and beta-Bi ₂ O ₃ reflected in the butadiene se- lectivity through changing the reducibility and dispersion properties. The catalyst with moderate loading of 20 wt% Ni and 10 wt% Bi exhibited a high advantage in the n-butane conversion: 30 % and butadiene selectivity: 49 % at 450 °C compared to the less and excess loaded catalysts. The catalytic performance of other mesoporous silica support catalysts also changed differently depending on Bi ₂ SiO ₅ and beta-Bi ₂ O ₃ phases.

1. Introduction

The global demand for butadiene in the manufacturing of synthetic rubber was about 12.3 million tons in 2018 and it is expected to grow by 4.5 % annually during the next five years [1]. On-purpose production methods have been investigated to supplement the decrease in butadiene supply due to the shift from naphtha to ethane crackers.

Oxidative dehydrogenation (ODH) reaction is one of the promising methods aimed at bridging the gap between the growing demand and supply of butadiene. Many researchers have investigated n-butane oxidative dehydrogenation to butenes/butadiene mainly using vanadium based catalysts composed of V₂O₅/SiO₂ [2], V₂O₅/silica gel [3], V/supports (TiO₂, ZrO₂ and Al₂O₃) [4,5], V/TiO₂-SiO₂ [6], Mg₃(VO₄)₂ species over Al₂O₃, ZrO₂, MgO and CeO₂ [7,8], VO_x/supports (USY, NaY, γ -Al₂O₃, α -Al₂O₃) [9], VO_x/SBA-15 [10], V/supports (HMS, SBA-16, SBA-15, MCM-48) [11], VO_x/Ti-HMS [12], V-MCM-41 [13], V/Ti-SBA-15 [14], and Mo-V-MgO [15]. On the other hand, Bi-Mo-O based catalysts are well-known for ODH of n-butenes to butadiene. Referring to these literatures, the functions of the catalysts in the first (butane to 1-butene/2-butenes) and second (butenes to 1,3-butadiene) step

dehydrogenations were focused on. Our prior studies [16–19] utilized nanoparticles of binary oxide Ni-Bi-O species deposited on commercially available Al_2O_3 , SiO_2 , and ZrO_2 for the ODH of n-butane with high selectivity to butadiene. The contribution of Bi oxide without Mo in stabilizing the active site NiO nanoparticles selective to butadiene [16], the role of calcination (two steps of 350 and 590 °C in air) in controlling the Bi oxide beta-Bi₂O₃ phase formations [17], and the synergetic effects of the active site NiO modification by partial substitution with Co and Fe [18], have been reported. The role of support in controlling the redox character of the active species, metal-support interaction and acid-base properties have been highlighted [19]. In an advanced studies on the effect of supports, an enhanced performance was obtained with SiO₂ sol supported catalysts or the sol supported ones.

Mesoporous silica support shows enhanced performance in catalytic applications through stabilizing the performance of the impregnated metal oxides nanoparticles with a uniform dispersion. This is mainly due to their ordered structure, high surface area, high chemical and thermal stabilities, and well-defined pore sizes [20–23]. Mesoporous

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siliceous carriers (SBA-15, silica foam and MCM-41) are utilized in the synthesis of highly dispersed tungsten oxide catalyst for butene metathesis reaction [24-26]. Nanoparticles of vanadium deposited on mesoporous silica supports have been utilized for the ODH of n-butane [10-14]. Supports of highly ordered mesoporous silica (SBA-15, silica foam, and MCM-41) loaded with 20 wt% Ni and 30 wt% Bi, were also utilized in our previous study [27]. The binary-oxide impregnated catalysts were probed for n-butane ODH to butadiene and compared with traditional silica gel catalysts. Mesoporous silicas as catalyst support are superior to the traditional silica gels, where the SBA-15 mesoporous silica supported catalyst gave the best performance [27]. The interaction of BiO_x species with microporous and mesoporous silicon oxides was reported by Dumitru et al. [28]. The BiO_x species were incorporated into the ZSM-5 pores during hydrothermal synthesis and it was concluded that the well-dispersed and occluded BiOx clusters are effective for the liquid-phase oxidation of hydrocarbons. The strength and/or type of acid sites present and the redox properties of the catalyst were controlled by the BiO_x species and its interaction with the support [28]. This was extended in a series of papers by different authors, for mainly oxidation and photocatalytic studies [29-35].

This manuscript reports the effect of cooperating BiO_x species with SBA-15 mesoporous silica support on the redox property of the active Ni species and on the overall catalytic performance during n-butane oxidative dehydrogenation. The metal oxides-support cooperation was clearly studied using X-ray diffraction, X-ray photoelectron spectroscopy and temperature programmed reduction. Other mesoporous silica supports including silica foam, silica sol, and the traditional silica gel catalysts have also been utilized in this study as references.

2. Experimental

2.1. Catalyst preparation

SBA-15 mesoporous silica carrier was prepared using tri-block copolymer as a structure directing agent. 4 g of Pluronic P123 was introduced into 30 ml of de-ionized water. Stirring continued until clear solution was achieved. 70 g of 0.28 M HCl was added to the solution with continuous stirring for 2 h. 9 g of Tetraethyl orthosilicate (TEOS) was introduced and stirring continued for 24 h at 40 °C and finally heated for 48 h at 100 °C. Filtration was utilized in recovering the solid product, de-ionized water was used several times for washing the residue and then dried at 100 °C overnight. Calcination was done at 550 °C for 6 h for template removal [36]. The other mesoporous silicas used were silica gel Q10; procured from Fuji Silysia Chemicals Limited, Japan. MCM-41 was prepared following the method reported by Palani et al. [37]. Silica foam was prepared using the method obtained in the literature [38], and silica sol was purchased from Sigma Aldrich.

Co-impregnation technique was utilized in synthesizing all the supported catalysts to obtain enhanced cohabitation of mixed oxide nanoparticles [39]. Ni and Bi precursors utilized were respectively Ni $(NO_3)_2$ ·6H₂O (99 %, Fisher Scientific) and Bi $(NO_3)_3$ ·5H₂O (98 %, Fluka Garantie). In a typical synthesis, 990 mg of Ni precursor was dissolved in 80 ml of de-ionized water. 700 mg of Bi precursor was introduced after dissolution with continuous stirring. 1000 mg of the support was then introduced. The mixture was left overnight for Bi species equilibrium adsorption and followed by evaporative drying at 80 °C for enforced deposition of Ni species. The product was dried further for 3 h at 120 °C and two steps calcination at 350 °C for 1 h and 590 °C for 2 h at the rates of 10 °C/min and 15 °C/min, respectively, was carried out.

2.2. Catalytic testing

ODH reaction of n-butane was conducted in an automated fixed-bed reactor obtained from Microtrac Bel Company, Japan. 300 mg of the synthesized catalyst was introduced into the reactor to form the catalyst bed. The contact time of n-butane was fixed at 0.42 h·g/mol. Total

reactants flow rate was kept at 31.2 ml/min. The performance of the catalysts were evaluated at $450 \,^{\circ}\text{C}$ and Oxygen to n-butane ratio = 2.0 mol/mol. Analyses of products was achieved with an online gas chromatograph (GC) system (Agilent, 7890 N). Flame ionization detector (FID) with GC-Gas Pro capillary column was utilized in oxygenates and hydrocarbons identification. All the gases were identified with a Thermal conductivity detector (TCD) having He and Ar as carriers for the TCD columns. Standard samples were used for confirming the products. The conversion of n-butane and the selectivities of the products were obtained using based on carbon mass balance.

2.3. Characterization of catalysts

The physical properties were obtained using N2 adsorption-desorption isotherm with Micromeritics ASAP 2020 instrument, Norcross, GA. BJH adsorption method was used in obtaining the pore surface area, pore volume and average pore diameter. X-ray diffraction (XRD) patterns of the calcined catalysts were recorded from 5° to 90° diffraction angle using X-ray diffractometer (Rigaku Miniflex II) utilizing Cu K α radiation at $\lambda = 1.5406$ Å and 30 mA and 40 kV operating parameters, at a speed of 0.5°/min and step size of 0.02°. High Resolution Transmission Electron Microscopy (HRTEM), JEM-2100 F model having an acceleration voltage of 200 kV was used in analyzing the morphologies of the catalysts. Temperature Programmed Reduction (TPR) was used in determining the catalysts reducibility. This was achieved with a chemisorption instrument [27]. H₂/Ar (5 vol%/95 vol %) gas mixture at a flow rate of 50 cm³/min was used in the TPR measurement. 100 mg of the calcined catalyst was preheated for 3 h at 300 °C under inert He and then cooled to room temperature. It was then increased up to 1000 °C at the rate of 20 °C /min. The intake of H₂ was measured with TCD and CuO was applied as a reference for H₂ consumption calibration. The catalysts binding energy and bonding states were analyzed using X-ray photoelectron spectroscopy (XPS) with a PHI 5000 Versa Probe II, ULVAC-PHI Inc. spectroscope. The samples were disc-pelletized and put under a high vacuum prior to the XPS measurement.

3. Results and discussion

3.1. Catalyst property

3.1.1. Surface area and porosity

The dispersion of active sites is mainly determined using the BET surface area and catalysts pore structure [40]. The surface areas calculated using the BET equation in the linear region of the N₂ adsorption-desorption isotherms ($P/P_o = 0.05-0.3$), all the catalysts pore properties calculated using the BJH method, are presented together with the support values in Table 1. A decrease in surface area was observed for all the catalysts compared to that of the support. The same trend was also observed in the catalysts pore structure.

The N_2 adsorption-desorption isotherm of the 20 Ni-30 Bi-O/SBA-15 catalyst (normalized to support weight) and SBA-15 support is presented in Fig. 1(a) while the pore size distribution (normalized to support weight) using the adsorption branch isotherm is shown in Fig. 1(b). The isotherms are typical of type IV of the IUPAC classification due to the existence of the type H1 hysteresis loop, which is common for mesoporous materials having a well-defined cylindricallike pore channel [40]. Adsorption and desorption paths of the isotherm coincide at low relative pressure (up to $P/P_0 \approx 0.5$) which is an indication that there exists monolayer-multilayer adsorption [41]. The beginning of the hysteresis loop signifies capillary condensation within the pores, and its end corresponds to the filling of the pores. Metal loading resulted in the decrease in the height of the loop due to pore volume decrease caused by the introduction of metal species within the support mesopore [42]. The pore size distribution gave a sharp peak for both the support and the catalyst, averaged around 8-10 nm, which

Table 1

Catalysts and supports physical properties.

Catalyst:20 wt% Ni-30 wt% Bi-O/ support (Support)	BET surface area		Pore surface area		Pore volume		Average pore
	[m ² /g-catalyst] ^a	[m ² /g-support] ^b	[m ² /g-catalyst] ^c	[m ² /g-support] ^d	[cm ³ /g-catalyst] ^e	[cm ³ /g- support] ^f	nameter [nm] ^g
CSG	158	251	171	272	0.71	1.13	16.8
(SiO ₂ gel)		(242)		(263)		(1.22)	(18.6)
CSB	269	427	309	491	0.33	0.52	4.2
(SBA-15)		(657)		(1080)		(1.08)	(4.1)
CSF	388	616	397	630	1.55	2.46	15.6
(SiO ₂ foam)		(540)		(554)		(2.27)	(16.4)
CSS (SiO ₂ sol)	91	144	87	138	0.64	1.02	29.1

^aBET surface area, ^{c,e,g}Surface area, pore volume and average pore diameter measured using BJH isotherm, ^{b,d,f}Surface area and pore volume calculated to support weight base by using the equation: SA or $PV \times [\mathbb{G}(MO_x/M) + 100]/100$, where M = metal wt%; $MO_x = metal oxide wt\%$; SA = surface area; PV = pore volume.

indicate a narrow mesopore size distribution, typical of mesoporous SBA-15 material [42,43].

The pore size distribution was divided into three regions to carefully examine the effect of the metal loading on the support. The pore surface area and pore volume of the support and catalyst are presented in Table 2. The pore surface area and the pore volume of the SBA-15 catalysts decreased to almost 50 % of the support. The main decrease is observed in the region of smaller pore diameter (1.7–3.9 nm). An approximately 1.1 nm thickness of the main pore inside surface of the support has been covered by the metal oxides impregnation. This is an indication that the Ni and Bi oxide species have been loaded uniformly into both the smaller pores and main mesopores of SBA-15.

The surface area, pore volume and the average pore diameter of the catalysts with reduced Ni and/or Bi loading can be found in the supplementary material [S1]. The catalysts exhibited a decrease in surface area and pore volumes relative to the supports. Average pore diameter remained unchanged in all the catalysts.

3.1.2. X-ray diffraction (XRD)

XRD patterns of the mesoporous and conventional silica supported catalysts are presented in Fig.2. The patterns were recorded from $2\theta = 5-90^{\circ}$ and then, $2\theta = 25-35^{\circ}$ was selected to carefully study the Bi oxide phases in the catalysts. For Ni-Bi-O/SiO₂ catalyst, the main phases identified are beta-Bi₂O₃ and Bi₂SiO₅ respectively at $2\theta = 27.38^{\circ}$ and 29.0° . This new phase was previously assigned as Bi₂O_{3-a} in our previous report [27]. However, this has been confirmed as bismuth silicate phase (JCPDS 00-0287), resulting from the strong interaction of small Bi oxide species and silica support. All the characteristic peaks associated with this new phase have been successfully identified in the silica sol supported catalysts. A pure Bi₂SiO₅ phase with

Table 2

Pore	size	distribution	of Ni-Bi-O/SE	3A-15	catalyst	and	suppor	t.
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Material	Support: SBA-15		Catalyst CSB: Ni-Bi-O/SBA-15		
Pore diameter (nm)	Pore surface area (m ² /g)	Pore volume (cm ³ /g)	Pore surface area (m ² /g- support)	Pore volume (cm ³ /g- support)	
1.7-3.9 3.9-5.6 5.6-266 Total	714 (66.1) 60 (5.5) 306 (28.4) 1080 (100)	0.523 (48.4) 0.066 (6.1) 0.491 (45.5) 1.080 (100)	213 (43.2) 53 (10.9) 225 (45.9) 491 (100)	0.096 (18.5) 0.060 (11.5) 0.364 (70.0) 0.520 (100)	

peaks at $2\theta = 28.95^{\circ}$, 32.33° and 33.38° with (3,1,1), (0,2,0) and (0,0,2) diffraction lines, respectively, were identified in Ni-Bi-O/SBA-15 catalyst. This new phase assignment as Bi₂SiO₅ agreed with the reports in the literature [44–48].

To further study the degree of the Bi_2SiO_5 phase formation, the metal loadings of Ni and Bi on SBA-15 were varied and the results are presented in Fig. 3. The extent of the new phase formation depended on the presence of Ni and mainly Bi species. For NiO/SBA-15 catalyst, only NiO phase (JCPDS 00-1159) diffraction peaks at $2\theta = 36.8^{\circ}$ and 42.9° were identified. Though an optimum loading for pure Bi_2SiO_5 phase is the 20 wt% Ni and 30 wt% Bi on SBA-15 as presented in Fig. 2, the XRD data of Bi_2SiO_5 phase shown in Fig. 3 were obtained as reasonably changing with Ni loading amount. The peak intensities ascribed to Bi_2SiO_5 and beta- Bi_2O_3 were similar in 30 wt% Bi solely loaded on SBA-15. The result means that both phases were derived from the cooperation between Bi species and SBA-15, possible without Ni co-impregnation. The cooperation was caused by 1st step calcination of Bi nitrate impregnated SBA-15 at the decomposition temperature of the nitrate. The nitrate ion partially dissolves an array of silanol inside SBA-



Fig. 1. (a) N₂ adsorption-desorption isotherm; (b) pore size distribution (Blue/unfilled: SBA-15, Red/Filled: Ni-Bi-O/SBA-15). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 2. XRD profiles for 20 wt%Ni-30 wt%Bi-O/support catalyst: micro-mesoporous SiO₂: CSS, CSG, CSB, CSF.



Fig. 3. XRD patterns for loaded species in 20 Ni/SBA-15, 30 Bi/SBA-15, 20 Ni-10 Bi-O/SBA-15, 14 Ni-10 Bi-O/SBA-15, and 10 Ni-10 Bi-O/SBA-15 catalysts.

15 mesopores with semi-dry conversion method. On the other hand, the peak intensity derived from Bi_2SiO_5 was increased by increasing the Ni loading from 10 to 20 wt% while that of beta- Bi_2O_3 decreased. The Bi_2SiO_5 on SBA-15 was increased by co-impregnated Ni nitrate similar to Bi nitrate.

The well-ordered array of silanol inside SBA-15 mesopores preferably caused the Bi_2SiO_5 shell formation on SBA-15. Therefore, reverse core-shell structure with uniform mesoporosity was successfully synthesized with semi-dry conversion method. The shell was formed as Bi_2SiO_5 /SBA-15 by partially dissolving an array of silanol inside SBA-15



Fig. 4. (a) Temperature programmed reduction profile for 20 Ni-30 Bi-O/support catalyst: CSG (SiO₂ gel), CSS (SiO₂ sol), CSB (SBA-15) and CSF (SiO₂ foam). Fig. **4(b)** TPR profile for impregnation methods in Ni-Bi-O, catalyst: CSG (SiO₂ gel) and EQA-CSG (SiO₂ gel).

mesopores with impregnated bismuth nitrate. The Bi_2SiO_5 of the shell was increased by co-impregnated nickel nitrate. The layered core faced to mesopore was formed as NiO/beta- Bi_2O_3 on the shell.

3.1.3. Temperature programmed reduction

Temperature programmed reduction (TPR) was utilized to determine the level of active species reducibility (reduction temperature and extent of reduction) which is very significant for catalysts activity and selectivity to butadiene. H₂-TPR profiles of the mesoporous silica supported catalysts are presented in Fig. 4(a) and was compared with conventional silica gel and sol catalysts.

SiO₂ gel supported catalyst (CSG) showed a reduction peak of high intensity at 500 °C and a small reduction peak from 625 °C to 700 °C. This ease of reduction indicates the presence of NiO and BiO_x species with large particles and having weak metal-support interaction. The SiO₂ sol supported catalyst showed a similar pattern with SiO₂ gel catalyst even though it produced a shoulder peak with high intensity aside from the main peak at 500 °C. Mesoporous supported catalysts (CSB and CSF) however produced a broad peak at higher reduction temperature indicating the formation of highly dispersed NiO on nonreducible Bi₂SiO₅ species (caused by the strong interaction of Bi oxide species with mesoporous supports). This confirmed the existence of surface heterogeneity which is having more than one species contributing to the overall reduction process [40]. The amount H₂ consumed by the various catalysts is presented as divided into the three temperature reduction ranges in Table 3. The three ranges, low, medium, and high temperatures previously reported [19] were used to maintain continuity of discussion on the effect of support. The overall hydrogen consumption depended on the availability of easily reducible oxide species that are weakly bonded to the support surface. The medium temperature region reflects the stability of the redox cycle for

Table 3

Amount of H₂ consumed in TPR of supported 20 wt% Ni-30 wt% Bi-O catalysts.

Catalyst (Support)		Amount of H_2 consumed [m mol/g] (T _M [°C])			
	I (350–550 °C)	II (550–650 °C)	III (650–850 °C)	Total	
CSG (SiO ₂ gel)	3.74	1.12	0.13	4.99	
CSB (SBA-15)	0.88	1.04	2.43	4.35	
CSF (Foamed SiO ₂)	0.70	1.01	2.51	4.22	
CSS (SiO $_2$ sol)	3.75	1.10	0.38	5.23	

dehydrogenation.

The TPR profile comparison for conventional SiO_2 gel supported catalyst (20 Ni-30 Bi/SiO₂) and a catalyst formed using equilibrium adsorption EQA (4 Ni-22 Bi-O/SiO₂) as previously reported [19], is shown in Fig. 4(b). The EQA catalyst contained a decreased amount of NiO species, hence the main component present is Bi oxide species. Two Bi species exist on the support surface which are Bi_2O_3 and Bi_2SiO_5 and these are responsible for the two distinct reduction peaks at 500 °C and 700 °C, respectively. The decreased Ni amount resulted in a stronger anchoring of Bi species on the support. This has increased the difficulty in reducibility of the EQA catalyst compared to the conventional silica supported catalyst.

To further study the reduction profile of mesoporous support and its interaction separately with the active metal species, TPR measurement was carried out on NiO/SBA-15 and BiO_x/SBA-15 and the result is presented in Fig. 5. Structured SBA-15 can anchor both Ni and Bi species strongly more than the conventional silica. The TPR profile showed the difficulty in the reducibility of NiO and Bi oxide species on SBA-15 separately still remained after co-impregnation. It is evident that oxygen species of NiO are strongly bound to the support surface. Similarly, the Bi oxide deposition on the support led to the formation of two species similar to the case of EQA catalyst. This also agrees with the XRD profiles discussed earlier. The TPR profiles of the various combination of Ni and Bi oxides on SBA-15 support are shown in Fig. S1 (Supplementary information). All the profiles followed the same pattern indicating a stable active species redox cycle.

3.1.4. X-ray photoelectron spectroscopy

The chemical states and dispersion of the active metal oxide species in the catalysts were examined with X-ray photoelectron spectroscopy (XPS) using the Ar-etching method. A) XRD undetectable Ni oxide species highly dispersed on Bi₂SiO₅, and B) Bi₂O₃ layer sandwiched with SiO₂ layers in layered crystal Bi₂SiO₅ were successfully measured by XPS, because XPS is selectively effective for highly dispersed oxide. The XPS spectra are presented in Fig. 6. The spectra showed before (upper layer) and after (lower layer) etching spectrum of Bi and Ni species. Surface Bi species showed XPS peaks of Bi $4f_{7/2}$ at 158.9 eV and





 $4f_{5/2}$ at 164.3 eV which gave good agreement with reference data of Bi_2O_3 [49], and identified as beta phase using XRD result. Inner surface Bi species showed XPS peaks of Bi $4f_{7/2}$ at 158.4 eV and $4f_{5/2}$ at 163.8 eV having 0.5 eV decrease of binding energy from reference data of Bi_2O_3 , which was assigned as Bi_2SiO_5 phase using XRD result. Bi in this phase is slightly reduced to lower valency like Bi_2O_{3-a} where a is estimated around 0.6 based on decreasing percentage to Ni metal's value.

Surface Ni species showed XPS peaks of Ni $2p_{3/2}$ at 854.4 eV which also gave good agreement with reference data of NiO [50], which is identified as nano-particle NiO using XRD result. Inner surface Ni species showed XPS peaks of Ni $2p_{3/2}$ at 853.7 eV having 0.7 eV decrease of binding energy from reference data of NiO, which was assigned for partially reduced NiO phase using XRD result. Ni in this phase is slightly reduced to lower valency like NiO_{1-b} where b is estimated around 0.4 based on decreasing percentage to Ni metal's value. These changes suggest a moderately strong interaction between the Ni and Bi nanoparticle species with the siliceous SBA-15 support. It is also an indication of charge transfer between Ni and Bi [33].

3.1.5. High-resolution transmission electron microscopy (HRTEM)

The HRTEM image of SBA-15 supported catalyst as presented in Fig. 7 shows the size and morphology of the highly ordered pores in an array with long 1D channels. The HRTEM image agrees with the result of pore distribution measurement by N_2 adsorption. A lattice spacing of 0.21 nm which corresponded to that of the XRD detected NiO has already been presented previously [27]. XRD undetectable NiO is dispersed through Bi species phase in SBA-15. This implies that the oxides, (i) ordered silica in mesopore of SBA-15, (ii) Bi₂SiO₅ (and beta-Bi₂O₃) ordered on the silica of SBA-15 framework and (iii) NiO species dispersed on the Bi species form a reverse core-shell layered catalyst system.

3.2. Catalyst performance evaluation

3.2.1. Schematic conversion route of n-butane to products

The proposed conversion route from the n-butane to the main product together with the byproducts is presented in Scheme 1. The major pathways are the 1st dehydrogenation from n-butane to butenes (1-butene and 2-butene), 2nd step dehydrogenation to butadiene, and cracking (to mainly ethylene, propylene, methane, CO, and CO_2). The selectivity to either dehydrogenation or cracking pathways depend on the strength of the acid and basic sites. The role of the active metal oxide species in enhancing the production of the desired product is discussed in the next section.

3.2.2. Effect of bismuth oxide loading

The effect of Bi amount loaded to the Ni-Bi-O/mesoporous silica SBA-15 system on the catalyst performance is presented as comparison between 30 wt% and 10 wt% loading as presented in Table 4. Decreasing the Bi amount slightly improved both n-butane conversion (activity) and butadiene (BD) selectivity resulting to increase in BD yield increase. This is mainly due to an increase in 2nd step dehydrogenation selectivity. Comparing the Bi oxide species present in 20 Ni-30 Bi and 20 Ni-10 Bi as depicted by XRD measurements (Figs. 2 and 3), the beta-Bi₂O₃ phase appeared in the case of 10 wt% Bi loading. While Bi₂SiO₅ species is still major in the Ni-Bi-O/mesoporous silica SBA-15 system, the presence of beta-Bi₂O₃ species thereby enhancing the catalyst activity with selectivity towards 2nd step dehydrogenation pathways.

3.2.3. Effect of nickel oxide loading

The effect of Ni amount loaded to the Ni-Bi-O/mesoporous silica SBA-15 system on the catalyst performance is presented as comparison from 10 wt% to 20 wt% loading as shown in Table 4. The BD yield



Fig. 6. XPS spectra for 20 Ni- 30 Bi-O on SBA-15: [a] Bi [b] Ni, upper: surface, lower: inner surface.



Fig. 7. HRTEM image of 20 Ni-30 Bi-O/SBA-15 mesoporous silica catalyst.

slightly increase with successive increase in Ni amount due to increase of activity, while BD selectivity slightly decreased. Comparing the Bi oxide species present in 10 Ni-10 Bi, 14 Ni-10 Bi and 20 Ni-10 Bi as depicted by XRD measurements (Fig. 3), the beta-Bi₂O₃ phase decreased with increasing Ni amount while Bi₂SiO₅ phase increase. The presence of beta-Bi₂O₃ species works important role for BD selectivity in the Ni-Bi-O/mesoporous silica SBA-15 system, while the activity and

 Table 4

 Comparison of Ni/Bi as the metal amo

Comparison of Ni/Bi as the metal amount in the supported catalyst at 450 $^\circ\text{C}$ and $O_2/n\text{-}C_4H_{10}$ = 2.0.

Catalyst	CSB HN-HB	CSB HN-LB	CSB MN-LB	CSB LN-LB
Support Ni/Bi [wt%]/[wt%]	SBA-15 20/30	SBA-15 20/10	SBA-15	SBA-15
(Ni/Bi atomic ratio)	(2.4)	(7.2)	(5.0)	(3.6)
n-C ₄ H ₁₀ conversion [%] Selectivity ^a [C%]	28.9	30.0	2/./	23.5
DH	75.2	71.8	78.4	83.5
2-C ₄ H ₈	15.4	14.6	15.0	17.8
1-C ₄ H ₈	12.3	7.8	10.2	11.2
BD	47.5	49.4	53.2	54.5
PO	24.8	28.2	21.6	16.5
OC	19.7	28.2	17.1	12.1
CO	5.1	0.0	4.5	4.4
$(1-C_4H_8 + BD)^b$	59.8	57.2	63.4	65.7
$BD/(1-C_4H_8 + BD)$ % ^c	79.4	86.3	83.9	82.9
BD yield	13.7	14.8	14.7	12.8

^a DH: dehydrogenation products, BD: butadiene, PO: partial oxidation products, OC: oxygenates and the cracked, and CO: carbon monoxide.

^b 1-butene selectivity at 1st step dehydrogenation.

^c Selectivity at 2nd step dehydrogenation.

2nd step dehydrogenation selectivity depend on amount of Ni oxide species. The beta- Bi_2O_3 species improved Ni oxide species thereby enhancing selectivity toward 2nd step dehydrogenation pathways with



Scheme 1. Schematic representation of n-butane conversion route to products.

Table 5

Comparison of Bi/Ni 0.42 to 0.14 as sub metal amount in Ni-Bi-O/support catalysts at 450 °C, O_2/n -C₄H₁₀ = 2.0.

Catalyst	CSG-LB (HB)	CSB-LB (HB)	CSF-LB (HB)	CSS-LB (HB)
Support Ni/Bi [wt%]/[wt%] Ni/Bi atomic ratio n- C ₄ H ₁₀ conversion	SiO ₂ gel 20/10 (20/ 30) 7.2 (2.4) 29.3	SBA-15 20/10 (20/ 30) 7.2 (2.4) 30.0	SiO ₂ foam 20/10 (20/ 30) 7.2 (2.4) 34.1	SiO ₂ sol 20/10 (20/ 30) 7.2 (2.4) 35.7 (35.6)
[%]	(17.6)	(28.9)	(29.2)	
PO OC CO (1- $C_4H_8 + BD$)* ² BD/(1- $C_4H_8 + BD$) %* ³	67.5 (79.1) 16.6 (21.7) 18.0 (25.5) 32.9 (31.9) 32.6 (20.9) 26.7 (17.5) 5.9 (3.4) 50.9 (56.4) 64.6 (55.6)	71.8 (75.2) 14.6 (15.4) 7.8 (12.3) 49.4 (47.5) 28.2 (24.8) 28.2 (19.7) 0.0 (5.1) 57.2 (59.8) 86.3 (79.4)	69.0 (77.6) 18.8 (17.2) 11.4 (14.8) 38.8 (45.6) 31.0 (22.4) 30.5 (21.0) 0.5 (1.4) 50.2 (60.4) 77.3 (75.4)	57.4 (78.3) 11.3 (18.6) 11.1 (18.1) 35.0 (41.6) 42.6 (21.6) 41.2 (20.5) 1.4 (1.1) 46.1 (59.7) 76.0 (69.7)
BD yield	9.6 (5.6)	14.8 (13.7)	13.2 (13.3)	12.5 (14.8)

 $*^{1}$, $*^{2}$ and $*^{3}$ are same as Table 4.

suppressed cracking. The mixture-balanced 20 wt% Ni-10 wt% Bi-O/SBA-15 catalyst effectively works as NiO-(beta-Bi₂O₃)-Bi₂SiO₅/SBA-15 system for oxidative dehydrogenation of n-butane to butadiene.

3.2.4. Effect of Bi amount loaded in Ni-Bi-O/mesoporous SiO_2 system on catalyst performance

The effect of Bi amount decreased from 30 wt% to 10 wt% on the catalyst performance was investigated for the different silica supports in Ni-Bi-O/support system. The results are presented in Table 5. Decreasing Bi amount showed negative effect for BD selectivity over SiO₂ foam and SiO₂ sol catalyst systems. The decreased caused a small improvement of BD selectivity in SiO₂ gel catalyst system while the activity was largely improved until equivalent to the other systems. It was considered that these negative or minor effects of decreased Bi amount on BD selectivity are due to the existence of beta-Bi₂O₃ species in the 20 wt% Ni- 30 wt% Bi-O/support shown in Fig. 2. As 1) the importance of beta-Bi₂O₃ species for BD selectivity and 2) the preparation of the XRD undetected Ni oxide with the beta-Bi₂O₃ species through

controlled calcination as reported in Ni-Bi-O/gamma-Al₂O₃ catalyst system [16,17], Ni oxide species work in synergy with the beta-Bi₂O₃ species to enhance BD selectivity also in the mesoporous SiO₂ support system.

3.3. Model of catalyst system from characterization and catalyst performance

Based on the characterization by instrumental analyses with catalyst preparation pathway and catalyst performance in oxidative dehydrogenation of n-butane to butadiene, the schematic drawing of the new mesoporous mixed oxides NiO-(beta-Bi₂O₃)-Bi₂SiO₅/SBA-15 system is shown in Scheme 2. NiO hierarchically on (beta-Bi₂O₃)-Bi₂SiO₅ nano-particle cohabitation/SBA-15 reflects the preparation scheme for Ni-Bi-O/SBA-15 catalyst as "reverse core-shell" structure.

4. Conclusion

New NiO-(beta-Bi2O3)-Bi2SiO5/SBA-15 catalyst system showed good performance in the oxidative dehydrogenation of n-butane to butadiene, resulting from the formation of beta-Bi₂O₃ and Bi₂SiO₅ phases on the catalyst. The change in phase between beta-Bi₂O₃ and Bi₂SiO₅ was determined by the Ni/Bi ratio. Reverse core-shell structure with uniform mesoporosity catalytically active for ODH of n-butene to butadiene was successfully synthesized with semi-dry conversion method. The shell was formed as Bi2SiO5/SBA-15 by partially dissolving an array of silanol inside SBA-15 mesopores with impregnated bismuth nitrate. The Bi2SiO5 of the shell was increased by co-impregnated nickel nitrate. The layered core faced to mesopore was formed as catalytically active NiO/beta-Bi₂O₃ on the shell. The degrees of formation of Bi₂SiO₅ and beta-Bi₂O₃ phase reflected in the butadiene selectivity through reducibility as evident from TPR and XRD studies. The catalyst with balanced loadings of 20 wt% Ni and 10 wt% Bi exhibited a clear superiority in the catalytic performance compared to the other catalysts. The existence of beta-Bi₂O₃ phase enhanced BD selectivity of active NiO species with suppressed cracking.

CRediT authorship contribution statement

G. Tanimu: Investigation, Methodology, Writing - original draft, Writing - review & editing. **A.M. Aitani:** Conceptualization, Writing review & editing. **S. Asaoka:** Conceptualization, Methodology,



Scheme 2. Preparation scheme for Ni-Bi-O/SBA-15 catalyst: NiO on hierarchical (beta-Bi₂O₃)-Bi₂SiO₅ nano-particle cohabitation/SBA-15 as "reverse core-shell" structure.

Supervision, Writing - review & editing. H. Alasiri: Conceptualization, Resources, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110893.

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