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Faujasite silicalites for oxidative dehydrogenation of *n*-octane: Influence of alkali metals, gallium, and boron on catalyst activity

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ABSTRACT

The sol-gel method was used to synthesize faujasite type silicalites bearing gallium and boron in the framework. Barium and sodium were used as charge balancing cations since isomorphic substitution of SI^{4+} by Ga^{3+} or B^{3+} results in a negative excess charge of the framework. The successful synthesis of this type of silicalites (GaBaY-S, BBaY-S, GaBBaY-S(IE), GaNaY-S) was confirmed using powder-XRD. SEM analysis showed that the morphology of the catalysts with respect to particle size depended on the framework metals and the charge balancing cation used. Framework Ga containing catalysts showed smaller particle size compared to B containing catalysts. So-dium also yielded a smaller particle-sized catalyst compared to barium. The catalysts were tested in the continuous flow oxidative dehydrogenation (ODH) of *n*-octane, and the catalytic results showed dependence on the active metal reducibility and acid-base character of the catalysts. At iso-conversion of 8 \pm 1 %, the least acidic BBaY-S gave the highest selectivity to octenes (40 %) and the lowest selectivity to COX (28 %), and the most acidic GaNaY-S showed the opposite results with octenes at 17 % and COX at 56 %. The catalysts (BBY-S and GaBBaY-S(IE) with least total acidity had the greatest quantity of strong acid sites which were attributed to Lewis acid sites, confirmed by the pyridine IR analysis. The GaNaY-S, with the highest total acidity, had the least strong acid sites.

1. Introduction

Zeolite materials belong to the tectosilicate family of minerals and are known for their pronounced acidity. They are used industrially as adsorbents, and as cracking and isomerization catalysts [1]. Zeolites have interesting properties, such as thermal stability, high surface area, well-defined pores; also their ease of synthesis and modification has attracted the use of these materials in several catalytic applications [2, 3]. However, the use of zeolites in the ODH of paraffins is yet to be fully exploited, even though there have been some studies carried out, which focused on the ODH of paraffins using zeolitic materials.

Rahmani et al. [4] prepared a Cr-ZSM-5 catalyst promoted with different loadings of ceria for the ODH of ethane using CO_2 as the oxidant. Catalytic results in this study showed that CeO_2 addition enhanced catalytic activity of Cr-ZSM-5 and also suppressed the deactivation rate of the catalyst. The achieved overall ethene yield for this study was 61.1 %. The drawback of this reaction was the elevated temperatures used which were up to 700 °C.

In another study by Alamdari and Karimzadeh [5], ODH of liquid

petroleum gas was carried out using a modified H-ZSM-5 within an electric field. The parent zeolite was modified by impregnation to yield Na, Cu, Zn, and Fe modified H-ZSM-5. At 510 $^{\circ}$ C, FeH-ZSM-5 showed superior activity, yielding 50.54 % of olefins at 92.81 % conversion. The catalysts showed coking at the end of the reaction, though less than other conventional methods.

Cheng et al. reported a study on the ODH of ethane using CO_2 as the oxidant and Ga supported on Na-ZSM-5 as a catalyst. Conversion above 10 % and ethene selectivity above 90 % were obtained at 650 °C, and the catalytic behavior of the prepared catalysts was explained as a result of the dispersion of GaO_x species on the surface of the zeolite, resulting in a large number of Lewis acid sites for the dissociative adsorption of ethane [6].

Apart from the MFI type zeolite, other forms of zeolites have been used in the ODH of paraffins. FAU (NaY, NaX), LTA (NaA), Mordenite, and clinoptilolite were used by Aliev et al. for the ODH of cyclohexane. Clinoptilolite gave better results in terms of conversion (23.5 %) and hexene yield (15.8 %). All other tested catalysts suffered from similar limitations, which was favoring more side reactions leading to the

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formation of oxygenates and carbon oxides [7].

Even though zeolites are used extensively in the ODH of short-chain alkanes, quick deactivation due to coke deposition and their tendency to promote deep oxidation is the reason why most researchers shy away from using zeolites in ODH reactions involving medium to long-chain paraffins. Because of the already mentioned superior properties of zeolites [2,3], there is still a need to find a method of modification that can eradicate the undesirable properties of zeolites while maintaining their stability in the ODH of medium to long-chain paraffins. Low-value linear medium-chain alkanes provide potentially a cheaper alternate feedstock to chemical reactions such as olefins and aromatics which are one of the key building blocks in the chemical industry.

Zeolites offer a variety of methods in which they can be tuned, viz. ionic exchange, isomorphic substitution, dealumination, and desilication. For this study, we looked at modifying a faujasite type zeolite by isomorphic substitution of framework aluminium with gallium and boron to yield another type of material called a silicalite. A silicalite is defined as a silica polymorph with a structure similar to zeolite [8]. Previous studies focussed on the syntheses and modification of the MFI and MCM type silicalites [9-13]. The use of MCM type zeolites analogs is mainly as adsorbents, and they are studied very little in paraffin activation owing to their low stability. MFI silicalites are known and have been used in several catalytic reactions. The most known MFI silicalite is the titanium-based TS-1 silicalite [14,15]. Both MCM and MFI type zeolites have been studied for ODH of alkanes, and both systems suffer from deactivation and production of COx as one of the main products [16,17]. Therefore, using a relatively weak acidic material (FAU) with relatively bigger pores, composed of boron or gallium in the framework, which possesses relatively low acidity and better dehydrogenation activity compared to aluminium in the zeolite matrix [18,19], could improve the catalytic activity of this material in ODH of n-octane. Therefore, we now report on these studies.

2. Materials and experimental methods

2.1. Catalysts preparation

Three of the studied catalysts (BBaY-S, GaBaY-S, GaNaY-S) were prepared using a modified sol-gel method [20]. Catalysts coding was based on the constituents used for the synthesis, where B = boron, Ba = barium, Ga = gallium, Na = sodium, Y = faujasite type and S = Silicalite. For BBaY-S synthesis, a 500 mL sealable Teflon beaker was used to dissolve 14.53 g of BaCl₂.2H₂O (Merck NT Laboratory Suppliers) in 37.5 g of distilled water. This was followed by the addition of 1.144 g of boric acid (Merck Chemicals) under agitation for 2 h to yield a borate solution. After 2 h, 30 wt% colloidal silica solution (Sigma Aldrich - 26.44 g) was slowly poured into the barium borate solution under vigorous stirring. The beaker was tightly sealed and transferred to a 25 °C oil bath and aged for 24 h with constant stirring. Thereafter the solution was aged at 40 °C for 24 h, and finally at 80 °C for 48 h with no stirring. The recovered solid was filtered under vacuum and washed with double distilled water until the pH was 8-9 and dried at 110 °C overnight. The remaining catalysts were prepared using a similar procedure as described above. Synthesis of GaBaY-S and GaNaY-S used 3.358 g of gallium nitrate (Sigma Aldrich) in place of boric acid. For GaNaY-S, sodium chloride (Sigma Aldrich - 20.28 g) was used in place of barium chloride as a charge balancing cation. The Si/M (M = Ga or B) was kept constant at 2.7 \pm 0.3 for all the prepared catalysts. The fourth and last catalyst was prepared by ionic exchange [21], where 8 g of the previously prepared BBaY-S was mixed in a round bottom flask with a 100 mL solution of gallium nitrate (0.90 g) dissolved in double-distilled water. The mixture was then stirred at 80 °C for four hours, and then the catalyst was filtered under vacuum and washed repeatedly with double distilled water and then dried at 110 °C overnight. The resulting catalysts were coded as GaBBaY-S(IE). The prepared catalysts were all calcined under flowing air at 550 °C for six hours before characterization

and testing.

2.2. Catalysts characterization

Powder X-ray diffraction patterns for structure and phase identification were carried out using a Bruker D8 advance diffractometer equipped with a graphite monochromatic filter operated at 40 kV and 40 mA. The radiation source was CuK α with a λ of 1.5406 nm. The data collection was done at a step and scanning speed of 0.02° and 0.2 s^{-1} respectively and at a 2-theta range of 5°–90 °. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed to quantify the elemental composition of the material using a Perkin Elmer Optima 5300 DV spectrometer. Standards of 1000 ppm Ga, Na, B, Ba, and Si were all purchased from Fluka. N2 physisorption analysis was performed using a Micromeritics Tristar II Surface area and porosity analyzer operated at - 196 °C. Finely ground samples were degassed for one hour at 90 °C, then at 200 °C for another hour, and then at 400 °C for 6 h under the flow of N₂ before analysis, using a Micromeritics Flow Prep 060 instrument. A Micromeritics 2920 Autochem II Chemisorption Analyser was used for all temperature-programmed experiments. Temperature programmed reduction (TPR) profiles were obtained by a published procedure [22]. Ammonia temperature-programmed desorption (NH₃-TPD) experiments were carried out using about 0.06 g of catalysts by a reported procedure [23]. CO₂-TPD was carried out using 0.06 g of catalyst. The sample was heated to 400 °C under a stream of helium (30 mL/min) for 30 min, followed by a temperature decrease to 80 °C under the same stream of helium before loading the sample with carbon dioxide. The TPD tests were carried out by heating the samples at 10 °C/min until 900 °C in a constant He flow. Pyridine IR spectra were collected using a Perkin Elmer Spectrum 100 FT-IR Spectrometer equipped with a Universal ATR Sampling Accessory. Samples of 0.5 g were treated with 1.0 mL of liquid pyridine. After 3 h the samples were heated to 100 $^\circ\text{C}$ and 150 $^\circ\text{C}$ under vacuum to remove excess and physisorbed pyridine. The samples were cooled to room temperature before collecting the spectra in the region of $1400-1700 \text{ cm}^{-1}$. For morphology and surface structure, SEM images were obtained using a Zeiss Ultra Plus field emission gun scanning electron microscope (FEG-SEM) with Smart SEM Software. Before analysis, the samples were coated with gold using a Q150R series high vacuum Quorum sputter coater.

2.3. Catalytic testing

Catalysts testing was conducted at a temperature of 450 $^\circ\text{C}$ in a laboratory-scale continuous-flow fixed-bed, gas phase reactor. The reactor tube was stainless steel with an inner diameter of 10 mm. Different ratios of Air and N2 were delivered to the reactor as the oxidant and diluent gas respectively to achieve iso-conversion. Reactions were performed with *n*-octane (Merk, assay > 98 %) and concentration in a gaseous mixture (v/v) above *n*-octane's upper flammability limit. For all the reactions the concentration of n-octane was kept at 6 %. A calibrated Lab Alliance Series II HPLC Pump was used to feed n-octane into the system and the mass delivered was weighed using an electronic balance. The n-octane fed was maintained in the gaseous phase by the heated feed lines at 130 °C using heating tape. The temperature was controlled using a CB-100 RK temperature control unit with an internal replay and monitored using K-type thermocouples. All the reactions were carried out using 1.0 mL of a pelletized catalyst (pellet sizes were between 600 and 1000 µm) between two thin layers of glass wool positioned at the hottest zone of the calibrated reactor block. The spaces in the reactor tube were packed with 24 grit carborundum and stoppered by glasswool on both ends. Total gas flow was measured using a Ritter drum type wet gas flow meter. All liquid products and unreacted feed were collected in a cylindrical stainless-steel vessel, cooled to \approx 3.0 °C. A Perkin Elmer Clarus 400 GC fitted with a 30 m $\times 530$ µm Supelco Carboxen 106 PLOT column and a thermal conductivity detector was used

to analyze COx products. Liquid and gaseous products were analyzed using a Shimadzu GC-2025, fitted with a 50 m $\times 200$ µm PONA capillary column and flame ionization detector. All the data points were obtained at least in triplicate with carbon balances ranging from 95 to 102 % and an error of \pm 2 %.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. Powder XRD

Zeolites are separated into different families which are named according to three-letter designations by the International Zeolite Association Structure Commission. Therefore each group is shown by the specific fingerprint when it comes to powder XRD of the material. For the faujasite type silicalites synthesized in this study, the XRD diffractograms obtained showed typical peaks associated with the faujasite framework (Fig. 1) [24–26]. All the prepared catalysts showed peaks at slightly shifted 2-theta ranges, and the shifts were different with the different metals incorporated in the framework and extra framework positions of the silicalites. The shifts are due to the chemical shifts induced by the alteration of the lattice parameters as a result of Na, Ba, Ga, and B incorporation with different electrostatic forces and atomic radii [27]. The ionic exchange procedure did not affect the framework of the faujasite materials prepared. This was confirmed by the sharpness of the XRD peaks that were attained after this procedure. The sharpness of the XRD peaks obtained also gives insights into the high crystallinity of the silicalites. No oxide peaks were detected in all the silicalite catalysts, confirming that the metal loadings were well dispersed in the framework and extra framework of the catalysts [28].

3.1.2. Scanning electron microscopy

The synthesis of silicalites is generally done in the presence of basic charge balancing cations, which influence the crystallization rate, crystal morphology, and size. Apart from the charge balancing cations, different heteroatoms also have different effects on the silicalite nucleation and crystal growth [29]. The synthesized catalysts for this study contain both barium (BBaY-S, GaBBaY-S(IE), and GaBaY-S) and sodium (GaNaY-S) as charge balancing cations. SEM images in Fig. 2 show that all the catalysts have the typical cubic shape of the faujasite type materials [30]. However, the crystal sizes of the catalysts differ, with sodium-based GaNaY-S having the smallest crystals. The small size of



the sodium-based silicalite crystals may be due to Na⁺ weak solubility to metallosilicate gels, which leads to the formation of aggregates of very small crystals [29]. Amongst the barium based silicalites, Ga containing catalysts showed a smaller crystal size than the boron-containing catalyst. This could be attributed to the differences in atomic radii of gallium and boron, which influence crystal growth differently [30].

3.1.3. Surface studies

The molar compositions of the prepared catalysts obtained from ICP-OES were as follows, GaNaY-S was (7.7 Na₂O: 2.40 Ga₂O₃: 11.6 SiO₂: 288 H₂O), GaBBaY-S(IE), (3.9 BaO: 1.8.0 B₂O₃: 1.0 Ga₂O₃: 11.6 SiO₂: 288 H₂O), GaBaY-S (3.9 BaO: 2.4.0 Ga₂O₃: 11.6 SiO₂: 288 H₂O) and BBaY-S (3.9 BaO: 1.8.0 B₂O₃: 11.6 SiO₂: 288 H₂O). Brunauer-Emmett-Teller (BET) surface area analysis (Table 1) showed that the catalysts with the smallest crystals (GaNaY-S) have the highest surface area and BBaY-S with the biggest crystals showed the smallest surface area [29–31]. Pore volume and size decreased with the increase in surface area [32], with the Na containing catalyst having the smallest size. The synthesis techniques and modifications used in the study have resulted in larger pores compared to most FAU-type zeolites, and similar observations have been reported [32,33].

3.1.4. Temperature programmed desorption with NH₃ and CO₂

Ammonia TPD was carried out to study the changes in acidity influenced by the introduction of Na, Ba, Ga, and B species at different silicalite locations. The obtained results (Table 2) for the prepared samples showed three characteristic regions of ammonia desorption, at the low-temperature from 200 °C to 300 °C (weak acid sites, W), medium temperature from 300 °C to 400 °C (medium strength acid sites, M), and high-temperature from 400 °C to 600 °C (strong acid sites, S) (Fig. S3) [34]. Weak acid sites in zeolitic materials are due to the adsorption of NH3 on the extra framework protons to form a loosely bound NH₄⁺, in the absence of protons, the adsorption is usually associated with Na⁺ [34]. Amongst the prepared catalysts, the Na containing catalysts contained more weak acid sites which can be associated with weak Lewis acid sites. The medium strength acid sites may be attributed to Brønsted acid sites, and the framework gallium containing catalysts (GaBaY-S and GaNaY-S) showed to have more of these sites, due to the high electronegativity of Ga compared to B, which increases the acid strength of the Si-OH-Ga bridging group [35]. Above 400 °C, the acid sites in that region can be assigned both to Lewis acid sites due to Ga^{3+}/B^{3+} and Brønsted acid sites. Framework boron-containing samples (BBaY-S and GaBBaY-S(IE)) showed more of these strong acid sites, and because of the small electronegativity of B compared to Ga species, the Si-OH-B bridging group strength is lower, and thus this adsorption may be associated with Lewis acid sites. GaNaY-S showed a low quantity of the strong acid sites, and because of the higher strength of the Si-OH-Ga bridging group in this catalyst, this was attributed to Brønsted acid sites. Gallium introduced by ionic exchange increased both the adsorption of NH₃ and CO₂ by the sites assigned as Lewis acid sites, and this agrees with the results since Ga introduced by ionic exchange sits on the Lewis acid sites of the catalyst (extra framework) [36, 37]. The total acidity of the catalysts increased with the introduction of Ga instead of B, and that is in line with previous studies [1,38].

CO₂-TPD analysis was carried out and adsorption peaks at three regions were obtained, at 50 °C–160 °C for weak basic sites (W), 160 °C–400 °C for moderate basic sites (M), and 550 °C–700 °C for strong basic sites (S) [39,40]. Boron containing catalysts contained stronger and more basic sites, while gallium decreased the basicity of the prepared catalysts (Table 3). This is due to the strong covalent hydroxyl bond for the boron-containing catalysts which lowers its acidity. Barium is more alkaline compared to sodium and it increases the basicity of the oxygen atoms present in the silicalite framework, hence GaBaY-S is more basic than GaNaY-S.



Fig. 2. SEM micrographs of (A) BBaY-S, (B) GaBBaY-S(IE), (C) GaBaY-S, (D) GaNaY-S.

Table 1

BET Surface properties analysis of the fresh silicalite	es catalysts.
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Catalysts	BET (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
BBaY-S	492	0.32	3.95
GaBBaY-S(IE)	665	0.30	3.26
GaBaY-S	697	0.28	3.20
GaNaY-S	709	0.22	3.06

Table 2

Acid properties of different silicalite catalysts studied by NH₃-TPD.

	Acidity amount (μ mol g $-^1$)			
Catalysts	W (200 °C–300 °C)	M (300 °C–400 °C)	S (400 °C–600 °C)	Total acidity
BBaY-S	0.80	0.62	3.9	5.3
GaBBaY-S	2.8	0.44	5.5	8.7
(IE)				
GaBaY-S	7.5	4.8	0.60	12.9
GaNaY-S	15.9	2.8	1.11	19.8

Table 3

Base properties of different silicalite catalysts studied by CO2-TPD.

	Basicity amount (µmol g ⁻¹)			
Catalysts	W (0 °C–160	M (160 °C–400	S (> 400	Total
	°C)	°C)	°C)	Basicity
BBaY-S	3.6	18.7	6.4	28.7
GaBBaY-S	1.5	10.5	11.1	23.1
GaBaY-S	9.1	6.8	1.44	17.3
GaNaY-S	2.6	3.7	5.0	11.3

3.1.5. Pyridine IR

The nature of acid sites analysis was carried out by adsorption and desorption of pyridine at 100 °C and 150 °C. At 100 °C, (Fig. S1) all samples showed similar IR bands due to physisorption of pyridine at 1440, 1482, 1580, a shoulder at 1595, and a weak band at 1633 cm⁻¹. The bands at 1440 and 1633 cm⁻¹ corresponds to pyridine molecules on Lewis acid sites, while the band at 1482 cm⁻¹ can be attributed to both Lewis and Brønsted acid sites. The bands at 1580 and 1595 cm⁻¹ correspond to pyridine molecules on Brønsted acid sites [41–43]. The sample without gallium (BBaY-S) showed a decrease in the intensity of all the bands, which can be related to the low number of acid sites. This is in agreement with the ammonia TPD results. The Intensity of all the bands shows that the samples contain more Lewis sites compared to Brønsted sites.

Upon increasing the temperature to 150 °C, (Fig. 3). All the bands associated with Brønsted acid sites disappeared, except for the most acidic silicalite (GaNaY-S). This suggests that GaNaY-S contained stronger Brønsted acid sites compared to the Ba containing catalysts. These results suggest that the group two alkaline earth metals poison the Brønsted acid sites of the catalysts while increasing the Lewis acid sites caused by the framework Ba²⁺ [44].

3.1.6. Temperature programmed reduction

To get insight into the catalytic activity of the prepared catalysts in ODH reactions, the redox properties of the active metal oxide are important. Temperature programmed reduction profiles of the prepared catalysts are shown in Fig. 4. No reduction peak was observed for BBaY-S, since the boron hydrogen reaction energy barrier is very high, therefore oxides of boron did not reduce under analysis conditions. The reduction peaks at a lower temperature for all the catalysts are due to the chemisorption of hydrogen to Ga⁺ species. For GaBBaY-S(IE), there was a small broad reduction peak starting around 360 °C to above 450 °C



Fig. 3. Pyridine FT-IR of (A) BBaY-S, (B) GaNaY-S, (C) GaBaY-S(IE), (D) GaBaY-S. *Pyridine evacuation carried out at a temperature of 150 °C.



Fig. 4. Temperature Programmed Reduction profiles of (A) GaBBaY-S(IE), (B) GaNaY-S, (C) GaBaY-S.

associated with the reduction of extra framework Ga^{3+} to Ga^+ . Both GaBaY-S and GaNaY-S showed this Ga^{3+} to Ga^+ broad reduction peak at temperatures above 500 °C to up to 700 °C [45]. This suggests that Ga in the lattice does not reduce easily compared to Ga located at the outside of the lattice. The reduction peak of GaBBaY-S(IE) was smaller because of the lower gallium content used in the synthesis. The trace for GaBaY-S did not come back to the baseline, which could suggest an incomplete reduction of gallium in this sample.

3.2. Catalytic results

To achieve iso-conversion, the prepared catalysts were tested at varying GHSV ranging from 6000 h^{-1} to 8000 h^{-1} . Boron based BBaY-S (not reducible) and GaBaY-S (high-temperature reduction profile) were tested at 6000 h^{-1} and GaBBaY-S(IE) and GaNaY-S (low-temperature reduction profiles) at 8000 h^{-1} , to achieve iso-conversion of about 8 %. The testing of all the prepared catalysts gave an array of the previously reported products in the ODH of *n*-octane [22,23]. The activity of BBaY-S in ODH of *n*-octane, with no active metal (Ga) comes from the

ability of boron to abstract hydrogen from the hydrocarbon by the -O-B-O- Lewis sites, to form the B-OH species (Scheme S1). This activity is low, and the catalyst deactivates quickly by coke deposition (Figs. S2 & S3). The introduction of gallium increased the dehydrogenation activity of the catalysts and increased the stability of the catalysts against coke deposition. Gallium incorporated in the catalysts facilitates the burning of coke to form CO₂, hence Ga containing catalysts showed more selectivity to COx products compared to BBaY-S. Results in Fig. 5 show that BBaY-S gave selectivity of 40 % to octenes, which is the highest of all the tested catalysts, followed by another boron-containing catalyst (GaBBaY-S(IE)) with a selectivity of 35 %. GaBaY-S and GaNaY-S gave octene selectivities of 33 % and 17 % respectively. The lower octene selectivity of the last two mentioned catalysts is due to the high acidity (adsorbs the formed octene) and low basicity of the catalysts, which limits olefin desorption and leads to deep oxidation (combustion) of the olefin products. The presence of the strong Brønsted acid sites on the GaNaY-S also leads to the deep oxidation of the feed molecule, increasing COx formation. Therefore, the catalyst with the lowest octene selectivity has the highest COx selectivity (56 %) and vice versa.



Fig. 5. Product selectivity towards cracked products, aromatics, carbon oxides, oxygenates and octene isomers at iso-conversion (8 \pm 1%) of *n*-octane at a fixed temperature of 450 °C.

Aromatic products' selectivity of the framework gallium-based catalysts were both above 10 %, whereas the extra framework substituted gallium (GaBBaY-S(IE)) and BBaY-S produced less aromatic products. This agrees with previous findings that aromatization takes place more inside the lattice of the shape-selective zeolitic materials [46]. Oxygenates production for all the catalysts was constant at around 9–10 %, except for the Na based catalyst which facilitated the decomposition of these products to COx owing to its strong Brønsted acid sites.

The cracked products distribution showed to be influenced by the charge balancing cations (Fig. 6). Barium containing catalysts favored the formation of pentene and hexene more than ethene and propene. The Na based catalyst was more selective towards the formation of ethene and propene. The different charge balancing cations (Ba and Na) lead to different pore volumes and sizes, with Ba containing catalysts having bigger pore volumes and sizes. This allowed oligomerization of the C-2 and C-3 fragments to form C-5 and C-6 fragments in the mesopores of the catalysts. Over the Na containing catalyst, the higher alkene was easily cracked on strong Brønsted acid sites, resulting in high contents of C-2 and C-3 alkene fragments. There were no C-1 cracked products observed in the product distribution of all the tested catalysts, and this was due to the mild temperature and pressure used to carry out the reactions. Under mild temperature and pressure, primary carbonium ions are unstable. The absence of alkane cracked products observed in the product spectrum was due to the high Lewis acidity of the catalysts compared to their Brønsted acidity. Comparing the results obtained from this study to a previous study where a commercial NaY zeolite was modified by barium [46], the selectivities to octenes and COx obtained

were both just above 30 %, whereas this study was able to achieve octene selectivities of about 40 % and COx selectivity of less than 30 %.

4. Conclusions

In this study, we were able to synthesize a series of faujasite type silicalites containing different heteroatoms in the framework. Characterization by powder XRD and SEM reiterated that different heteroatoms affect the lattice parameters and the crystal size of the catalysts, but do not change the overall shape of the material. Boron incorporation in the framework of the metallosilicates enhances the covalency of the OH bond, which results in a less acidic catalyst compared to the gallium incorporated catalysts. Barium exchanged catalysts showed less Brønsted acid sites and more basic sites compared to sodium exchanged catalyst. The activity of the prepared catalysts was proportional to the reducibility of the active metal as confirmed by the TPR analyses. The study also demonstrated that the non-reduceable boron in the silicalite framework was active towards the ODH of n-octane and also leads to the most selective catalyst towards octene production. The drawback of these catalysts was deactivation due to coke formation. The introduction of gallium by an ionic exchange in the extra framework of BBaY-S produced a catalyst that is stable against coke deactivation, but the octene selectivity was compromised, 40 % for BBaY-S and 35 % for GaBBaY-S (IE) at similar conversion. The study also showed that Na based catalysts favoured the formation of C-2 and C-3 alkenes, whereas Ba favoured C-5 and C-6 alkenes more, which could be attributed to the different atomic sizes of Na and Ba, which leads to the different



Fig. 6. Selectivity towards different cracked products, at iso-conversion (8 \pm 1%) of *n*-octane at a fixed temperature of 450 °C.

regioselectivity.

CRediT authorship contribution statement

Siyabonga S. Ndlela: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. Holger B. Friedrich: Conceptualization, Methodology, Resources, Data curation, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. Mduduzi N. Cele: Conceptualization, Methodology, Data curation, Writing - review & editing, Visualization, Supervision.

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

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