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# Barium promoted Ni/Sm<sub>2</sub>O<sub>3</sub> catalysts for enhanced CO<sub>2</sub> methanation

Nur Athirah Ayub, Hasliza Bahruji \* and Abdul Hanif Mahadi

Low temperature CO<sub>2</sub> methanation is a favorable pathway to achieve high selectivity to methane while increasing the stability of the catalysts. A Ba promoted Ni/Sm<sub>2</sub>O<sub>3</sub> catalyst was investigated for CO<sub>2</sub> methanation at atmospheric pressure with the temperature ranging from 200–450 °C. 5Ni–5Ba/Sm<sub>2</sub>O<sub>3</sub> showed significant enhancement of CO<sub>2</sub> conversion particularly at temperatures ≤ 300 °C compared to Ni/Sm<sub>2</sub>O<sub>3</sub>. Incorporation of Ba into 5Ni/Sm<sub>2</sub>O<sub>3</sub> improved the basicity of the catalysts and transformed the morphology of Sm<sub>2</sub>O<sub>3</sub> from random structure into uniform groundnut shape nanoparticles. The uniformity of Sm<sub>2</sub>O<sub>3</sub> created interparticle porosity that may be responsible for efficient heat transfer during a long catalytic reaction. Ba is also postulated to catalyze oxygen vacancy formation on Sm<sub>2</sub>O<sub>3</sub> under a reducing environment presumably *via* isomorphic substitution. The disappearance of a high temperature (~600 °C) reduction peak in H<sub>2</sub>-TPR analysis revealed the reducibility of NiO following impregnation with Ba. However, further increasing the Ba loading to 15% formed BaNiO<sub>3</sub>–BaNiO<sub>2.36</sub> phases which consequently reduced the activity of the Ni–Ba/Sm<sub>2</sub>O<sub>3</sub> catalyst at low temperature. Ni was suggested to segregate from BaNiO<sub>3</sub>–BaNiO<sub>2.36</sub> at high temperature thus exhibiting comparable activity with Ni/Sm<sub>2</sub>O<sub>3</sub> at 450 °C.

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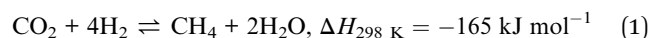
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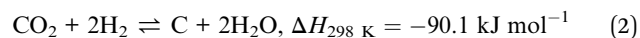
## Introduction

Carbon dioxide is a naturally occurring gas occupying ~0.04% of air in the atmosphere. CO<sub>2</sub> is produced from natural processes such as biomass decomposition, or human activities that are associated with the burning of fossil fuel. Primary consumption of fossil fuel as an energy provider results in the rising level of CO<sub>2</sub> in the atmosphere. This greenhouse gas contributes to global warming, which ultimately caused a devastating impact to the environment in particular through extreme climate change.<sup>1</sup> Current analysis by the UNEP (United Nations Environment Programme) indicated that the global temperature was expected to elevate by more than 2 °C by 2050, and more than 4 °C by 2100.<sup>2</sup> Over the years, scientists have investigated multiple approaches to overcome the issue of CO<sub>2</sub> emission. Carbon capture and utilization (CCU) has gain worldwide attention as a method to control CO<sub>2</sub> emission *via* conversion of CO<sub>2</sub> into useful products such as urea and fuel.<sup>3</sup>

Since CO<sub>2</sub> is continuously emitted from industrial processes, the conversion of CO<sub>2</sub> to methane (CH<sub>4</sub>) was identified as an ideal route to recycle the most oxidative carbon compound into active carbon species.<sup>4</sup> Catalytic hydrogenation of CO<sub>2</sub> with hydrogen gas produced CH<sub>4</sub> and water, which was discovered by Paul Sabatier in 1902<sup>2</sup> and referred to as the Sabatier reaction or CO<sub>2</sub> methanation (eqn. (1)).



Since CO<sub>2</sub> methanation is an exothermic reaction, production of methane favors a lower reaction temperature. However as a stable molecule, catalyst was required for the reaction to achieve optimum rate. Competing reactions such as carbon formation (eqn (2)) and reverse-water-gas-shift (RWGS) (eqn (3))<sup>5</sup> occurred predominantly at high temperatures. High temperature reaction also caused coke deposition that eventually contributed to the deactivation of catalysts.



Metal oxides such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> were commonly investigated as metal supports for Ni-based catalysts.<sup>6</sup> Rare earth element was generally used as promoter to enhance CO<sub>2</sub> methanation primarily due to the high cost of obtaining the element. Sm<sub>2</sub>O<sub>3</sub> was often investigated as promoter for various catalytic reaction such as water gas shift reaction,<sup>7</sup> ammonia synthesis,<sup>8</sup> and photocatalytic removal of organic pollutants.<sup>9</sup> As promoter in Co/CeO<sub>2</sub> catalysts, samarium improved the reducibility of Ce<sup>4+</sup> by facilitating the electron transfer from Co to CeO<sub>2</sub> and enhanced the surface oxygen vacancies.<sup>7</sup> Sm<sub>2</sub>O<sub>3</sub> was reported to enhance Ni dispersion, reduced coke deposition, hence enhanced both stability and activity of Ni/SBA-15 catalyst.<sup>10</sup> Ni exhibited high selectivity towards CH<sub>4</sub> and inexpensive, in comparison to noble metals.<sup>5</sup>

Centre of Advanced Material and Energy Sciences, Universiti Brunei Darussalam Jalan Tungku Link, BE 1410, Brunei Darussalam. E-mail: hasliza.bahruji@ubd.edu.bn



The use of alkali and rare earth oxides as promoter further increased the metal-support interaction and metal dispersion.<sup>5</sup> However, Ni was easily sintered during rapid temperature increase and exothermic nature of the methanation reaction. Coke deposition onto the active sites of Ni-based catalysts also caused premature deactivation.<sup>11</sup> W. J. Lee *et al.*<sup>12</sup> stated that highly dispersed Ni particles can be achieved by essentially enhancing the surface defects of the support.

This research aimed to investigate the ability of rare earth metal oxide,  $\text{Sm}_2\text{O}_3$ , as active catalyst for  $\text{CO}_2$  methanation reaction. The potential of  $\text{Sm}_2\text{O}_3$  as support for  $\text{CO}_2$  methanation was relied on its basic properties and redox potential, which was ideal to enhance  $\text{CO}_2$  adsorption and dissociation. However, studies on  $\text{Sm}_2\text{O}_3$  as catalysts support for  $\text{CO}_2$  methanation was rarely reported. Muroyama *et al.* showed utilization of  $\text{Ni}/\text{Sm}_2\text{O}_3$  as catalyst produced a higher  $\text{CH}_4$  yield when compared to  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$ , although the catalysts showed deactivation within 5 h of the reaction.<sup>13</sup> The formation of  $\text{Sm}_2\text{O}_3$  xerogel *via* epoxide addition method showed high activity and thermal stability of  $\text{Ni}/\text{Sm}_2\text{O}_3$ , however 39 wt% of Ni was required to ensure such performances.<sup>14</sup> In this work,  $\text{Ni}-\text{Ba}/\text{Sm}_2\text{O}_3$  was investigated as catalysts for  $\text{CO}_2$  methanation reaction to enhance the activity and the stability of the catalysts. Ba as alkali earth metal was introduced as promoter to enhance the basicity of the catalysts and to improve  $\text{CO}_2$  adsorption and dissociation.<sup>15</sup> Ba showed a high affinity towards  $\text{CO}_2$  to form carbonate, which was a highly important step towards  $\text{CO}_2$  decomposition at mild temperatures.<sup>16</sup> To our knowledge, studies on the effect of Ba as promoter to enhance  $\text{Ni}/\text{Sm}_2\text{O}_3$  activity has not yet been reported.  $\text{Ni}-\text{Ba}/\text{Sm}_2\text{O}_3$  catalysts was synthesized using wet impregnation method at variation of Ba loading while using 5 wt% of Ni. The enhanced activity was correlated with the basicity, reducibility and morphology of the catalysts determined using FE-SEM, HRTEM, XRD,  $\text{H}_2$ -TPR,  $\text{CO}_2$ -TPD and XPS analysis.

## Results

### XRD analysis

Fig. 1a showed the XRD analysis of  $\text{Sm}_2\text{O}_3$ ,  $5\text{Ni}/\text{Sm}_2\text{O}_3$  and  $5\text{Ni}-x\text{Ba}/\text{Sm}_2\text{O}_3$  at different Ba loading ( $x = 5\%$ ,  $10\%$  and  $15\%$ ) after calcination in air at  $500^\circ\text{C}$ . The main characteristic peaks of  $\text{Sm}_2\text{O}_3$  were observed at  $2\theta = 28.2^\circ$ ,  $32.7^\circ$ ,  $46.9^\circ$  and  $55.6^\circ$  which were indexed to (222), (400), (440) and (622) accordingly (JCPDS 043-1029). Following impregnation with Ni and Ba, some of the  $\text{Sm}_2\text{O}_3$  diffraction peaks were disappeared. As seen in Fig. 1b, narrow angle XRD analysis showed NiO peaks on  $5\text{Ni}/\text{Sm}_2\text{O}_3$  and  $5\text{Ni}-x\text{Ba}/\text{Sm}_2\text{O}_3$  at  $2\theta = 38.9^\circ$  and  $42.0^\circ$ , indexed at (111) and (200) respectively (JCPDS 004-0835), proving that NiO nanoparticles were formed following calcination at  $500^\circ\text{C}$ . However, at 10% of Ba loading,  $\text{BaNiO}_3$  peak was observed at  $2\theta = 18.8^\circ$ ,  $36.8^\circ$  and  $42.3^\circ$  (JCPDS 072-0403).<sup>17</sup> Increasing the Ba loading to 15%,  $\text{BaNiO}_{2.36}$  peaks appeared at  $2\theta = 21.9^\circ$ ,  $38.3^\circ$ ,  $48.9^\circ$  and  $50.4^\circ$  corresponded to (110), (020), (220), (131), (310) and (240) planes respectively (JCPDS 072-0403).  $\text{BaNiO}_3$  was reported as less stable than  $\text{BaNiO}_{2.36}$ , which will be decomposed gradually at higher temperatures.<sup>18</sup>

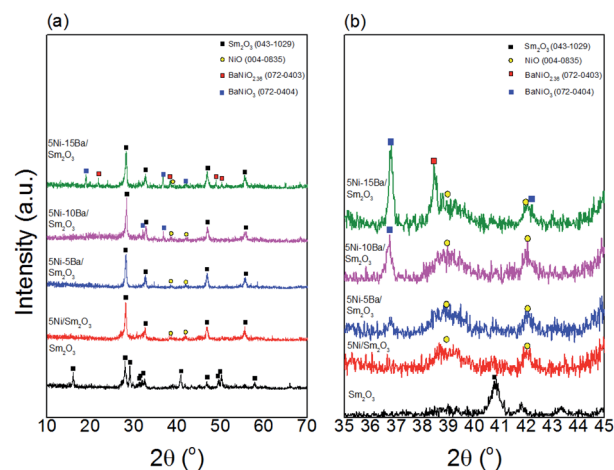


Fig. 1 (a) Wide and (b) narrow angle XRD patterns of pure  $\text{Sm}_2\text{O}_3$ ,  $5\text{Ni}/\text{Sm}_2\text{O}_3$  and  $5\text{Ni}-x\text{Ba}/\text{Sm}_2\text{O}_3$  with different Ba loading after calcination at  $500^\circ\text{C}$ .

### $\text{N}_2$ adsorption–desorption analysis

The textural properties of  $5\text{Ni}/\text{Sm}_2\text{O}_3$  and  $5\text{Ni}-x\text{Ba}/\text{Sm}_2\text{O}_3$  were analyzed using  $\text{N}_2$  adsorption–desorption (Fig. 2a). The isotherms of the catalysts were categorized as Type III isotherm with H3-hysteresis loop, according to IUPAC isotherm classification. The H3 loop was related to the adsorbed multi-layer metastability and delayed capillary condensation which occurs in slit-shaped macropores resulted from a low level of pore curvature and flexibility of the aggregate structure.<sup>19,20</sup> The increase of Ba loading slightly enhanced the surface area of the catalysts.  $5\text{Ni}/\text{Sm}_2\text{O}_3$  showed  $9\text{ m}^2/\text{g}$ , and the surface area was enhanced  $14\text{ m}^2\text{ g}^{-1}$  for  $5\text{Ni}-10\text{Ba}/\text{Sm}_2\text{O}_3$ . However, the surface area was reduced to  $12\text{ m}^2\text{ g}^{-1}$  on  $5\text{Ni}-15\text{Ba}/\text{Sm}_2\text{O}_3$  presumably due to the formation of  $\text{BaNiO}_2$ . Hysteresis loop presence at high relative pressure ( $p/p_o > 0.7$ ) implied a broad pore size distribution, comprising both meso- and macropores in the catalysts structure.<sup>21</sup> Pore size distribution analysis (Fig. 2b)

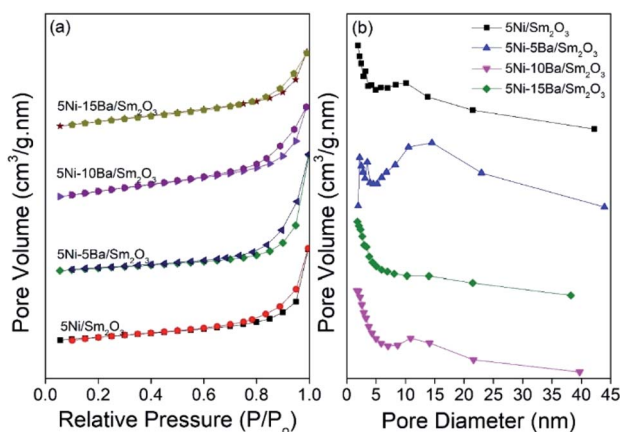


Fig. 2 (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution of  $5\text{Ni}/\text{Sm}_2\text{O}_3$  and  $5\text{Ni}-x\text{Ba}/\text{Sm}_2\text{O}_3$ ,  $x = 5\%$ ,  $10\%$  and  $15\%$  after calcination at  $500^\circ\text{C}$ .



**Table 1** Textural properties of 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-*x*Ba/Sm<sub>2</sub>O<sub>3</sub>, *x* = 5%, 10% and 15% Ba loading

Catalyst	<i>S</i> <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore size (nm)	<i>T</i> <sub>H<sub>2</sub></sub> desorption (°C)	H <sub>2</sub> uptake <sup>a</sup> (mmol g <sub>cat</sub> <sup>-1</sup> )	CO <sub>2</sub> uptake <sup>b</sup> (μmol g <sub>cat</sub> <sup>-1</sup> )
Sm <sub>2</sub> O <sub>3</sub>	13	N.D	N.D	410	0.74	6.9
5Ba/Sm <sub>2</sub> O <sub>3</sub>	N.D	N.D	N.D	526, 555, 863	15.8	13.2
5Ni/Sm <sub>2</sub> O <sub>3</sub>	9	0.0419	2, 11	412, 516, 635	34.5	10.0
5Ni-5Ba/Sm <sub>2</sub> O <sub>3</sub>	9	0.0532	3, 15	373, 443, 552	40.9	18.3
5Ni-10Ba/Sm <sub>2</sub> O <sub>3</sub>	14	0.0414	—	386, 538	97.9	16.5
5Ni-15Ba/Sm <sub>2</sub> O <sub>3</sub>	12	0.0342	—	495	59.8	6.9

<sup>a</sup> H<sub>2</sub> consumption obtained from H<sub>2</sub>-TPR profiles. <sup>b</sup> The amount of adsorbed CO<sub>2</sub> was determined from CO<sub>2</sub>-TPD. N.D – not determined.

showed the formation of mesopores on 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> catalyst. A broad pore distribution was observed on 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> with a slight enhanced of pore volume compared to 5Ni/Sm<sub>2</sub>O<sub>3</sub>. The data summarized in Table 1 indicated the pore volume was increased to 0.050 cm<sup>3</sup> g<sup>-1</sup> in 5% Ba loading compared to 0.040 cm<sup>3</sup> g<sup>-1</sup> in 5Ni/Sm<sub>2</sub>O<sub>3</sub> catalyst.

### Morphology analysis

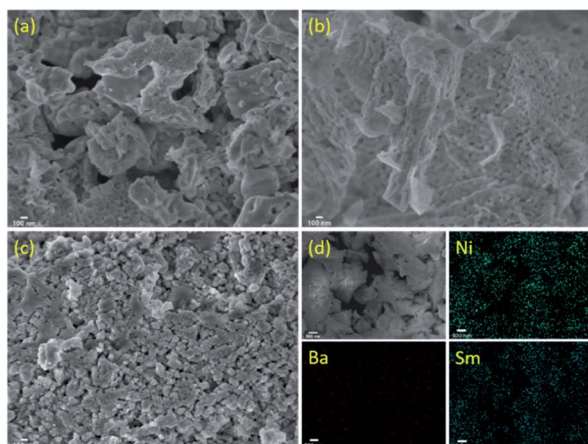
Surface morphology of 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-*x*Ba/Sm<sub>2</sub>O<sub>3</sub> catalysts were characterized using FESEM-EDX and HRTEM analysis. Fig. 3a displayed the morphology of 5Ni/Sm<sub>2</sub>O<sub>3</sub> after calcination in air at 500 °C for 3 hours. The SEM image showed a non-uniform crystallites structure with no apparent pattern on the morphology. Following addition of 5% Ba on Ni/Sm<sub>2</sub>O<sub>3</sub>, the morphology was significantly changed into interconnected uniform nanoparticles resembled to a groundnut-like structure. The presence of uniform pores was observed from the interaction between particles in 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> catalyst (Fig. 3b). The addition of Ba significantly reduced the size of crystallites to be within nanoscale length. However, following impregnation with 15% of Ba loading, the uniform groundnut-like structures disappeared and turned into non-uniform crystallites. The uniform porosity was no longer visible as the amount of Ba increased to 15% loading (Fig. 3c). The formation of non-uniform morphology of 5Ni-15Ba/Sm<sub>2</sub>O<sub>3</sub> may be associated with the formation of

BaNiO<sub>3</sub>-BaNiO<sub>2.36</sub> phases as shown in XRD analysis. EDX analysis was carried out to study the Ni and Ba dispersion on Sm<sub>2</sub>O<sub>3</sub>. EDX mapping (Fig. 3d) of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> showed Ni and Ba particles were evenly dispersed on Sm<sub>2</sub>O<sub>3</sub> surface. The homogeneous dispersion can promote synergetic effect between Ni and Ba to improve CO<sub>2</sub> adsorption and to increase catalytic activity.

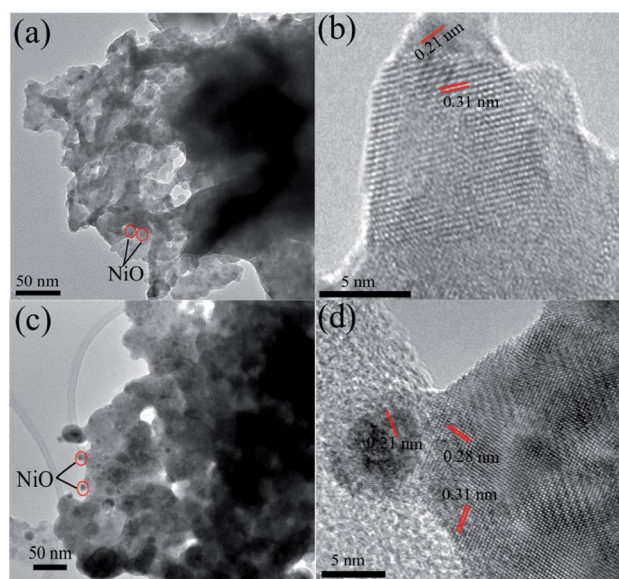
HRTEM analysis of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> in Fig. 4a and b showed homogeneous dispersion of NiO nanoparticles. The average NiO particle diameter was determined at approximately 3.5 ± 0.5 nm. The interplanar spacing of NiO nanoparticles was measured at 0.21 nm corresponded to (111) plane (16). The interplanar spacing determined at 0.31 nm was in a good agreement with the Sm<sub>2</sub>O<sub>3</sub> (222) (*d*<sub>222</sub> = 3.142 Å) plane.<sup>22</sup> HRTEM analysis of 5Ni-15Ba/Sm<sub>2</sub>O<sub>3</sub> (Fig. 4c and d) estimated the diameter of NiO nanoparticles as 4.5 ± 0.4 nm with interplanar spacing at 0.21 nm. The presence of BaNiO<sub>2.36</sub> was evident from 0.28 nm crystal plane adjacent to Sm<sub>2</sub>O<sub>3</sub>.<sup>23</sup>

### H<sub>2</sub>-TPR analysis

H<sub>2</sub>-TPR analysis of the catalysts provided information on the reducibility of NiO and the metal support interaction (Fig. 5). In



**Fig. 3** FESEM images of 5Ni-*x*Ba/Sm<sub>2</sub>O<sub>3</sub> at (a) 0% Ba, (b) 5% Ba, (c) 15% Ba and (d) EDX mapping of 5Ni-*x*Ba/Sm<sub>2</sub>O<sub>3</sub> at 5% Ba after calcination.



**Fig. 4** HRTEM analysis of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> (a and b) and 5Ni-15Ba/Sm<sub>2</sub>O<sub>3</sub> (c and d) after calcination in air at 500 °C.





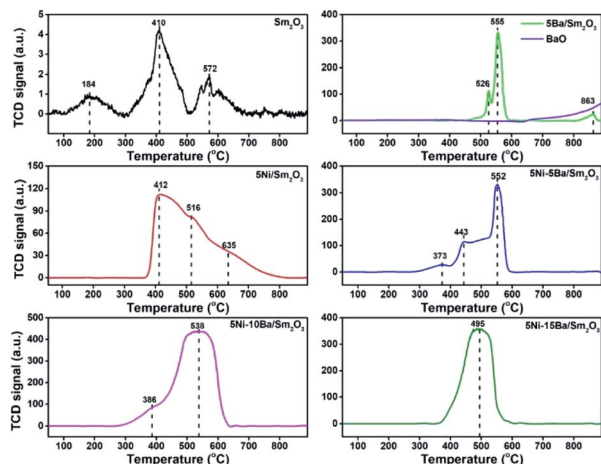


Fig. 5  $H_2$ -TPR profiles of 5Ni/Sm $_2$ O $_3$ , 5Ba/Sm $_2$ O $_3$ , BaO, and 5Ni- $x$ Ba/Sm $_2$ O $_3$  at different Ba loading. The catalysts were calcined in air at 500 °C prior to the analysis.

general,  $\alpha$ -type NiO species peak was located at low-temperature region (300–500 °C) signifying bulk NiO particles.  $\beta$ -Type NiO peak can be seen at mild-temperature region (500–700 °C) demonstrating a weak interaction between NiO and support. Meanwhile a high temperature peak >700 °C was assigned to  $\gamma$ -type NiO species with strong interaction with the support.<sup>24–26</sup> Sm $_2$ O $_3$  only showed a very low  $H_2$  uptake (0.74 mmol g $_{cat}^{-1}$ ) suggesting the high stability of Sm $_2$ O $_3$  which only slightly reduced to SmO. Following impregnation with 5% Ba on Sm $_2$ O $_3$ , sharp TPR peaks appeared at 526 °C and 555 °C, and a small peak at much higher temperatures, 863 °C. The amount of  $H_2$  uptake was increased to 15.2 mmol g $_{cat}^{-1}$ . The  $H_2$  TPR analysis of 5Ba/Sm $_2$ O $_3$  was compared with  $H_2$  TPR analysis of BaO, which indicated BaO stability under reducing environment. The reduction of Sm $_2$ O $_3$  upon Ba addition could be due to migration of Ba $^{2+}$  to Sm $_2$ O $_3$  lattice. The close interaction between Ba $^{2+}$  and Sm $^{3+}$  enhanced the reducibility of Sm $^{3+}$  to Sm $^{2+}$  thus promoting the formation of oxygen vacancy. The hypothesis was postulated from the behaviour of CeO $_2$  system when doped with cation with a lower charge such as Co $^{2+}$  that leads to charge compensation.<sup>27</sup> This charge compensation mechanism from isomorphic substitution of Ba $^{2+}$  in Sm $^{3+}$  enhanced the formation of surface oxygen vacancies.

All Ni catalysts showed the reduction peaks were formed within  $\alpha$ - and  $\beta$ -type ranges and shifted to the lower temperatures with the addition of Ba. 5Ni/Sm $_2$ O $_3$  showed a broad reduction peaks at 412 °C, with shoulder peaks at 516 °C and 635 °C. The broad reduction peak formation suggested multiple interaction of NiO species with the Sm $_2$ O $_3$  support.<sup>26</sup> Large NiO particles required a long reduction time and high temperatures in order to ensure complete reduction into its metallic state, hence displayed a broad reduction peak at high temperature region.<sup>21</sup> The  $H_2$ -TPR profile of 5Ni-5Ba/Sm $_2$ O $_3$  showed the appearance of small reduction peak at 373 °C, followed with a broad peak started at 443 °C. A sharp reduction peak at 552 °C showed a similar feature as 5Ba/Sm $_2$ O $_3$ . Impregnation with 5Ni-5Ba on Sm $_2$ O $_3$  also showed the disappearance of NiO reduction peak at 635 °C which implied the incorporation of Ba into 5Ni/

Sm $_2$ O $_3$  improved the reducibility of NiO nanoparticles. The volume of  $H_2$  consumption was also significantly enhanced with increasing Ba loading presumably due to the combination of  $H_2$  consumption for NiO reduction and the formation of oxygen vacancies on Ba/Sm $_2$ O $_3$ . However, the amount of  $H_2$  uptake was reduced to 59.8 mmol g $_{cat}^{-1}$  on 5Ni-15Ba/Sm $_2$ O $_3$  presumably due to the formation of BaNiO $_3$ -BaNiO $_{2.36}$  phases restricting the evolution of oxygen vacancies.

### CO $_2$ -TPD analysis

Surface basicity and distribution of basic sites of 5Ni- $x$ Ba/Sm $_2$ O $_3$  catalysts at different Ba loadings were determined using CO $_2$ -TPD as shown in Fig. 6. CO $_2$  is a weak Lewis acid that can adsorb on the catalysts to distinguish the types and the strengths of basic sites. The CO $_2$  desorption peak at temperature below 100 °C was corresponded to CO $_2$  interaction with a weak basic site on the catalysts surface. This feature was negligible on all catalysts. CO $_2$ -TPD analysis of Sm $_2$ O $_3$  showed the CO $_2$  desorption peaks centered at 172 °C and 363 °C that were associated with the medium interaction between CO $_2$  molecules and moderate basic sites. The peaks formed in the medium basic site region also indicated the formation of carbonate species on the catalysts surface.<sup>28,29</sup> These carbonate species, specifically monodentate carbonate were susceptible towards hydrogenation to form CH $_4$ .<sup>30</sup> Following impregnation of Sm $_2$ O $_3$  with 5% Ba, the amount of CO $_2$  uptake was enhanced from 6.9  $\mu$ mol g $_{cat}^{-1}$  on Sm $_2$ O $_3$  to 13.2  $\mu$ mol g $_{cat}^{-1}$  on 5Ba/Sm $_2$ O $_3$ . The CO $_2$  desorption peak also slightly shifted to lower temperatures. The results clearly showed the presence of Ba enhanced surface basicity of Sm $_2$ O $_3$ . No peak associated with the strong interaction between CO $_2$  molecules and basic sites was observed at temperature above 500 °C.<sup>21,31</sup> Ni/Sm $_2$ O $_3$  also showed enhanced CO $_2$  uptake at 10.9  $\mu$ mol g $_{cat}^{-1}$ . Synergy between Ni, Ba and Sm $_2$ O $_3$  was further evidenced on the increase of desorption peak at 150 °C for 5Ni-5Ba/Sm $_2$ O $_3$  compared to 5Ni/Sm $_2$ O $_3$  and 5Ba/Sm $_2$ O $_3$ . The amount of adsorbed CO $_2$  was quantified based on the deconvoluted peak and tabulated in Table 1. The results clearly indicated the addition of Ba into Ni/Sm $_2$ O $_3$  tremendously

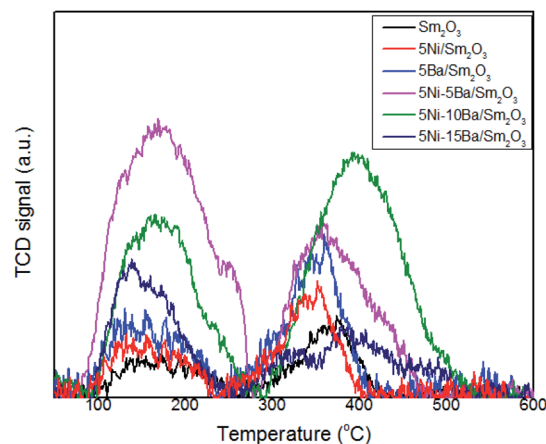


Fig. 6 CO $_2$ -TPD profiles of 5Ni/Sm $_2$ O $_3$ , 5Ba/Sm $_2$ O $_3$  and 5Ni- $x$ Ba/Sm $_2$ O $_3$  with different Ba loading at  $x$  = 5%, 10%, 15%.



improved the surface basicity of the catalysts through the formation of a new basic sites originating from the Ba.<sup>32,33</sup> 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> demonstrated the highest CO<sub>2</sub> uptake at 16.5 μmol g<sub>cat</sub><sup>-1</sup>. The role of Ba to provide the additional basic sites was further consolidated by the reduction of CO<sub>2</sub> uptake on 5Ni-15Ba/Sm<sub>2</sub>O<sub>3</sub> at 6.9 μmol g<sub>cat</sub><sup>-1</sup>. The formation of BaNiO<sub>3</sub>-BaNiO<sub>2.36</sub> as evidenced by the XRD analysis reduced the ability of Ba to increase the surface basicity of the catalyst.

### XPS analysis

XPS analysis is a surface analysis method that provided the information of the outer layer of heterogeneous catalysts responsible for catalytic reaction. XPS analysis was conducted following air calcination at 500 °C and reduction at 450 °C (Fig. 7). The presence of Ni and Sm were observed on 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub>, although Ni 3d signal appeared significantly low in intensity due to the low Ni loading. Analysis of O1s XPS spectra between 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> indicated the presence bulk lattice oxygen. There were no significant differences on the O1s signal following Ba addition. The Sm 3d XPS signal showed doublet peaks appeared at 1083.8 eV and 1150 eV corresponded to Sm<sup>3+</sup> species.<sup>34</sup> Ni was analyzed at 856.1 eV and 861.8 eV originated from NiO. However, the Ni<sup>0</sup> at 853.1 eV was absent presumably due to the surface oxidation of Ni<sup>0</sup> when the catalyst was exposed to air during the transfer process for XPS measurement.<sup>35</sup> There were no significant differences on the XPS signal of Sm 3d following impregnation with Ba suggesting that no alteration of Sm<sup>3+</sup> oxidation states. The presence of surface oxygen vacancies on Sm<sub>2</sub>O<sub>3</sub> following impregnation with Ba cannot be deduced from the XPS analysis due to the absence of Sm<sup>2+</sup> peak generally appeared at binding energy ~1095.9 eV and 1121.3 eV.<sup>36,37</sup> XPS also confirmed that dissolution of Ni or Ba into Sm<sub>2</sub>O<sub>3</sub> lattice did not take place on the 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> catalysts even after reduction at 450 °C.

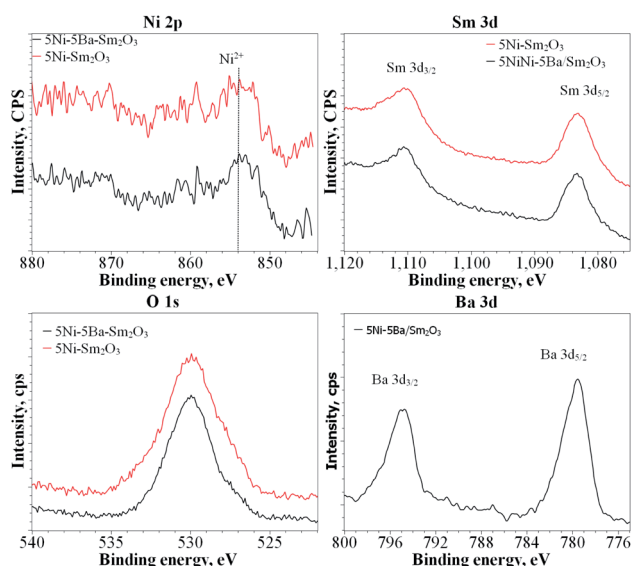


Fig. 7 Ni 2p, Sm 3d, O 1s and Ba 3d XPS spectra of 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> after reduction at 450 °C.

### Catalytic activity

The activity of 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-xBa/Sm<sub>2</sub>O<sub>3</sub> on the variation of Ba loading was investigated at 200–450 °C (Fig. 8). No activity was observed at 200 °C, and all the catalysts showed CO<sub>2</sub> conversion at 250 °C with 100% selectivity to methane. Increasing the temperature to 300 °C significantly enhanced the conversion of CO<sub>2</sub>. 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> showed the highest CO<sub>2</sub> conversion at 38.9% followed with 5Ni-10Ba/Sm<sub>2</sub>O<sub>3</sub> at 29%. The conversion was significantly higher than 5Ni/Sm<sub>2</sub>O<sub>3</sub> with only 20% at 300 °C. 5Ni-15Ba/Sm<sub>2</sub>O<sub>3</sub> was less active than 5Ni/Sm<sub>2</sub>O<sub>3</sub> at temperature below 350 °C presumably due to the formation of BaNiO<sub>2</sub>. Evidently, as the amount of Ba loading increased to 10% and 15%, the CO<sub>2</sub> conversions were comparable with 5Ni/Sm<sub>2</sub>O<sub>3</sub> at 400 °C and 450 °C. Reaction at 450 °C showed 72.7% of CO<sub>2</sub> conversion on 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub>, which was slightly higher than 5Ni/Sm<sub>2</sub>O<sub>3</sub>, 5Ni-10Ba/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-15Ba/Sm<sub>2</sub>O<sub>3</sub> at ~66.8%. It is apparent that the addition of Ba enhanced the activity of Ni catalysts at temperature below 350 °C. Meanwhile at temperature above 400 °C, the reaction was dictated by the thermodynamic of the reaction thus restricting the catalytic performances of all the catalysts. It is also interesting to note that all the 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-xBa/Sm<sub>2</sub>O<sub>3</sub> catalysts exhibited 100% selectivity to methane. When the Ni-Ba/Sm<sub>2</sub>O<sub>3</sub> catalysts were compared with the results previously reported on Ni/metal oxides (Table 2), it is apparent that Ni-Ba/Sm<sub>2</sub>O<sub>3</sub> selectively transformed CO<sub>2</sub> to methane and prevented CO formation. The activity of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> was further investigated for 28 h to show the stability of the catalysts (Fig. 9). The conversion was observed at 39% with 100% selectivity towards methane, with similar conversion was observed up to 28 h.

Fig. 10 summarized the effect of reduction temperature on the activity of 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> in order to further elucidate the role of Ba in enhancing Ni activity. These studies also provided insight into the importance of reducing the catalysts prior to the reaction, to ensure the catalysts gained high catalytic activity. Reduction at 250 °C showed the CO<sub>2</sub> conversion of 5Ni/Sm<sub>2</sub>O<sub>3</sub> was significantly lower in comparison to 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub>. 5Ni/Sm<sub>2</sub>O<sub>3</sub> was only active at 350 °C, to give

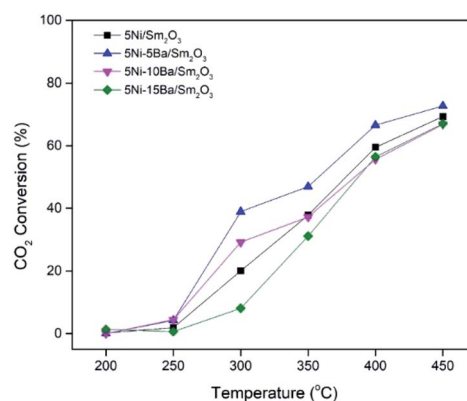
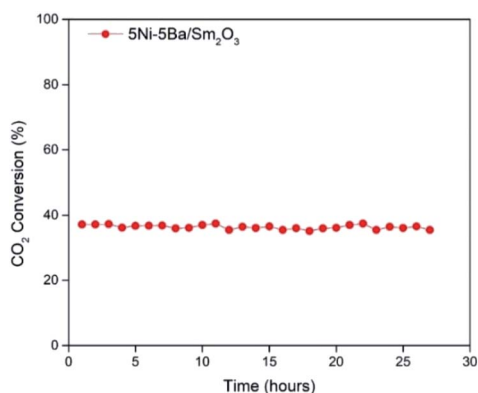
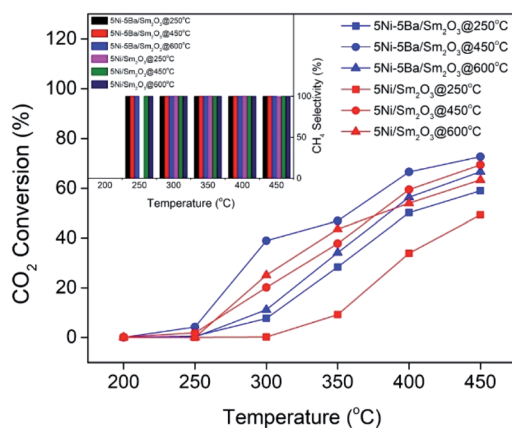


Fig. 8 CO<sub>2</sub> conversion for 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-xBa/Sm<sub>2</sub>O<sub>3</sub> at x = 5%, 10%, 15%. The catalysts was pre-reduced *in situ* under H<sub>2</sub> for 3 h at 450 °C.

**Table 2** Catalytic performance comparison among various Ni-based catalysts prepared using wet impregnation as CO<sub>2</sub> methanation catalysts

Catalysts	Reaction condition	X <sub>CO<sub>2</sub></sub> (%)	S <sub>CH<sub>4</sub></sub> (%)	Reference
5Ni/Sm <sub>2</sub> O <sub>3</sub>	450 °C, 1 bar	69.3	100	This work
5Ni-5Ba/Sm <sub>2</sub> O <sub>3</sub>	450 °C, 1 bar	72.7	100	This work
5Ni-10Ba/Sm <sub>2</sub> O <sub>3</sub>	450 °C, 1 bar	66.8	100	This work
5Ni-15Ba/Sm <sub>2</sub> O <sub>3</sub>	450 °C, 1 bar	67.0	100	This work
5Ni/NaY-DM	400 °C, 1 bar	67	94	39
5Ni/MSN	300 °C, 1 bar	64.1	99.9	40
10Ni/SiO <sub>2</sub>	400 °C, 1 bar	73.2	98.7	41
10Ni/MgO	400 °C, 1 bar	28.9	9.0	
10Ni/SiO <sub>2</sub> + 10Ni/MgO	400 °C, 1 bar	66.5	96.8	
10Ni/CeO <sub>2</sub>	350 °C, 1 bar	79.1	76.5	42
5Ni/CZ <sub>imp</sub>	350 °C, 1 bar	59.8	97.3	30

**Fig. 9** Catalytic stability of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> catalysts at 300 °C for 28 h.**Fig. 10** CO<sub>2</sub> conversion and selectivity of 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> at different reduction temperature.

9.2% of CO<sub>2</sub> conversion. The result was indirect contrast to 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub>, in which 7.9% conversion was analysed at 300 °C following pre-reduction at 250 °C and increased to 28.4% at 350 °C. When the reaction temperature was further increased to 450 °C, the conversion was enhanced to give 49% for 5Ni/Sm<sub>2</sub>O<sub>3</sub> and 59% for 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub>. Following reduction at 450 °C, no methane was produced at 200 °C but significant conversion was observed at 250 °C for both catalysts. 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> showed

4.3% conversion at 250 °C meanwhile Ni/Sm<sub>2</sub>O<sub>3</sub> only showed 1.9% of CO<sub>2</sub> conversion. Increasing the reaction temperature to 300 °C, further increased CO<sub>2</sub> conversion of 39% on Ba promoted catalysts compared to reduction at 250 °C with only 7.7%. When 5Ni/Sm<sub>2</sub>O<sub>3</sub> was reduced at 600 °C, the catalysts achieved 24% of CO<sub>2</sub> conversion at 300 °C, slightly higher than 5Ni/Sm<sub>2</sub>O<sub>3</sub> reduced at 450 °C. Fully reduction of NiO at 600 °C according to H<sub>2</sub>-TPR analysis (Fig. 5) was suggested to improve 5Ni/Sm<sub>2</sub>O<sub>3</sub> activity. However, reduction of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> at 600 °C reduced the CO<sub>2</sub> conversion. H<sub>2</sub>-TPR analysis of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> showed the catalyst was fully reduced at temperature below 500 °C, thus high temperature reduction may cause particle sintering.<sup>38</sup> Nevertheless, all the catalysts showed 100% selectivity towards CH<sub>4</sub>. The results obtained on the effect of reduction temperature is highly important to show the role of Ba in improving the activity of Ni catalysts particularly for CO<sub>2</sub> methanation at low temperature.

## Discussions

The effect of Ba on Ni/Sm<sub>2</sub>O<sub>3</sub> activity was observed particularly when the reaction was carried out at temperature below 300 °C. The activity of most nickel catalysts for CO<sub>2</sub> methanation was reported to have insignificant increment at the temperature above 350 °C mainly due to the thermodynamic restriction.<sup>43</sup> Reaction at temperatures above 400 °C showed the gap between CO<sub>2</sub> conversions on 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> and 5Ni/Sm<sub>2</sub>O<sub>3</sub> were only slightly varied. At low temperature, the methanation was restricted by kinetic due to the stability of CO<sub>2</sub>.<sup>44</sup> The results proved the synergy between Ni, Ba and Sm<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> conversion at mild temperatures. The combination of increased basicity, surface oxygen vacancies, NiO reducibility and interparticle meso-porosity of 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> enhanced the activity and stability of 5Ni-xBa/Sm<sub>2</sub>O<sub>3</sub> catalyst. It is also interesting to note that, 5Ni-5Ba/Sm<sub>2</sub>O<sub>3</sub> exhibited 100% selectivity towards methane even when the reaction was carried out at 450 °C. Sm<sub>2</sub>O<sub>3</sub> is a rare earth metal oxide, with mild basicity and redox properties which is ideal for CO<sub>2</sub> adsorption and hydrogenation. Barium as alkali earth metal promoter further enhanced the basicity of the catalysts evidenced by the increase of adsorbed CO<sub>2</sub> volume determined using CO<sub>2</sub>-TPD. There is





a possibility that introduction of  $\text{Ba}^{2+}$  in  $\text{Sm}_2\text{O}_3$  enhanced the mobility of oxygen species consequently facilitated the formation of oxygen vacancies on reducible metal oxides.<sup>45</sup> The presence of surface oxygen vacancies during catalytic reaction promotes  $\text{CO}_2$  activation and dissociation.<sup>46</sup> Although the XPS analysis showed no evidence of  $\text{Sm}^{2+}$  species, there is a possibility that  $\text{Sm}_2\text{O}_3$  as redox active metal oxide, to be responded with the changes of oxidation states under reducing environment, alternating between  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$ .<sup>34</sup>  $\text{CO}_2$  adsorbed on the metal oxide surface to form monodentate or bidentate carbonate species depending on the oxygen vacancies within the vicinity of Ni nanoparticles.<sup>28</sup> Furthermore, the presence of surface oxygen vacancies on  $\text{Sm}_2\text{O}_3$  following the addition of Ba enhanced the hydrogenation of carbonate into formate intermediates.<sup>28</sup> Formate intermediate will further undergo C–O dissociation and hydrogen insertion to form methane, thus preventing decomposition into  $\text{CO}$ .<sup>28</sup>

However at higher Ba loading (15%), the formation of  $\text{BaNiO}_3$ – $\text{BaNiO}_{2.36}$  was observed after calcination at 500 °C.  $\text{BaNiO}_{2.36}$  is a stable crystalline phase resulting from the oxidation of Ba and Ni precursors to form zig-zag chains of  $\text{Ni}^{2+}$  ion.<sup>47</sup> The average oxidation states of Ni in  $\text{BaNiO}_2$  is 2+, and it is interchangeable to 4+ under oxygen at high temperature to form  $\text{BaNiO}_3$ .<sup>17</sup> Since it was crucial for Ni to be in its reduction state in order to catalyze hydrogen dissociation in  $\text{CO}_2$  methanation reaction,<sup>48</sup> the formation of  $\text{BaNiO}_3$ – $\text{BaNiO}_{2.36}$  reduced the activity of 5Ni–15Ba/ $\text{Sm}_2\text{O}_3$ . Furthermore,  $\text{BaNiO}_3$ – $\text{BaNiO}_{2.36}$  inhibited the contribution of Ba as the additional basic sites evidenced by the  $\text{CO}_2$ -TPD analysis thus resulting in a low catalytic activity at temperature below 350 °C. However, as the temperature was increased to 450 °C, there is a possibility that NiO segregating from  $\text{BaNiO}_3$ – $\text{BaNiO}_{2.36}$  under the presence of  $\text{H}_2$ . Although we have no evidence on the segregation of NiO from  $\text{BaNiO}_2$  during reaction at 450 °C, the comparable activity with Ni/ $\text{Sm}_2\text{O}_3$  implied such processes may occur *in situ* under the flow of reactant gases.

Impregnation of barium also altered the morphology of  $\text{Sm}_2\text{O}_3$  to form uniform particles within ~100 nm of size with interparticle porosity. It is suggested that partial dissolution of  $\text{Sm}_2\text{O}_3$  during impregnation changed the morphology, which was essential to improve the uniformity of nanoparticles. The formation of uniform nanoparticles with interparticle porosity may be beneficial to facilitate carbon dioxide adsorption and diffusion in order to react with the dissociated H atom on Ni sites to form  $\text{CH}_4$ .<sup>5,49</sup> Porosity was also improved the heat transfer capacity that allowed the catalysts to overcome the heat released during the exothermic reaction.<sup>50</sup>

## Experimental

### Catalysts preparation

All the catalysts were prepared using wetness impregnation method. Nickel(III) nitrate hexahydrate was obtained from Emsure, 99.0%, barium nitrate from Emsure, 99.0%, samarium oxide from Aldrich, 99%. 5Ni– $x\text{Ba}/\text{Sm}_2\text{O}_3$  catalysts were prepared with different Ba loading, and  $x = 5$  wt%, 10 wt% and 15 wt%. The amount of Ni was kept at 5 wt% relative to the weight of  $\text{Sm}_2\text{O}_3$ .  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Sm}_2\text{O}_3$

were weighed accordingly and physically mixed, which later then dissolved in 10 mL of distilled water. The mixture was stirred continuously for 3 h at 60 °C to ensure thorough dispersion. The catalysts were dried at 200 °C for 2 hours and then calcined at 500 °C for 3 hours in air atmosphere with a heating rate of 10 °C  $\text{min}^{-1}$ .

### Catalyst characterization

Field Emission Scanning Electron Microscope (JSM-7610F equipped with EDX) was used to investigate the surface morphology of the catalysts. Energy Dispersive X-ray analysis was carried out to determine the Ni and Ba dispersion onto  $\text{Sm}_2\text{O}_3$ . The morphological analysis at micro and nano-scales resolution was carried out using high-resolution field emission transmission electron microscopy (HRTEM) Tecnai G2 F20 STWIN at 200 kV. Prior to the analysis, the catalyst was ground and dispersed in water, and the suspension was dropped on the TEM grid and leave to dry at ambient condition. X-ray powder diffraction (Shimadzu XRD-700 X-ray Diffractometer) was carried out to analyze the crystalline structure of the catalysts by utilizing Cu-K $\alpha$  radiation at  $\lambda = 1.54$  Å, with operating conditions of 60 kV and 50 mA. The scanning angle range,  $2\theta$ , was 10–70° with a scan rate of 2°  $\text{min}^{-1}$ . The crystalline structure size was calculated using Scherrer's equation (eqn (4)).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (4)$$

where D is the crystallite size (nm),  $\lambda$  is the wavelength of X-ray (0.15406 nm),  $\theta$  is the peak position (radians),  $k$  is Scherrer constant and  $\beta$  is the FWHM (radians).

Surface area, average pore volume and pore diameter of 5Ni/ $\text{Sm}_2\text{O}_3$  and 5Ni– $x\text{Ba}/\text{Sm}_2\text{O}_3$  at different Ba loading were determined using  $\text{N}_2$  adsorption at 77 K (Micromeritics ASAP 2020). The samples were degassed under carbon degassing conditions for 2 hours at 300 °C. Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area and Barret–Joyner–Halenda (BJH) equation for pore volume and diameter calculation. The pore volume was determined based on three different measurement with standard deviation was measured at  $8.91 \times 10^{-5}$ . X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra-DLD XPS spectrometer with a monochromatic Al K $\alpha$  source (75–150 W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). The XPS data was analysed using CASA XPS software and all the samples were calibrated by adjusting the C 1s position to 284.5 eV.  $\text{H}_2$  temperature-programmed reduction (Quantachrome ChemBET Pulsar TPR/TPD, equipped with TCD) was performed to study the reducibility of the catalyst. Catalyst was pre-treated in  $\text{N}_2$  stream with flow of 75 mL  $\text{min}^{-1}$  at 100 °C for 1 hour and cooled down to 40 °C. The catalysts were heated to 900 °C with a heating rate of 10°C  $\text{min}^{-1}$  in a 5%  $\text{H}_2/\text{N}_2$  gas mixture with a flow rate of 75 mL  $\text{min}^{-1}$ .  $\text{CO}_2$  temperature-programmed desorption was conducted to study the surface basicity and basic sites distribution of the catalysts. Catalysts were heated to 600 °C for 1 hour under 5%  $\text{H}_2/\text{N}_2$  gases, which later cooled to room temperature under He flow. Catalyst was exposed to  $\text{CO}_2$  gas stream for 30 minutes and then flushed out



with He for 1 hour. TPD was finally carried out from 40–600 °C with a heating rate of 10 °C min<sup>-1</sup>.

### Catalytic activity

CO<sub>2</sub> methanation reaction was conducted in a stainless-steel plug flow reactor at atmospheric pressure and reaction temperature ranging from 200 to 450 °C. 0.5 g of catalyst was placed in a tubular fixed bed reactor and reduced *in situ* with H<sub>2</sub> gas (99.9%) with flow rate of 20 mL min<sup>-1</sup> at 450 °C for 3 h. The catalyst was cooled down to room temperature and CO<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> (15%/60%/25%) gases at 20 mL min<sup>-1</sup> were flowed in the reactor. The gas effluent from the reactor was analyzed by GC (Shimadzu GC-2014 with TCD detector). Reaction temperature was increased by 50 °C every hour and the gas were sampled using GC. CO<sub>2</sub> conversion (eqn (5)), CH<sub>4</sub> selectivity (eqn (6)) and CO selectivity (eqn (7)), and CH<sub>4</sub> yield (eqn (8)) were calculated according to the previous method (ref. 48) as follows:

$$x_{\text{CO}_2} = \left[ \frac{m_{\text{CH}_4} + m_{\text{CO}}}{m_{\text{CO}_2} + m_{\text{CH}_4} + m_{\text{CO}}} \right] \times 100\% \quad (5)$$

$$S_{\text{CH}_4} = \left[ \frac{m_{\text{CH}_4}}{m_{\text{CH}_4} + m_{\text{CO}}} \right] \times 100\% \quad (6)$$

$$S_{\text{CO}} = \left[ \frac{m_{\text{CO}}}{m_{\text{CH}_4} + m_{\text{CO}}} \right] \times 100\% \quad (7)$$

$$Y_{\text{CH}_4} = x_{\text{CO}_2} S_{\text{CH}_4} \quad (8)$$

where  $x_{\text{CO}_2}(\%)$  is the CO<sub>2</sub> conversion,  $S_{\text{CH}_4}(\%)$  is the CH<sub>4</sub> selectivity,  $S_{\text{CO}}(\%)$  is the CO selectivity,  $Y_{\text{CH}_4}(\%)$  is the CH<sub>4</sub> yield and  $m$  is the number of moles of the gases.

## Conclusions

The activity of Ni–Ba/Sm<sub>2</sub>O<sub>3</sub> catalysts was investigated to enhance CO<sub>2</sub> methanation at moderate reaction temperatures. 5Ni–5Ba/Sm<sub>2</sub>O<sub>3</sub> demonstrated a higher CO<sub>2</sub> conversion with 100% CH<sub>4</sub> selectivity in comparison to 5Ni/Sm<sub>2</sub>O<sub>3</sub>. The effect of increasing Ba loading on 5Ni/Sm<sub>2</sub>O<sub>3</sub> exhibited the changes of porosity and uniformity of the catalysts structure, and the reducibility of NiO. Ba as promoter also enhanced the number of basic sites and surface oxygen vacancies, and transformed the non-uniform aggregates Sm<sub>2</sub>O<sub>3</sub> into uniform size nanoparticles. The basicity originated from Ba promoter enhanced CO<sub>2</sub> adsorption meanwhile the porosity facilitated the heat transfer process during catalytic reaction which consequently increased the catalytic stability. However, further increasing the Ba loading to 15% destroyed the uniform nanostructure and porosity of the catalysts, due to the formation of BaNiO<sub>3</sub>–BaNiO<sub>2.36</sub> phases thus reducing the catalytic performance at low temperatures.

## Conflicts of interest

There are no conflicts to declare.

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