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Optimizing acido-basic profile of support in Ni supported $\text{La}_2\text{O}_3+\text{Al}_2\text{O}_3$ catalyst for Dry Reforming of Methane

Fahad Al-Mubaddel^{1,2}, Rawesh Kumar³, Mahmud Lanre Sofiu¹, Francesco Frusteri⁴, Ahmed Aidid Ibrahim¹, Vijay Kumar Srivastava³, Samsudeen Olajide Kasim¹, Anis Hamza Fakeeha¹, Ahmed Elhag Abasaheed¹, Ahmed I. Osman⁵, Ahmed Sadeq Al-Fatesh^{1*}

¹ Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia.

² King Abdullah City for Atomic & Renewable Energy, Energy Research & Innovation Center (ERIC) in Riyadh, Riyadh 11451, Saudi Arabia.

³ Sankalchand Patel University, Visnagar, Gujarat, India, 384315

⁴ CNR-ITAE, Istituto di Tecnologie Avanzate per Energia "Nicola Giordano", Via S. Lucia sopra Contesse 5, 98126, Messina, Italy

⁵ School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, UK.

* Corresponding author. E-mail addresses: aalfatesh@ksu.edu.sa (A.S. Al-Fatesh)

Abstract

The increasing alarm of global warming always draws interest in reactions like dry reforming of methane (DRM) where both global warming gases (CO_2 and CH_4) are converted into value-added chemical building blocks, such as syngas. Nickel catalyst active sites along with support acid-base profiles play a key role in DRM. Herein, $x\text{La}_2\text{O}_3+(100-x)\text{Al}_2\text{O}_3$ ($x = 0, 10, 15, 20\%$) supports are prepared and followed by NiO dispersion over the produced support by impregnation method. It was tested for DRM reaction and characterized with TGA, XRD, TEM, IR, Surface area and porosity measurement, H_2 -TPR, CO_2 -TPD and NH_3 -TPD techniques. Upon increasing the basic lanthana proportion in the acidic alumina support, the crystallinity of alumina and acidity of total support decline. Up to 15% Lanthana addition in support claims a low acid and rich basic surface including super basic sites (related to unidentate carbonates) which governed optimum catalytic performance 64% CH_4 conversion, 79% CO_2 conversion and $\text{H}_2/\text{CO} \sim 1$ up to 460-minute in time on stream test. 20% lanthanum oxide loading led to inferior performance due to rapid loss of surface area, pore-volume, pore diameter, acidity and

medium basic strength sites. Fine-tuning of acid-base lanthana-alumina support with dispersed Ni species are a means for understanding DRM.

Keywords: Acid-basic property, DRM, Super basic sites, Lanthana-Alumina

1. Introduction

Dry reforming of methane (DRM) always draws global attention due to converting two global warming causing gases, CH₄ and CO₂, into useful syngas, CO and H₂, feedstock. It is a catalytic induced process generating syngas used as a viable fuel alternative to fossil fuel and a precursor for substantial chemicals such as methanol, ammonia, and synthetic hydrocarbon fuel production [1]. The application of inexpensive and readily available DRM catalysts with performance to outstandingly yield syngas has been the focal point of research and development in modern times. Versatile cheap catalysts for DRM are of utmost demand from the industry as well as environmental community. The Ni-based catalytic system is most trusted after noble metals Pt, Ru and Rh for DRM [2, 3, 4, 5, 6, 7]. Due to cheap and wide availability, Ni is investigated deeply for DRM by the research community. Dissociation of CH₄ over the Ni surface into carbon deposits and H₂ (irreversible dehydrogenation reaction) and thereafter oxidation of carbon deposit by CO₂ into CO (reversible Boudouard reaction) of DRM is widely accepted (Equation (1) & (2)) [8]. At high temperature, the Boudouard reaction shifts towards CO disproportionation, which is likely to decrease CO yield and decrease CO₂ conversion and enhance carbon deposition.

54 Overall, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ $\Delta H = 247\text{kJ/mol}$ ---(3)

55 However, overall CH_4 conversion, CO_2 conversion and H_2/CO ratio are altered by other parallel
56 reaction over the catalyst surface: (1) Reaction of product H_2 with substrate CO_2 gives CO and
57 H_2O ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$). This reaction is popularly known as reverse water gas shift
58 reaction (RWGS), which causes a remarkable decrease in H_2 yield, increase in CO yield and
59 increase of CO_2 conversion. (2) Gasification of carbon deposit by hydrogen gas into CH_4 ($\text{C} +$
60 $2\text{H}_2 \rightarrow \text{CH}_4$) causes a decrease in H_2 yield and a decrease of CH_4 conversion [9]. (3)
61 Gasification of carbon deposit by H_2O into CO and H_2 ($\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$) causes an
62 increase of H_2 yield and CO yield.

63 Various attempts were reported to disperse the Ni on proper support with synthetic
64 methodologies and conditions such that the maximum and stable catalytic conversion could be
65 achieved. As DRM reaction is highly endothermic and catalyst supports like SiO_2 , Al_2O_3 and
66 ZrO_2 can sustain a high reaction temperature and hold the dispersed nickel species even at the
67 high reaction temperatures. Among all supports, Al_2O_3 support is the cheapest and handy for
68 industrial applications. Among the $\gamma\text{-Al}_2\text{O}_3$ and $\beta\text{-Al}_2\text{O}_3$ support, $\gamma\text{-Al}_2\text{O}_3$ supported Ni catalyst
69 was found more suitable for DRM reaction as it holds large numbers of C_a species (completely
70 dehydrogenated carbides carbon) over its surface which resulted into higher CO_2 conversion
71 [10]. Presence of NiAl_2O_4 phases in the Al_2O_3 supported Ni catalyst system showed strong
72 metal-support interaction, presenting high resistance against sintering and coking [11,12].
73 Al_2O_3 nanosheet support provides superior anchoring surface (100) for Ni nanoparticle where
74 Al_2O_3 nanofiber support provides abundant confined space for steady chemisorption behaviour
75 [13]. So, the earlier catalyst showed high catalytic conversion ($> 85\%$ CO_2 and CH_4 conversion)
76 with excellent H_2 and CO selectivity whereas later catalyst system showed superior catalytic
77 stability. Xiuzhong Fang et al.; has applied evaporation-induced self-assembly methodology
78 (EISA) to prepare Al_2O_3 supported nickel-based catalyst [14]. The catalyst prepared by the

EISA method had more dispersed, small and uniform Ni particle over-ordered mesopores support. This methodology claimed remarkable activity and potent coke resistance than that of the conventional impregnated catalyst. R.L.B.A. Medeiros et al.; had applied microwave-assisted combustion method (MAC) using urea [15]. The catalyst prepared by low urea content (2g) showed a high degree of reduction and high specific surface area of $266 \text{ m}^2/\text{g}$ which promoted better activity and 33% lower deactivation levels. Yu Zhao et al.; prepared sandwiched catalyst $\text{Al}_2\text{O}_3/\text{Ni}/\text{Al}_2\text{O}_3$ by atomic layer deposition of porous Al_2O_3 thin-film over $\text{Ni}/\text{Al}_2\text{O}_3$ [16]. Sandwich model of catalyst prevented Ni gathering as well as facilitates double interaction of Ni with Al_2O_3 . Despite preparation complexity, this catalyst system had attained nearly 100% CO_2 and CH_4 conversion with absolute selectivity towards CO and H_2 .

Apart from these, Al_2O_3 support also tunes acid-basic profile and reducibility of promoted/modified catalytic surface. Promotional addition of various basic (Mg, Sr)[17,18], acidic (B)[19], transition metal (Mn, Co, W)[20,21, 22] and redox (Ce, Zr, La)[23,24, 25] promoters had shown a remarkable effect on activity and coke resistance. Basicity enhances CO_2 absorption, whereas acidity encounters CH_4 dissociation. Cobalt controls Ni's ensemble size, whereas Mn partially blocks large Ni particles to slow down the coke formation [20,21]. W formed catalytic important Ni-W alloy species which hindered the carbon deposition inside the lattice, and further tungsten carbide was supposed to carry out carbon gasification [22]. Among the redox set, ceria was found promising to facilitate accessible mobile oxygen in the lattice for accelerating surface oxidation reactions during DRM [23]. ZrO_2 addition enhanced the dissociation of CO_2 at Ni- ZrO_2 boundary, and its redox property gasified the coke afterwards [24]. Recently, Al-Fatesh et al.; used BO_x , SiO_2 , TiO_2 , ZrO_2 , MoO_x and WO_x promoted Ni supported Al_2O_3 catalyst for DRM reaction where Si and W promoted catalyst nourished “excellent Ni dispersion” as well as “strongly interacted NiO species with support (or NiAl_2O_4 species)”. This catalyst system conquered >64% CH_4 conversion, >70% CO_2

conversion and >0.90 mol H_2/CO ratio [26]. Fakeeha et al.; used Ni supported Al_2O_3 catalysts promoted by CuO, ZnO, Ga_2O_3 and Gd_2O_3 among which Gd_2O_3 promoted catalyst claimed 87% H_2 yield with $H_2/CO \sim 1$ through DRM reaction [27]. The role of lanthana as a thermal stabilizer of Al_2O_3 at very high temperature (1000-1100°C) was found substantial [28]. However, at DRM reaction condition (600-800°C), the following significant surface catalytic features were attained in favor of DRM after lanthana addition. (1) Increasing metal-support interaction (Ni--Al) or enhancing Ni dispersion [29, 30]. (2) Optimizing the size of nickel particles for DRM [31, 32]. (3) Enhancing the basic characteristics which may induce the CO_2 adsorption for oxidation of carbon deposits [33,34]. Again, upon increasing CO_2 concentration, Boudouard equilibrium may shift towards CO formation, resulting in carbon deposit removal. (4) Enhancing the redox potential of $La_2O_3/La_2O_2CO_3$, which could also gasify the carbon species [25, 35, 36, 37]. (5) Minimizing the H_2 consumption by inhibiting the reverse water gas shift reaction (RWGS) [38, 39].

Moreover, for bearing such qualities over catalyst surface, lanthana is also needed to be dispersed in alumina vicinity. Herein, we utilized the $x\%La_2O_3 + (100-x)\% Al_2O_3$ as support to weave a close network of lanthana with Al_2O_3 . Furthermore, Ni was deposited over $x\%La_2O_3 + (100-x)\% Al_2O_3$ support by the wet impregnation method. This combination facilitated good Ni dispersion and Ni-support interaction over “lanthana containing Al_2O_3 support”. The catalyst was abbreviated as 5Ni_xLa(100-x) Al (x = 0, 10, 15, 20 wt%).

2. Experimental

2.1. Materials

$La(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, deionized water, mesoporous $\gamma-Al_2O_3$, crucible, crusher (mortar with a pestle).

2.2. Catalyst Preparation

The weight of an empty crucible was measured and recorded. Depending on the catalyst's desired composition and mass, a calculated amount of the support (meso- γ - Al_2O_3) was weighed and poured into the empty crucible. Also, specific masses of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the crucible containing the support to obtain a powder mixture. The percentage weight of Ni in all of the synthesized catalysts was made at a fixed value of 5wt.%. The mixture was grounded thoroughly until all the greenish colour of nickel nitrate has disappeared. Deionized water was added dropwise to the ground powder mixture in the crucible to form a paste. It was well stirred, and the water was allowed to evaporate under ambient condition overnight. The crucible plus sample's weight was measured, and subsequently, that of the sample was determined after drying overnight. Thereafter, the dried sample was calcined at 700°C for 3 hours. The calcined 5 wt% Ni-x wt% La_2O_3 -(100-x) Al_2O_3 (x = 0, 10, 15, and 20 wt %) catalysts were abbreviated as 5Ni_xLa(100-x)Al where x = 1, 10, 15 and 20 wt%).

2.3. Catalytic reaction

The catalyst activity test is described in detail in the supporting information S1.

2.4. Catalyst characterization

The specification and analysis details are described in the supporting information S2.

3. Result

3.1. Catalytic activity and thermal gravimetric analysis results

The catalytic activity of 5Ni_xLa(100-x)Al (x = 0, 10, 15, 20 wt%) catalytic system is shown in **Fig. 1(A) -1(C)**. The 5Ni100Al catalyst showed 55-51% CH_4 conversion and 69-66% CO_2 conversion, $\text{H}_2/\text{CO} \sim 0.88$ to 0.85 up to 460 minutes in the time on stream test. 5%Ni impregnated on dual support (10% basic lanthana, and 90% acidic alumina) and was denoted as 5Ni10La90Al. It showed constant $\sim 57\%$ CH_4 conversion and constant $\sim 73\%$ CO_2 conversion and $\text{H}_2/\text{CO} \sim 0.93$ -0.89 up to 460 minutes in time on stream test. 5Ni15La85Al catalyst showed optimum catalytic activity of 64% CH_4 conversion and 79% CO_2 conversion

with $H_2/CO \sim 1$ up to 460-minute in the time on stream test. Lanthana loading of 20 wt.% (5Ni20La80Al) showed ~55% CH_4 conversion and ~70 CO_2 conversion, $H_2/CO \sim 0.87$ -0.82. The catalytic performance of 5Ni20La80Al was almost similar to the catalyst's performance without lanthana loading (5Ni100Al).

Thermal gravimetric analysis (TGA) result of spent 5Ni_xLa(100-x)Al (x = 0, 10, 15, 20 wt%) catalyst samples is shown in **Fig. S1**. Spent 5Ni100Al catalyst showed continuous weight loss up to 830°C. 3% weight loss in the initial 10 minutes (<200 °C) due to loss of moisture from the surface, 7% weight loss in next 10-35 minutes (<600 °C) due to loss of amorphous carbon and 17% weight loss in the range of 35-50 minute (600-800 °C) is due to loss of graphitic carbon [40]. The effect of Lanthana addition in support can be observed clearly. The major weight loss region 600-800 °C (due to graphitic carbon) is completely absent in all Lanthana containing catalyst. It may be expected that the basic property of Lanthana may improve CO_2 absorption and thereby enhancing the reverse Boudouard reaction to eliminate carbon deposits during the DRM reaction [41, 42].

Fig. 1. Catalytic activity of 5Ni_xLa (100-x)Al (x = 0, 10, 15, 20 wt%) catalyst samples (A) CH₄ conversion against time-on-stream (TOS), (B) CO₂ conversion against TOS, and (C) H₂/CO ratio against TOS

3.2. Characterization Results

3.2.1 X-ray diffraction: The XRD profiles of the different fresh and spent 5Ni_xLa(100-x)Al (x = 0, 10, 15, 20 wt%) catalyst samples are shown in **Fig. 2 (A-C)**. The 5Ni100Al catalyst showed diffraction lines that correspond to aluminium oxide (JCPDS card reference no. 00-001-1308, 01-080-1385) and nickel aluminium oxide crystalline (JCPDS card reference no. 00-001-1299) major peaks at $2\theta = 31.2^\circ$, 37.17° , 45.6° , 66° at plane (220), (311), (400), (440), respectively [43]. Nickel aluminium oxide's formation is generally reported on Al₂O₃ supported nickel system as it is a diffusion couple of NiO and Al₂O₃ [44]. It is interesting to observe that beyond the 15wt% lanthana loading, the crystallinity of the catalyst is faded and becomes amorphous. That means the basic addition of lanthana oxide dignified the acidic crystalline structures of

aluminium oxide and nickel aluminium oxide. **It indicates the role of basicity in promoting crystallinity.** Previously, Nortier et al; also reported that with decreasing acidity profile of alumina, alumina's surface crystallinity decreases from crystalline to amorphous phase [45]. XRD profile of spent catalyst showed bulk crystalline carbon diffraction lines at $2\theta = 44.2^\circ$ (JCPDS card reference no. 01-075-0410) and metallic nickel at $2\theta = 44.3^\circ$ and 51.6° (JCPDS card reference no. 00-001-1258), respectively in **Fig. 2(B-C)**. The crystallinity of aluminium oxide and nickel aluminium oxide was impacted during the DRM reaction as the intensity of (4, 4, 0) at $2\theta = 66^\circ$ brag angle was reduced. However, after lanthana addition with alumina support, the crystallinity was retained after the DRM reaction.

Fig. 2. The XRD profile of different fresh and spent 5Ni_xLa (100-x) Al (x = 0, 10, 15, 20wt%) catalyst sample.

3.2.2. Transmission Electron Microscopy (TEM): The TEM images of fresh and spent 5Ni_xLa (100-x)Al (x = 0, 10, 15, 20 wt%) catalyst samples are shown in **Fig. 3**. TEM image also

showed well-dispersed Ni species over $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ dual support. 5Ni15La85Al catalyst had well-dispersed Ni species of 4 nm average size. However, after the reaction, the size of the Ni species increased to 7-8 nm (**Fig. 3(C)**). 5Ni20La80Al catalyst also showed dispersed Ni species of an average size of 6.2 nm. In the TEM image of spent 5Ni20La80Al and 5Ni15La85Al catalyst system, the carbon nanotubes can be easily observed, which resulted from carbon deposition over the catalyst.

Fig. 3. TEM image of (A) 5Ni15La85Al catalyst; inset figure shows distribution curve of Ni species (B)-(C) spent 5Ni15La85Al catalyst (D) 5Ni20La80Al catalyst; inset figure shows distribution curve of Ni species (E)-(F) spent 5Ni20La80Al catalyst

3.2.3. The Infrared spectra: The Infrared spectra of 5Ni_xLa (100-x) Al (x = 0, 10, 15, 20 wt%) catalytic sample systems are shown in **Fig. 4 (A)**. $\gamma\text{-Al}_2\text{O}_3$ is characterized by the presence of all three absorption bands at 1635, 1517 and 1382 cm^{-1} [46, 47]. The absorption band at 2349 cm^{-1} is attributed to physically adsorbed CO_2 gases [48]. The absorption bands at 1730 and 1270 cm^{-1} indicated bidentate CO_2 chemisorbed species over γ -alumina [49]. After 10% lanthana addition with alumina dual supports, 1730 and 1270 cm^{-1} absorption bands disappeared, and an absorption band at 1517 cm^{-1} increased in intensity. Basic La_2O_3 would

interact with acidic CO₂ and may form unidentate carbonate. It indicates partial diffusion of La⁺³ into Al⁺³, and the infrared band for “unidentate carbonate species coordinated to La” showed impression on band especially around 1517-1530 cm⁻¹ [50,51,52]. Further lanthana addition at 15wt.% in 5Ni15La85Al catalyst showed absorption bands for both unidentate as well as bidentate carbonate species. However, when infra-red spectra of “CO₂-TPD treated 5Ni15La85Al” catalyst system was taken, the absorption bands that are attributed to a hydroxyl group (at 1635 and 3460 cm⁻¹) decreased in intensity and absorption bands attributed to bidentate carbonate species (at 1730 and 1270 cm⁻¹) are completely absent (**Fig. 4 B**) [53]. The absorption bands correspond to unidentate species at 1517 cm⁻¹ also got reduced. It indicates that at high temperature, surface hydroxyl species are reduced, and so CO₂ interactions on hydroxylated oxide surfaces were decreased such that CO₂ bidentate species were lost completely whereas unidentate species remained on the catalyst surface [54, 55]. Thus, under high reaction temperature, unidentate carbonate species were available on the 5Ni15La85Al catalyst surface. The absorption bands attributed to ionic anhydrous lanthanum carbonate at 1464, 1084 and 859 cm⁻¹ were completely absent in these catalytic systems [56].

Fig. 4. Infra-red spectra of 5Ni_xLa(100-x)Al (x = 0, 10, 15, 20 wt%) catalyst samples

3.2.4. Surface area and porosity measurement: Nitrogen sorption isotherms of 5Ni_xLa (100-x)Al (x = 0, 10, 15, 20 wt%) samples are plotted in **Fig. 5**, and the textural data are depicted in **Table 1**. All samples indicated typical type IV adsorption/desorption isotherms with H1 hysteresis loop. Point of inflection at a relative pressure was in the range of 0.6–0.75 corresponds to the capillary condensation, which indicated uniformity of the pores in mesoporous materials [57, 58]. After loading 10wt.% lanthana, the surface area, pore volume and pore diameter all decreased. It indicated a possible deposition of lanthanum oxide into the pores of the alumina support. On 15wt.% lanthana loading, the surface morphology was not only retained but improved. In XRD also; at 15wt% Lanthana loading, the crystallinity of catalyst is faded, which may improve the surface parameters [59]. It indicated that from 10-15wt.% lanthana loading, lanthanum is successfully incorporated into the aluminium network and expanded the framework. Hence improved the surface morphology of the catalytic system; thus, this loading was found optimum. So, at 15% La loading, pore occlusion was decreased (than 10% La loading) due to the expansion of surface parameters. Further loading at 20 wt.% lanthana, all the three texture parameters were significantly decreased, indicating rapid deposit of lanthana in the pores and forming clusters and hence blocked the pore structure of the parent alumina support.

Fig. 5. N₂ physisorption and BJH adsorption pore size distribution plots for 5Ni_xLa(100-x) Al (x = 0, 10, 15, 20 wt%) catalyst samples

Table 1. Textural properties (S_{BET} , P_v , and P_d) of 5Ni_xLa(100-x) Al (x = 0, 10, 15, 20 wt%) catalyst samples

Catalyst	S_{BET} , m ² /g	P_v , cm ³ /g	P_d , nm
5Ni100Al	185.6	0.64	12.4
5Ni10La90Al	161.7	0.55	12.2
5Ni15La85Al	162.2	0.61	12.9
5Ni20La80Al	134.9	0.49	12.2

3.3.5. H₂-Temperature Programmed Reduction (H₂-TPR)

H₂-temperature-programmed reduction profiles of 5Ni_xLa(100-x)Al (x = 0, 10, 15, 20%) samples are shown in Fig. 6. All catalyst samples showed H₂-TPR peaks after 600°C. This indicates the strong interaction between the Ni species with the support as hence there was no free NiO reduction peak in the low-temperature region. The TPR peak at around 750-850°C can be attributed to the reduction of NiAl₂O₄ spinel, which might be ascribed to the strong interaction between NiO and Al₂O₃ [31, 60, 61, 62]. The effect of La addition to support can be seen clearly. In the 5Ni10La90Al catalyst sample, reduction peaks of nickel aluminate were decreased. For the 5Ni15La85Al catalyst sample, reduction peak shifted to the higher temperature region, which signified the strong interaction of NiO with support. 5Ni20La80Al catalyst showed reduction profile very similar to 5Ni10La90Al catalyst.

Fig. 6. The H₂-TPR profiles of 5Ni_xLa(100-x) Al (x = 0, 10, 15, 20 wt%) catalyst system

3.3.6. CO₂-Temperature Programmed De-adsorption (CO₂-TPD)

To understand the catalyst surface's basic profile, CO₂-TPD has been carried out and shown in **Fig. 7 (A)**. The desorption CO₂ peaks qualitatively differentiated the catalyst surface into four types of basic regions [63]. The peak below 100°C indicated weak basic sites related to surface hydroxyl, below 200°C for intermediate strength -basic sites related to bidentate carbonates, peak 250°-400 °C for strong basic sites associated with isolated O₂⁻ species and peak at a high temperature of super basic sites associated with unidentate carbonates [64, 65]. All catalysts have a little amount of medium strength bidentate carbonate species. Interestingly, after the addition of 10% basic lanthana, basic sites regions decreased relative to 5Ni100Al. IR spectra also indicated the disappearance of bidentate carbonate species at 10% lanthana loading, affecting the density of the basic sites. After addition of 15wt.% basic lanthana, the basic sites are greatly nurtured at the catalyst surface. This surface was enriched with a wide variety of basic sites as well as it also bears a broad peak of super basic sites. IR spectra also indicated the presence of unidentate as well as bidentate carbonate species at 15% lanthana loading. It may be a clear indication of the best activity of the 5Ni15La85Al amongst the rest of the catalysts.

3.3.7. NH₃-Temperature Programmed De-adsorption (NH₃-TPD)

To understand the acid profile of the catalyst surface, NH₃-TPD has been carried out and are shown in **Fig. 7 (B)**. For catalyst 5Ni100Al, as the support is acidic, it had a wide range of acid sites over the catalyst surface. It was observed that with increasing La content on alumina supported Ni catalysts, the acid sites density decreased. It seems that the La addition to alumina played a crucial role in neutralizing the acidity of the alumina. Overall, the 5Ni15La85Al catalyst system can be characterized as the low acid profile catalyst system. Strong acidic catalyst system inhibits dissociative chemisorption of CO₂ onto the catalyst surface. Proper CO₂ dissociation and thereafter oxidation of carbon deposit can take place over low acidic catalyst system. So, the low acidic catalyst system is known for coke free DRM operation [66,67,68].

Fig. 7. Temperature Programmed Desorption profile of 5Ni_xLa(100-x)Al (x = 0, 10, 15, 20 wt%) catalyst system (A) CO₂-TPD (B) NH₃-TPD.

4. Discussion

Absence of NiO diffraction crystalline peaks in all catalyst samples showed that alumina and lanthana-alumina are good crystalline dual-support to carry dispersed Ni species at high temperature. In all catalytic systems, CO₂ conversion was higher than CH₄ conversion which indicated that CO₂ was also involved in other reaction such as RWGS reaction (CO₂ + H₂ → CO + H₂O) other than DRM [69]. Due to the RWGS reaction, H₂ was consumed, and CO is

315 released. So, H_2/CO ratio may be affected seriously. Now over 5Ni100Al, reducible nickel
316 aluminate amount, expanded surface parameters and a moderate amount of weak as well as
317 strong basic sites rendered good catalytic activity of 55% CH_4 conversion and 70% CO_2
318 conversion. Besides, the rich surface acid profile of 5Ni100Al competed for the methane
319 decomposition with lower H_2 yield and higher carbon accumulation [70]. So, it had the lowest
320 H_2/CO ratio of 0.88 and showed the highest carbon deposition (17% within 550-750°C) over
321 catalytic active sites, thus causing the catalyst deactivation.

322 Besides, the basic 10wt.% lanthana joined the acidic alumina as a dual-support system. The
323 crystallinity of alumina was lost (as observed in XRD), surface parameter (surface area, pore
324 volume and pore diameter) declined, and acid sites density slowly depleted (as observed in
325 NH_3 -TPD). Interestingly, bidentate carbonate species or basic sites are devastated (as observed
326 in CO_2 -TPD), but unidentate carbonates are gathered at the catalyst surface (as observed in IR).
327 Reducible nickel aluminate and vanishing acid sites (as observed in NH_3 -TPD) did not feed
328 excess carbon deposits to the catalyst surface, and carbon deposits are regularly washed away
329 by CO_2 through the oxidation process. Overall, this catalyst rendered constant CH_4 conversion
330 ~57% and constant CO_2 conversion ~73% up to 460 minutes in time on stream test with
331 minimum carbon deposition. Lower acid site density of 5Ni10La90Al led to higher H_2/CO ratio
332 0.93 relative to 5Ni100Al.

333 5Ni15La85Al had reducible “NiO supported species”, a wide range of basic site density
334 including super basic sites (related to unidentate carbonates) and a lower amount of acid site
335 density. Low acid profile and rich basic profile facilitated control of CH_4 dissociation and
336 supported CO_2 dissociative chemisorption onto catalyst surface to oxidate carbon deposits. The
337 fine-tuning of acid and basic sites inhibited the pulverization and graphitization of carbon
338 deposits responsible for the catalyst deactivation. Overall, it had an optimum catalytic activity

of 64% CH₄ conversion and 79% CO₂ conversion with H₂/CO ~ 1 up to 460-minute in the time on stream test.

Lanthana loading up to 20% with alumina supports claimed minimum crystallinity, most compact surface parameters (surface area, pore volume and pore diameter), minimum acidity, minimum strong basic site density and more carbon deposits after 5Ni100Al. However, it had a moderate amount of weak basic sites more than that of 5Ni100Al catalyst. Overall, CH₄ conversion and CO₂ conversion, H₂/CO ratio and even carbon deposits from the TGA profiles of 5Ni20La80Al remained very similar to that of 5Ni100Al catalyst.

5. Conclusion

NiO is well dispersed over alumina and lanthana-alumina dual-support. On increasing basic lanthana proportion in acidic alumina, the crystallinity of alumina and acidity of total support declined. 15wt.% lanthana was the optimum loading in the lanthana-alumina dual-support system, at 5Ni15La85Al, a wide range of basic site densities, including super basic sites (related to unidentate carbonates) are nurtured additionally. A combat balance between the acid sites and basic sites over the catalyst surface controlled the CH₄ decomposition, carbon deposit oxidation by CO₂ and inhibition of the pulverization and carbon deposit graphitization. Altogether, 5Ni15La85Al ensured low carbon deposit as well as the optimum catalytic activity of about 64% CH₄ conversion and 79% CO₂ conversion with H₂/CO ~ 1 up to 460-minute time on stream. At 20wt.% lanthana loading, it showed rapid loss of surface area, pore-volume, pore diameter, acidity and medium strength basic sites which herald inferior catalytic performance.

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- [1] M. M. Zain, A. R. Mohamed, An overview on conversion technologies to produce value added products from CH₄ and CO₂ as major biogas constituents. *Renew Sustain Energy Rev* 98 (2018) 56–63. <https://doi.org/10.1016/j.rser.2018.09.003>
- [2] Ş.Ö.-Aydınoglu, E. Özensoy, A. E. Aksoylu, The effect of impregnation strategy on methane dry reforming activity of Ce promoted Pt/ZrO₂, *Int. J. Hydrog. Energy* 34 (2009) 9711–9722. <https://doi.org/10.1016/j.ijhydene.2009.09.005>
- [3] S. M. S.-Williams, F. B. Noronha, G. Fendley, D. E. Resasco, CO₂ Reforming of CH₄ over Pt/ZrO₂ Catalysts Promoted with La and Ce Oxides, *J. Catal.* 194 (2000) 240–249. <https://doi.org/10.1006/jcat.2000.2939>.
- [4] K. Nagaok, M. Okamur, K. Aika, Titania supported ruthenium as a coking-resistant catalyst for high pressure dry reforming of methane, *Catalysis Catal. Commun.* 2 (2001) 255–260. [https://doi.org/10.1016/S1566-7367\(01\)00043-7](https://doi.org/10.1016/S1566-7367(01)00043-7).
- [5] P. Ferreira-Aparicio, I. Rodríguez-Ramos, J. A. Anderson, A. Guerrero-Ruiz, Mechanistic aspects of the dry reforming of methane over ruthenium catalysts, *Applied Appl. Catal. A: Gen.* 202 (2000) 183–196. [https://doi.org/10.1016/S0926-860X\(00\)00525-1](https://doi.org/10.1016/S0926-860X(00)00525-1).
- [6] L. V. Mattos, E. Rodino, D. E. Resasco, F. B. Passos, F. B. Noronha, Partial oxidation and CO₂ reforming of methane on Pt/Al₂O₃, Pt/ZrO₂, and Pt/Ce–ZrO₂ catalysts, *Fuel Process. Technol.* 83 (2003) 147 – 161. [https://doi.org/10.1016/S0378-3820\(03\)00063-8](https://doi.org/10.1016/S0378-3820(03)00063-8).
- [7] A. M. Efstathiou, A. Kladi, V. A. Tsiouriari, X. E. Verykios, Reforming of Methane with Carbon Dioxide to Synthesis Gas over Supported Rhodium Catalysts: II. A Steady-State Tracing Analysis: Mechanistic Aspects of the Carbon and Oxygen Reaction Pathways to Form CO, *Journal J. Catal.* 158 (1996) 64–75. <https://doi.org/10.1006/jcat.1996.0006>.
- [8] H. Cheng, G. Li, H. Zhao, X. Lu, Q. Xu, W. Tao, Effects of preparation technique and lanthana doping on Ni/La₂O₃ -ZrO₂ catalysts for hydrogen production by CO₂ reforming of coke oven gas. *Catal. Today* 318 (2018) 23–31. <https://doi.org/10.1016/j.cattod.2017.11.017>
- [9] U.-C. Chung, Effect of H₂ on Formation Behavior of Carbon Nanotubes. *Bull. Korean Chem. Soc.*, 25 (10) (2004) 1521. <https://doi.org/10.4028/www.scientific.net/MSF.475-479.3559>.
- [10] X. U Junke, Z. Wei, W. Jihui, L. I. Zhaojing, M. A Jianxin, Characterization and Analysis of Carbon Deposited during the Dry Reforming of Methane over Ni/La₂O₃/Al₂O₃ Catalysts, *Chin. J. Catal.*, 30 (11) (2009) 1076–1084. [https://doi.org/10.1016/S1872-2067\(08\)60139-4](https://doi.org/10.1016/S1872-2067(08)60139-4).
- [11] Y. Xu, X.H. Du, J. Li, P. Wang, J. Zhu, F.J. Ge, J. Zhou, M. Song, W. Y. Zhu, A comparison of Al₂O₃ and SiO₂ supported Ni-based catalysts in their performance for the dry reforming of methane. *Ranliao Huaxue Xuebao/Journal Fuel Chem. Technol.* **2019**, 47, 199–208, doi:10.1016/s1872-5813(19)30010-6.

-
- [12] L. Zhou, L. Li, N. Wei, J. Li, J.-M. Basset, Effect of NiAl_2O_4 Formation on $\text{Ni/Al}_2\text{O}_3$ Stability during Dry Reforming of Methane. *ChemCatChem* **2015**, 7, 2508–2516, doi:10.1002/cctc.201500379
- [13] D. Shen, M. Huo, L. Li, S. Lyu, J. Wang, X. Wang, Y. Zhang, J. Li, Effects of alumina morphology on dry reforming of methane over $\text{Ni/Al}_2\text{O}_3$ catalysts. *Catal. Sci. Technol.* **2020**, 10, 510–516, doi:10.1039/c9cy02093d
- [14] X. Fang, , C. Peng H. Peng, W. Liu, X. Xu, X. Wang, C. Li, Zhou, W. Methane Dry Reforming over Coke-Resistant Mesoporous $\text{Ni-Al}_2\text{O}_3$ Catalysts Prepared by Evaporation-Induced Self-Assembly Method. *ChemCatChem* **2015**, 7, 3753–3762, doi:10.1002/cctc.201500538
- [15] R.L.B.A. Medeiros, G.P. Figueredo, H.P. Macedo, Â. A.S. Oliveira, R.C. Rabelo-Neto, D.M.A. Melo, R.M. Braga, M.A.F. Melo, One-pot microwave-assisted combustion synthesis of $\text{Ni-Al}_2\text{O}_3$ nanocatalysts for hydrogen production via dry reforming of methane. *Fuel* **2020**, 119511, doi:10.1016/j.fuel.2020.119511
- [16] Y. Zhao, Y. Kang, H. Li, H. Li, CO_2 conversion to synthesis gas: Via DRM on the durable $\text{Al}_2\text{O}_3/\text{Ni/Al}_2\text{O}_3$ sandwich catalyst with high activity and stability. *Green Chem.* **2018**, 20, 2781–2787, doi:10.1039/c8gc00743h
- [17] Z. Alipour, M. Rezaei, F. Meshkani, Effects of support modifiers on the catalytic performance of $\text{Ni/Al}_2\text{O}_3$ catalyst in CO_2 reforming of methane. *Fuel* **2014**, 129, 197–203, doi:10.1016/j.fuel.2014.03.045
- [18] A.S. Al-Fatesh, M.A. Naeem, A.H. Fakeeha, A.E. Abasaheed, CO_2 Reforming of Methane to Produce Syngas over $\gamma\text{-Al}_2\text{O}_3$ -Supported Ni-Sr Catalysts. *Bull. Chem. Soc. Jpn.* **2013**, 86, 742–748, doi:10.1246/bcsj.20130002
- [19] A. Fouskas, M. Kollia, A. Kambolis, C. Papadopoulou, H. Matralis, Boron-modified $\text{Ni/Al}_2\text{O}_3$ catalysts for reduced carbon deposition during dry reforming of methane. *Appl. Catal. A Gen.* **2014**, 474, 125–134, doi:10.1016/j.apcata.2013.08.016.
- [20] S.H. Seok, H.C. Sun, E.D. Park, H.H. Sung, S.L. Jae, Mn-promoted $\text{Ni/Al}_2\text{O}_3$ catalysts for stable carbon dioxide reforming of methane. *J. Catal.* **2002**, 209, 6–15, doi:10.1006/jcat.2002.3627
- [21] N. Rahemi, M. Haghighi, A.A. Babaluo, M.F. Jafari, S. Khorram, Non-thermal plasma assisted synthesis and physicochemical characterizations of Co and Cu doped $\text{Ni/Al}_2\text{O}_3$ nanocatalysts used for dry reforming of methane. *Int. J. Hydrogen Energy* **2013**, 38, 16048–16061, doi:10.1016/j.ijhydene.2013.08.084.
- [22] D. Vroulias, N. Gkoulemani, C. Papadopoulou, H. W Matralis, –modified $\text{Ni/Al}_2\text{O}_3$ catalysts for the dry reforming of methane: Effect of W loading. *Catal. Today* **2020**, 355, 704–715, doi:10.1016/j.cattod.2019.05.066

-
- [23] R.Y. Chein, W.Y. Fung, Syngas production via dry reforming of methane over CeO₂ modified Ni/Al₂O₃ catalysts. *Int. J. Hydrogen Energy* **2019**, 44, 14303–14315, doi:10.1016/j.ijhydene.2019.01.113
- [24] S. Therdthianwong, C. Siangchin, A. Therdthianwong, Improvement of coke resistance of Ni/Al₂O₃ catalyst in CH₄/CO₂ reforming by ZrO₂ addition. *Fuel Process. Technol.* **2008**, 89, 160–168, doi:10.1016/j.fuproc.2007.09.003
- [25] K. Li, C. Pei, X. Li, S. Chen, X. Zhang, R. Liu, J. Gong, Dry reforming of methane over La₂O₂CO₃-modified Ni/Al₂O₃ catalysts with moderate metal support interaction. *Appl. Catal. B Environ.* **2020**, 264, 118448, doi:10.1016/j.apcatb.2019.118448
- [26] A. S. Al-Fatesh, R. Kumar, S. O. Kasim, A. A. Ibrahim, A. H. Fakeeha, A. E. Abasaheed, R. Alrasheed, A. Bagabas, M. L. Chaudhary, F. Frusteri, B. Chowdhury, The effect of modifier identity on the performance of Ni-based catalyst supported on γ -Al₂O₃ in dry reforming of methane, *Catal. Today* 348 (2020) 236–242. <https://doi.org/10.1016/j.cattod.2019.09.003>.
- [27] A. H. Fakeeha, A. A. Bagabas, M. S. Lanre, Ahmed I. Osman, S. O. Kasim, A. A. Ibrahim, R. Arasheed, A. Alkhalifa, A. Y. Elnour, A. E. Abasaheed and A. S. Al-Fatesh, Catalytic Performance of Metal Oxides Promoted Nickel Catalysts Supported on Mesoporous γ -Alumina in Dry Reforming of Methane, *Processes*, 8 (2020) 522. <https://doi.org/10.3390/pr8050522>.
- [28] H. Schaper, E. B. M. Doesburg, L. L. Van Reijen, H. Schaper, E.B.M. Doesburg, L.L. van Reijen, The influence of lanthanum oxide on the thermal stability of gamma alumina catalyst supports, *Appl. Catal.* 7 (1983) 211–220. [https://doi.org/10.1016/0166-9834\(83\)80009-8](https://doi.org/10.1016/0166-9834(83)80009-8).
- [29] N. D. Charisiou, L. Tzounis, V. Sebastian, S. J. Hinder, M.A. Baker, K. Polychronopoulou, M. A. Goula, Investigating the correlation between deactivation and the carbon deposited on the surface of Ni/Al₂O₃ and Ni/La₂O₃ -Al₂O₃ catalysts during the biogas reforming reaction. *Appl. Surf. Sci.* 474 (2019) 42–56. <https://doi.org/10.1016/j.apsusc.2018.05.177>.
- [30] R. M. Navarro, M. C. Álvarez-Galván, F. Rosa, J. L. G. Fierro, Hydrogen production by oxidative reforming of hexadecane over Ni and Pt catalysts supported on Ce/La-doped Al₂O₃, *Appl. Catal. A: Gen.* 297 (2006) 60–72. <https://doi.org/10.1016/j.apcata.2005.08.036>
- [31] W. Mo, F. Ma, Y. Ma, X. Fan, The optimization of Ni–Al₂O₃ catalyst with the addition of La₂O₃ for CO₂–CH₄ reforming to produce syngas. *Int. J. Hydrog. Energy* 44 (2019) 24510–24524. <https://doi.org/10.1016/j.ijhydene.2019.07.204>.
- [32] K. W. Siew, H. C. Lee, J. Gimbun, S. Y. Chin, M. R. Khan, Y. H. Taufiq-Yap, C. K. Cheng, Syngas production from glycerol-dry (CO₂) reforming over La-promoted Ni/Al₂O₃ catalyst, *Renewable Energy* 74 (2015) 441–447. <https://doi.org/10.1016/j.renene.2014.08.048>.
- [33] T. Hou, S. Zhang, Y. Chen, D. Wang, W. Cai, Hydrogen production from ethanol reforming: catalysts and reaction mechanism. *Renew Sustain. Energy Rev.* 44 (2015) 132–148. <https://doi.org/10.1016/j.rser.2014.12.023>.
- [34] M. Miyamoto, A. Hamajima, Y. Oumi, S. Uemiya, Effect of basicity of metal doped ZrO₂ supports on hydrogen production reactions, *Int. J. Hydrog. Energy* 43 (2018) 730–738. <https://doi.org/10.1016/j.ijhydene.2017.11.041>.

-
- [35] H. Chen, H. Yu, F. Peng, H. Wang, J. Yang, M. Pan, Efficient and stable oxidative steam reforming of ethanol for hydrogen production: effect of in situ dispersion of Ir over Ir/La₂O₃. *J. Catal.* 269 (2010) 281-290. <https://doi.org/10.1016/j.jcat.2009.11.010>.
- [36] M.-N. N. Shafiqah, H. N. Tran, T. D. Nguyen, P. T. T. Phuong, B. Abdullah, S. S. Lam, P. Nguyen-Tri, R. Kumar, S. Nanda, D.-V. N. Vo, Ethanol CO₂ reforming on La₂O₃ and CeO₂-promoted Cu/Al₂O₃ catalysts for enhanced hydrogen production, *Int. J. Hydrog. Energy* 45 (2020) 18398-18410. <https://doi.org/10.1016/j.ijhydene.2019.10.024>.
- [37] S. Isarapakdeetham, P. K.-Lohsoontorn, S. Wongsakulphasatch, W. Kiatkittipong, N. Laosiripojana, J. Gonge, S. Assabumrungrat, Hydrogen production via chemical looping steam reforming of ethanol by Ni-based oxygen carriers supported on CeO₂ and La₂O₃ promoted Al₂O₃, *Int. J. Hydrog. Energy* 45 (2020) 1477-1491. <https://doi.org/10.1016/j.ijhydene.2019.11.077>.
- [38] C. Chen, X. Wang, L. Zhang, X. Zou, W. Ding, X. Lu, Synthesis of mesoporous Ni–La₂O₃/SiO₂ by ploy(ethylene glycol)-assisted sol-gel route as highly efficient catalysts for dry reforming of methane with a H₂ /CO ratio of unity. *Catal. Commun.* 94 (2017) 38–41. <https://doi.org/10.1016/j.catcom.2017.02.018>.
- [39] J. Zhu, X. Peng, L. Yao, J. Shen, D. Tong, C. Hu, The promoting effect of La, Mg, Co and Zn on the activity and stability of Ni/SiO₂ catalyst for CO₂ reforming of methane, *Int. J. Hydrog. Energy* 36 (2011) 7094-7104. <https://doi.org/10.1016/j.ijhydene.2011.02.133>.
- [40] D. Liu, X.Y. Quek, H.A. Wah, G. Zeng, Y. Li, Y. Yang, Carbon dioxide reforming of methane over nickel-grafted SBA-15 and MCM-41 catalysts, *Catal. Today* 148 (2009) 243–265. <https://doi.org/10.1016/j.cattod.2009.08.014>.
- [41] Bartholomew CH. Mechanisms of catalyst deactivation. *Appl Catal Gen* 2001;212:17e60. [https://doi.org/10.1016/S0926-860X\(00\)00843-7](https://doi.org/10.1016/S0926-860X(00)00843-7).
- [42] V. Palma, E. Meloni, S. Renda, M. Martino, Catalysts for Methane Steam Reforming Reaction: Evaluation of CeO₂ Addition to Alumina-Based Washcoat Slurry Formulation, *J Carbon Research*. 6 (2020) 52. <https://doi.org/10.3390/c6030052>.
- [43] A. E. CLuna, M. E. Iriarte, Carbon dioxide reforming of methane over a metal modified Ni-Al₂O₃ catalyst, *Applied Appl. Catal. A: Gen.* 343 (2008) 10–15. <https://doi.org/10.1016/j.apcata.2007.11.041>.
- [44] F. S. Pettit, E. H. Randklev, E. J. Felten, Formation of NiAl₂O₄ by Solid State Reaction, *Journal of The American Ceramic Society*, 49 (1966) 199-203.
- [45] P. Nortier, P. Fourre, A.B. Mohammed Saad, O. Saur and J.C. Lavalley, *Appl. Catal.*, 61 (1990) 141.
- [46] C. Dyer, P. J. Hendra, Surface hydration of aqueous γ -Al₂O₃ studied by Fourier transform Raman and infrared spectroscopy—I. Initial results, *Spectrochim Acta*. 49A (1993) 691-705. [https://doi.org/10.1016/0584-8539\(93\)80092-O](https://doi.org/10.1016/0584-8539(93)80092-O).

-
- [47] L. Vlaev, D. Damyanov, M. Mohamed, Infrared spectroscopy study of the nature and reactivity of a hydrate coverage on the surface of γ -Al₂O₃, *Colloids Surf.* 36 (1989) 427-437. [https://doi.org/10.1016/0166-6622\(89\)80257-4](https://doi.org/10.1016/0166-6622(89)80257-4).
- [48] N. D. Parkyns, Influence of thermal pretreatment on the infrared spectrum of carbon dioxide adsorbed on alumina, *J. Phy. Chem.* 76 (1971) 526-531. <https://doi.org/10.1021/j100674a014>.
- [49] G. Busca, V. Lorenzelli, Infrared Spectroscopic Identification of Species Arising from Reactive Adsorption of Carbon Oxides on Metal Oxide Surfaces, *Material Chemistry* 7 (1982) 89-126.
- [50] Pham MH, Goujard V, Tatibouët JM, Batiot-Dupeyrat C. Activation of methane and carbon dioxide in a dielectric-barrier discharge-plasma reactor to produce hydrocarbons—Influence of La₂O₃/γ-Al₂O₃ catalyst. *Catal. Today* 171 (2011) 67–71. <https://doi.org/10.1016/j.cattod.2011.03.015>.
- [51] Barrera A, Fuentes S, Viniegra M, Avalos-Borja M, Bogdanchikova N, Campa-Molina J. Structural properties of Al₂O₃–La₂O₃ binary oxides prepared by sol–gel. *Mater. Res. Bull.* 42 (2007) 640–8. <https://doi.org/10.1016/j.materresbull.2006.08.001>.
- [52] D. Salinas, N. Escalonab, G. Pecchie, J. L. G. Fierro, Lanthanum oxide behavior in La₂O₃-Al₂O₃ and La₂O₃-ZrO₂ catalysts with application in FAME production, *Fuel* 253 (2019) 400-408. <https://doi.org/10.1016/j.fuel.2019.05.015>.
- [53] L. Vlaev, D. Damyanov, M. Mohamed, Infrared Spectroscopy Study of the Nature and Reactivity of a Hydrate Coverage on the Surface of γ-Al₂O₃, *Colloids Surf.*, 36 (1989) 427-437. [https://doi.org/10.1016/0166-6622\(89\)80257-4](https://doi.org/10.1016/0166-6622(89)80257-4).
- [54] J. Baltrusaitis, J. H. Jensen, V. H. Grassian, FTIR Spectroscopy Combined with Isotope Labeling and Quantum Chemical Calculations to Investigate Adsorbed Bicarbonate Formation Following Reaction of Carbon Dioxide with Surface Hydroxyl Groups on Fe₂O₃ and Al₂O₃, *J. Phys. Chem. B*, 110 (2006) 12005-12016. <https://doi.org/10.1021/jp057437j>.
- [55] Y. Pan, C.-J. Liu, Q. Ge, Adsorption and Protonation of CO₂ on Partially Hydroxylated γ-Al₂O₃ Surfaces: A Density Functional Theory Study, *Langmuir* 24 (2008) 12410-12419. <https://doi.org/10.1021/la802295x>.
- [56] D. Salinas, C. Sepúlveda, N. Escalona, J. L. G. Fierro, G. Pecchia, Sol–gel La₂O₃–ZrO₂ mixed oxide catalysts for biodiesel production, *J. Energy Chem.* 27 (2018) 565-572. <https://doi.org/10.1016/j.jechem.2017.11.003>.
- [57] Sandip Mandal, Chiranjit Santra, Rawesh Kumar, Malay Pramanik, Sumbul Rahman, Asim Bhaumik, Sudip Maity, Debasis Sen and Biswajit Chowdhury, Niobium doped hexagonal mesoporous silica (HMS-X) catalyst for vapor phase Beckmann rearrangement reaction, *RSC Adv.*, 4 (2014) 845–854. <https://doi.org/10.1039/C3RA41840E>.
- [58] S. Rahman, C. Santra, R. Kumar, J. Bahadur, A. Sultana, R. Schweins, D. Sen, S. Maity, S. Mazumdar, Biswajit Chowdhury, Highly active Ga promoted Co-HMS-X catalyst towards styrene epoxidation reaction using molecular O₂, *Appl. Catal. A: Gen.* 482 (2014) 61–68. <https://doi.org/10.1016/j.apcata.2014.05.024>.

-
- [59] M. Toyoda, Y. Nanbu, Y. Nakazawa, M. Hirano, M. Inagaki, Effect of crystallinity of anatase on photoactivity for methyleneblue decomposition in water, *Applied Catalysis B: Environmental* 49 (2004) 227–232. <https://doi.org/10.1016/j.apcatb.2003.12.012>
- [60] Z. Y. Hou, O. Yokota, T. Tanaka, T. Yashima. Characterization of Ca-promoted Ni/ α - Al_2O_3 catalyst for CH_4 reforming with CO_2 , *Appl. Catal. A*, 253 (2003) 381. [https://doi.org/10.1016/S0926-860X\(03\)00543-X](https://doi.org/10.1016/S0926-860X(03)00543-X).
- [61] X. Chen, K. Honda, Z. G. Zhang, CO_2 - CH_4 reforming over $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ in fixed-bed/fluidized-bed switching mode, *Catal. Today*, 93-95 (2004) 87. <https://doi.org/10.1016/j.cattod.2004.06.015>.
- [62] B. S. Liu, C. T. Au, Carbon deposition and catalyst stability over $\text{La}_2\text{NiO}_4/\gamma\text{-Al}_2\text{O}_3$ during CO_2 reforming of methane to syngas, *Appl. Catal. A*, 244 (2003) 181. [https://doi.org/10.1016/S0926-860X\(02\)00591-4](https://doi.org/10.1016/S0926-860X(02)00591-4).
- [63] D. Salinas, N. Escalona, G. Pecchi, J. L. G. Fierro, Lanthanum oxide behavior in La_2O_3 - Al_2O_3 and La_2O_3 - ZrO_2 catalysts with application in FAME production *Fuel* 253 (2019) 400-408. <https://doi.org/10.1016/j.fuel.2019.05.015>.
- [64] Di Serio M, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Ind. Eng. Chem. Res.* 45(9) (2006) 3009–3014. <https://doi.org/10.1021/ie051402o>.
- [65] Santório R, Veloso CdO, Henriques CA. Preparation, basic properties and catalytic activity of Mg/La and Al/La catalysts for biodiesel production from refined and acid soybean oil. *J. Mol. Catal. A Chem* 422 (2016) 234–47. <https://doi.org/10.1016/j.molcata.2015.12.006>.
- [66] Y. Vafaeian, M. Haghighi, S. Aghamohammadi, Ultrasound assisted dispersion of different amount of Ni over ZSM-5 used as nanostructured catalyst for hydrogen production via CO_2 reforming of methane, *Energy Convers. Manag.* 76 (2013) 1093-1103. <https://doi.org/10.1016/j.enconman.2013.08.010>.
- [67] F. Mirzaei, M. Rezaei, F. Meshkani, Coprecipitated Ni-Co bimetallic nanocatalysts for methane dry reforming, *Chem. Eng. Technol.* 37 (2014) 973-978. <https://doi.org/10.1002/ceat.201300729>.
- [68] S. Das, M. Sengupta, J. Patel, A. Bordoloi, A study of the synergy between support surface properties and catalyst deactivation for CO_2 reforming over supported Ni nanoparticles, *Appl. Catal., A* 545 (2017) 113-126. <https://doi.org/10.1016/j.apcata.2017.07.044>.
- [69] N. Wang, W. Chu, T. Zhang, X. S. Zhao, Synthesis, characterization and catalytic performances of Ce-SBA-15 supported nickel catalysts for methane dry reforming to hydrogen and syngas, *Int. J. Hydrog. Energy* 37 (2012) 19-30. <https://doi.org/10.1016/j.ijhydene.2011.03.138>.
- [70] J. Ashok, S. Naveen Kumar, A. Venugopal, V. Durga Kumari, M. Subrahmanyam, CO_x -free H_2 production via catalytic decomposition of CH_4 over Ni supported on zeolite catalysts, *J. Power Sources* 164 (2007) 809–814. <https://doi.org/10.1016/j.jpowsour.2006.11.029>.