

RESEARCH ARTICLE

Synergistic effect of Promoter addition and Nickel Loading for Catalysed Dry Reforming of Methane

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Abstract

This paper investigates the synergistic influence of both catalyst active sites Lanthanum promoter and Nickel loading on supported Ni catalysts for Dry Reforming of Methane (DRM) reaction. Alumina-supported nanosized Ni-based catalysts were synthesized using the impregnation method with varying percentages of Lanthanum promoter. Structural analysis via XRD, SEM and PSD show Nickel and lanthanum particles were homogeneously dispersed on Al₂O₃ supported catalyst with a size range of 40-90 nm were obtained. Lanthanum addition favors equilibrated reaction equivalent to the DRM mechanism. Increasing the La percentage and temperature however shifts the equilibrium to a higher conversion of CH₄ (72%) hence higher H₂ selectivity (70%).

Keywords: Greenhouse gases; CO₂ Utilization; Dry Reforming Methane; Catalyst

1.0 Introduction

Natural Gas utilization is the main source of energy in Malaysia with the largest natural gas reservoir in South East Asia. Recent studies estimate that burning 1 ton of carbon in fossil fuels produces above 3.5 tons of CO₂. Current carbon capture and storage (CCS) technologies focus mainly on capture from large intensive sources such as oil refineries and power plants. CO₂ disposal by sequestration in geological storage has been costly and possess some limitation such as leakage, storage capacity, and also operation and maintenance cost. However, the continuous development of this high CO₂ gas field has created a significant new challenge whereby the paradigm has shifted from Carbon Capture Sequestration (CCS) to Carbon Capture Utilization (CCU) [1-3]. The valorization of methane to liquid fuels has been extensively studied due to large volumes of methane resources. Methane which is a major component of natural gas is produced at

the offshore reservoir, hence transportation is a hassle. Dry Reforming of Methane combines the utilization of both CO₂ and CH₄ to produce syngas which is used extensively for conversion to value-added products. Nevertheless, the challenge arises from catalyst design and development as a high temperature (>700 °C) is needed for this highly endothermic reaction [3, 4]. Currently, available catalysts are noble metal catalysts such as Ru, Rh, and Pt due to their high activity and susceptibility to deactivation [5]. Nevertheless, current research is more leaning towards supported Nickel and Copper-based catalyst as they are preferred in the industry as it is cheaper and has comparable activity [6]. However, the major setback from this reaction is rapid catalyst deactivation due to coke formation from CO continuous disproportionation reaction which leads to catalyst sintering [7, 8]. To avoid this, an alkaline promoter was added to reduce carbon deposition. La promoter can reduce sintering by mesoporous framework confinement besides increasing the basic site. Coke deposition can also be reduced if the reaction temperature can be reduced [9]. Synthesis parameters play a major role in obtaining the suitable catalyst structure and morphology for the desired reaction [10, 11]. In this manuscript, the role of La promoter and Nickel loading along with the reaction parameters will be scrutinized to further understand the mechanism of DRM for further catalysts upgrading.

2.0 Materials and Methods

2.1 Catalyst Synthesis & Characterization

A series of Nickel (Ni) catalysts supported on Alumina was synthesized at 30 °C using the impregnation method. 5g of Aluminum oxide was added slowly to 100 ml of Nickel (II) chloride solution (5, 10 & 50 wt% Ni) while stirring. Lanthanum oxide was added as the same amount percentage as nickel. The solution was allowed to stir continuously for 1 hour and then evaporated to dryness at 80 °C. The solid powder obtained was dried in an oven at 60 °C for 24 hours to remove the excess water. The X-Ray Diffractograms (XRD) were obtained using a Bruker's Theta/2theta goniometer and a Scintillation counter detector. The data sets were collected in reflection geometry in the range of $2^\circ \leq 2\theta \leq 80^\circ$ with a step size of $\Delta 2\theta = 0.02^\circ$ analyzed using High Score Plus software for phase identification. The surface morphology and the particle size distribution were determined using FEI's Field Emission Scanning Electron Microscope-Energy Dispersive X-ray (FESEM-EDX) and Malvern's Zetasizer. The synthesized catalysts were then activated in a tubular furnace underflow of 20ml/min of synthetic air.

2.2 Catalyst Activity Evaluation

Prior to the reaction, the synthesized catalyst was reduced based on Temperature Programmed Reduction conducted in Thermo Finnigan's TPDRO 1100. The catalytic activity for Dry Reforming of Methane was evaluated in a fixed bed reactor (Nanoflow) equipped with a valve switching gas chromatographic system for a quantitative effluent gas analysis. 0.3 g of catalyst were loaded into each reactor tube and the volume of the catalyst bed was set at 5 ml by inert (SiC) packing. The flow rate of the reactant feed was set to 100 ml/min ($N_2/CO_2/CH_4 = 80:10:10$) and GHSV $10,000\text{ h}^{-1}$) into the reactor tube at a temperature range of 450 - 525 °C. The spent catalysts were sieved to separate the SiC packing particles and subjected again to XRD and PSD analysis.

3. Results & Discussion

3.1 Structural Properties of Synthesized Catalyst

Figure 1 shows the XRD Diffractograms of synthesized Ni-based nanocatalyst with high crystallinity. All diffractograms show peak characteristics indexed to Nickel Oxide, NiO, a cubic phase, (PDF File 022-1189) with prominent peaks matching at 37.3° (003), 43.3° (012) and 62.9° (110) though it appears to be shifted in Figure 1 (b). Figure 1 (b,c,d) exhibits the addition of La_2O_3 matching the diffractogram with Lanthanum oxide, cubic crystal structure (PDF File 040-1284) with prominent peaks at 28.0° , (110) 39.8° (002) and 49.2° (211) though peaks at 28 and 49.2° appear to be overlapping with Lanthanum Nickel Oxide (PDF File 089-1029). This may be due to the composite formed when La_2O_3 was used as support. There is an additional peak at 16° indexed to Lanthanum Hydroxide, $La(OH)_3$ (PDF File 075-1900). The addition of lanthanum did not alter the phase diffractogram drastically suggesting that there is no alteration to the crystal structure. Another match in Figure 1 (a,c,d) was the support used which is Aluminium Oxide, Al_2O_3 , rhombohedral phase, (PDF File 071-1124) with prominent peak matches at 25.6° (012), 35.2° (104), 43.4° (113) and 57.6° (116). No residue of used ligand was observed confirming pure phase synthesized nanocatalyst. SEM imaging with EDX mapping in Figure 2 shows the Nickel and La_2O_3 particles were homogeneously dispersed which will enable strong interaction with the Aluminium oxide support [6].

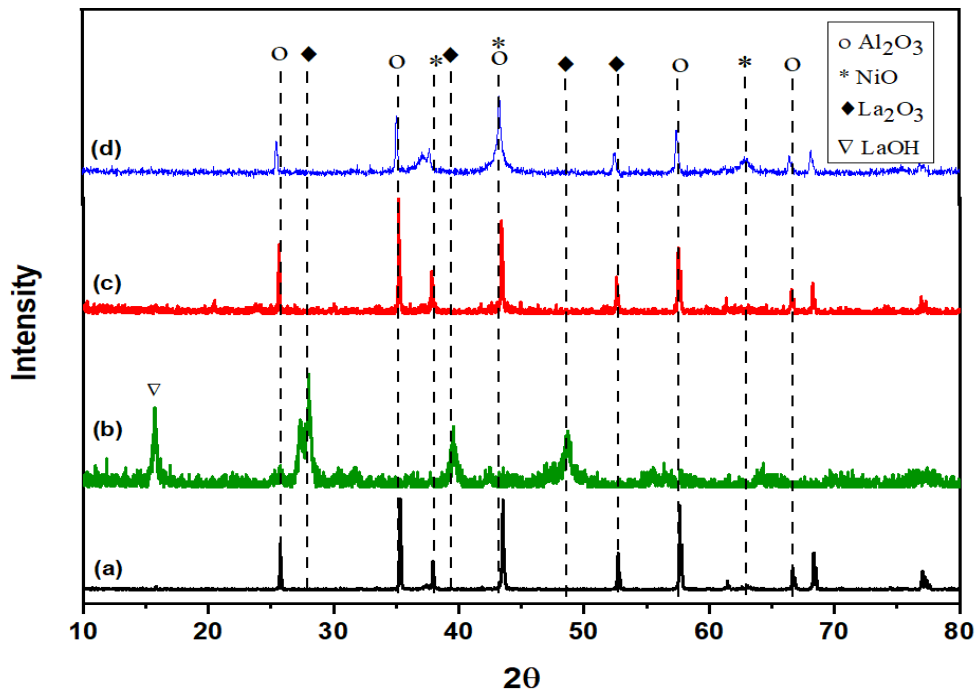


Figure 1: X-Ray powder diffractogram of synthesized (a) 5% Ni/Al₂O₃ (b) 5% Ni/La₂O₃ (c) 10% Ni/La/Al₂O₃ (d) 50% Ni/La/Al₂O₃

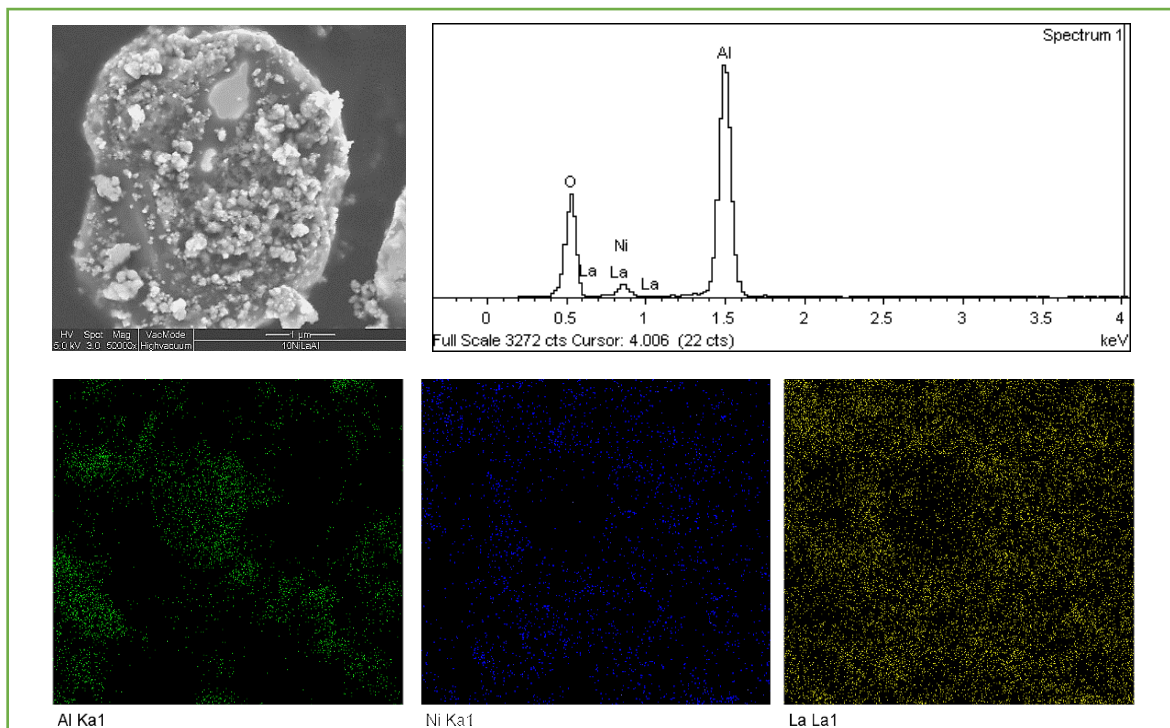


Figure 2: SEM - EDX mapping of synthesized 10% Ni/La/Al₂O₃

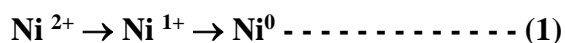
Particle size distribution (PSD) analysis shown in Table 1 shows that all synthesized Ni-based catalysts are within the nano range. This is essential for higher catalytic surface activity. Unsupported 5% Ni/La₂O₃ catalyst (Figure 3(b)) exhibits the smallest particle size with the mean range obtained was 42 nm while the mode of particle size was in the range of 33-38 nm. The addition of Alumina support increases the particle size to a mean average of 80 nm for both 5% Ni/Al₂O₃ and 10% Ni/La/Al₂O₃. 50% Ni/La/ Al₂O₃ exhibits the largest particle size among all synthesized catalysts with an average size of 95 nm.

Table 1. Catalyst Particle Size Distribution (PSD) before & after DRM reaction.

Catalyst	Pre-Reaction Size (nm)		Post Reaction Size (nm)	
	Mode	Mean	Mode	Mean
5% Ni/Al ₂ O ₃	60-90	80	141-190	173
5% Ni/La ₂ O ₃	33-38	42	68-92	82
10% Ni/La/Al ₂ O ₃	68-91	79	122-164	161
50% Ni/La/Al ₂ O ₃	78-105	95	140-191	150

3.2 Catalyst Activation Profile

TPR Profile shown in Figure 4 shows Ni is reduced at a lower temperature (400 °C) compared to the support & promoter used. Two distinct humps were observed indicating the Nickel active component was reduced in two stages as seen in Equation (1)



However, the TPR profile of 5% Ni/La₂O₃ shows another distinct hump at 693 °C which maybe the reducing temperature of Lanthanum Oxide (La₂O₃). The presence of La also shifted the Ni¹⁺ reduction peak to a slightly higher temperature from 400 °C to 450 °C, perhaps due to the formation of mixed nickel lanthanum oxides [12]. Hence, a longer reduction holding time is required for this catalyst. The inert alumina support is incredibly thermally stable and does not react in any way with the active component hence providing a stable base for nickel catalyst. This is an attractive alternative catalyst next to the expensive ruthenium-based catalyst.

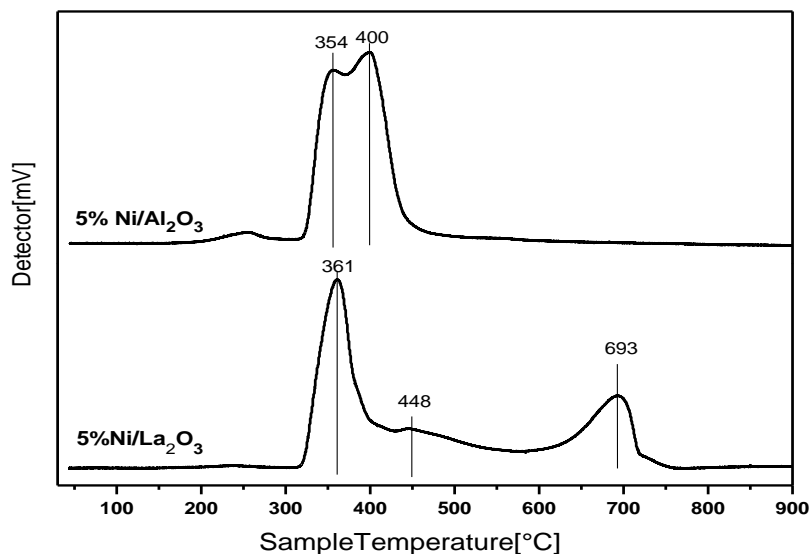


Figure 4: Temperature Programmed Reduction (TPR) of the synthesized catalyst

3.3 Dry Reforming of Methane Catalyst Activity Studies

Table 2: Catalytic performance of different Ni loading catalysts for DRM

Catalyst	Temperature (°C)	Conversion (XCO ₂ %)	Conversion (XCH ₄ %)	Selectivity (SH ₂ %)	Selectivity (SCO%)
Blank	500	0	3.68	100	0
	525	1.65	0	100	0
5% Ni/Al ₂ O ₃	500	19.28	86.97	65.96	34.04
	525	0	*93.27	*79.71	*20.29
5% Ni/La ₂ O ₃	500	42.30	40.28	44.24	55.76
	525	43.58	53.05	56.22	43.78
10% Ni/La/Al ₂ O ₃	500	37.56	57.13	66	34
	525	50.52	61.14	56.75	43.25
50% Ni/La/Al ₂ O ₃	500	39.93	50.85	56.93	43.07
	525	46.58	72.06	70.61	29.39

Reaction conditions: 1.0 MPa, 100 ml/min (N₂/CO₂/CH₄=80:10:10) and GHSV 10,000 h⁻¹

*Only 1 point of GC analysis were recorded

The Ni-based catalyst was reduced at 400 °C before DRM reaction to only reduce the Ni²⁺ to Ni⁰ since pure NiO surface is not active [13] without disruption to the structural integrity of Al₂O₃ and La₂O₃. To investigate the influence of lanthanum of the Dry Reforming of Methane, different

loading of Ni-based catalyst were evaluated against non-promoted Ni catalyst and also under blank conditions. The DRM mechanism is as follow (eq 2);

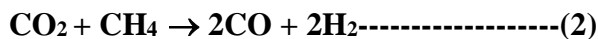


Table 1 displays the normalized conversion percentage of CO₂ and CH₄ and also the selectivity to CO and H₂. There was no significant conversion observed for blank reaction (Figure 5). As shown in figure 4, non-promoted 5%Ni/Al₂O₃ favors the conversion of CH₄ and can reach a maximum conversion of 87% amounting to 66% H₂ selectivity at 500 °C. These findings are consistent with extensive studies done previously exhibiting Nickel supported on Alumina catalyst as a favorable catalyst for DRM mechanism though it is conducted at a much higher temperature [8, 14]. However, there was no activity observed after raising the temperature to 525°C. Alumina has a higher sintering rate via surface diffusion thus an immediate reaction halt was observed after raising the temperature [15]. This may be due to coke deposits due to the high conversion of methane hence eliminating the presence of oxygen vacancies which is crucial for the catalyst active sites surface activity [6]. With the addition of lanthanum, there is almost an equal balance of both CO₂ and CH₄ conversion aligning with the reaction equation (2) and this is prominent with 10% Ni/La/Al₂O₃ catalyst. The selectivity of both H₂ and CO was also almost 50% matching the reaction stoichiometry of 1:1 ratio. By increasing the Nickel loading the selectivity shifted towards H₂. This may be caused by the larger particle size providing an increase of methane adsorption on the Ni surface [9]. At 525 °C, 50% Ni/La/Al₂O₃ catalyst shows the highest conversion of CH₄ at 72%. The addition of lanthanum inhibits the sintering process of alumina by maintaining the reactive surface area sites by increasing the Ni confinement [16, 17]. However, the attempt to increase the temperature to 550 °C was halted as there was no reactant flow and no activity was recorded. It may be inferred that by raising the temperature, the CO formed to continue to combust causing coking inhibiting the active sites and porosity that subsequently have stopped the flow of reactant gas to the catalyst.

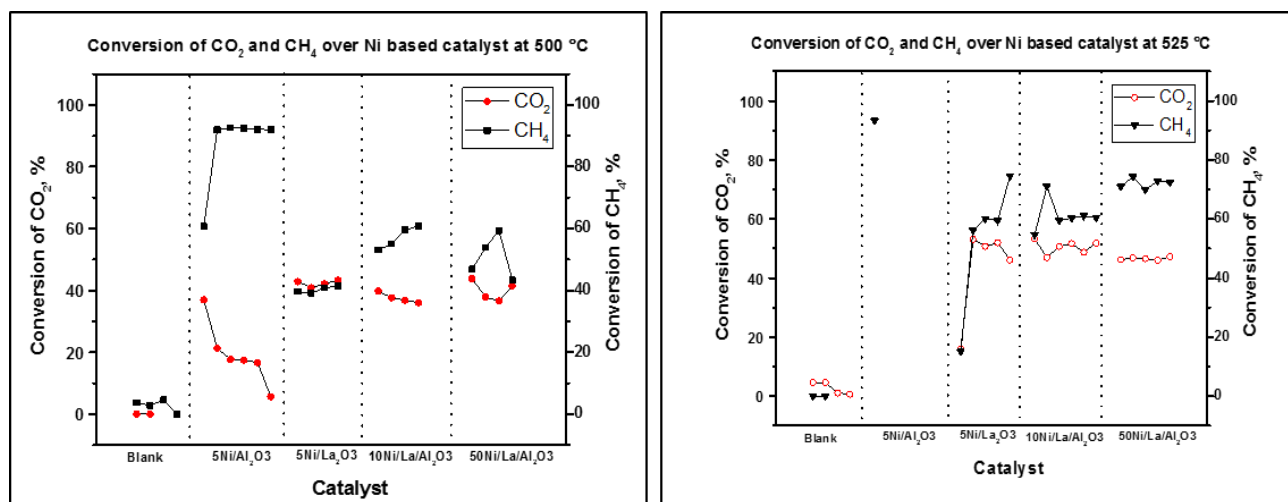


Figure 5: Catalytic conversion of CO₂ & CH₄ at (a) 500 °C (b) 525 °C

3.4 Post Reaction Characterization

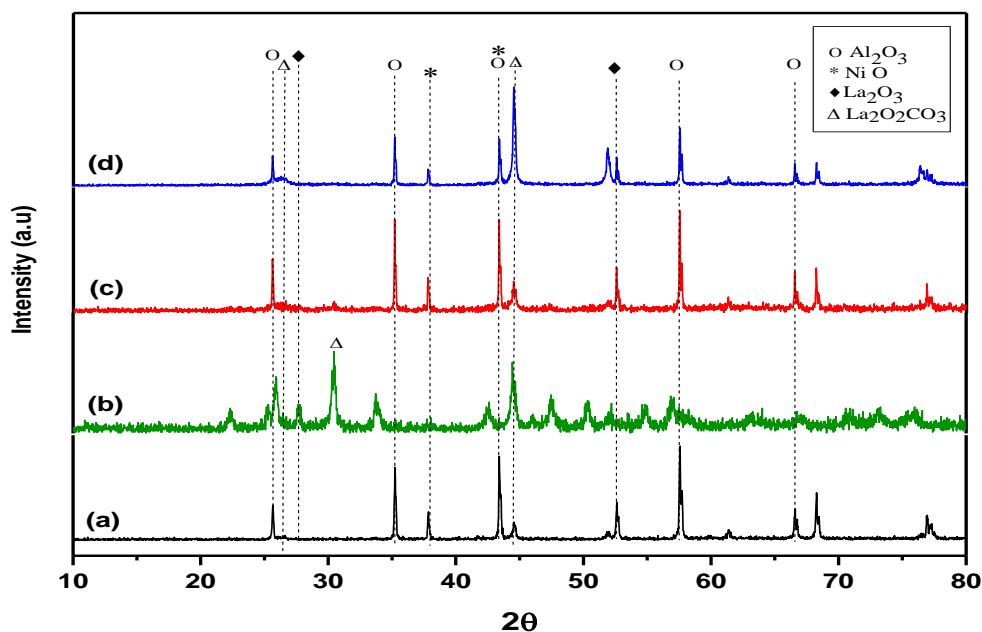


Figure 6: XRD of spent catalyst (a) 5% Ni/Al₂O₃ (b) 5% Ni/La₂O₃ (c) 10% Ni/La/Al₂O₃ (d) 50% Ni/La/Al₂O₃

All spent catalyst was extracted via sieving and subjected to post-reaction characterization using XRD and PSD analysis. Figure 6 shows the diffractograms of all the spent catalysts. The diffractograms are almost the same as the synthesized catalyst, however, there are additional peaks that appear when Lanthanum is matching Lanthanum oxide carbonate (La₂O₂CO₃), PDF-File No 022-0642. The major peaks are at 25.9° (101), 30.4° (103) and 44.5° (110). However, no carbide

formation was observed [18]. This suggests that a new composite has formed as a derivative from the carbon coking and sintering hence deactivating the active sites on Nickel. This can also be reflected by the PSD analysis of the spent catalyst whereby the size comparatively increased approximately twice the synthesized catalyst size (Table 1).

5. 0 Conclusion

Ni-based supported nanocatalysts were successfully synthesized via the impregnation method. This was supported by the XRD analysis exhibiting pure phase crystal structure and PSD analysis showing all synthesized catalysts were within nano range. The addition of lanthanum proves that DRM can take place at a lower temperature. Moderate addition of lanthanum; 10%Ni/La/Al₂O₃ shows the best conversion and selectivity parallel to the DRM mechanism. This was more prominent at a higher temperature at 525 °C. The addition of lanthanum shows that it can reduce sintering by mesoporous framework confinement thus increasing selectivity. However, by increasing the lanthanum loading the conversion of methane increases rapidly to 72% favoring higher H₂ selectivity at 70 %. Catalyst deactivation still poses a major problem as the synthesized catalyst was deactivated from sintering as a result of coking when the temperature was raised to 550 °C. To conclude, by controlling the synthesis parameters such as active site selection, DRM reaction can occur at a lower temperature range.

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Conflicts of Interest: The authors declare no conflicts of interest.

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