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Effect of Ce-promotion on iron catalysts activity through the synthesis of liquid fuels by the Fischer-Tropsch process

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Abstract. The main objective of this work is studying the effect of cerium promotion and reaction temperature on the catalysts activity and product selectivity, the iron-based catalysts utilized in this study were prepared by impregnation methods and characterized via temperature programmed reduction (TPR) and N₂ adsorption-desorption isotherms. Reaction experiments were accomplished in a stainless steel fixed bed reactor. The reaction experiments for unpromoted and promoted catalysts were done at pressure 20 bar, space velocity 1400 h⁻¹, H₂/CO=2 and different reaction temperature (250, 275, 300 and 325 °C). The results have shown the addition of promoter to iron-based catalyst enhanced the reducibility of Fe₂O₃ through a shift down in reduction temperature, furthermore, for both catalysts, conversion of carbon monoxide (CO) and selectivities of undesired products (CO₂, CH₄, and C₂-C₄) were found to be increased whereas the selectivity of desired products (C₅+) was decreased with increasing in a reaction temperature from 55.87 to 35.65% and from 73.03 to 61.59 % for unpromoted and Ce-promoted catalysts respectively. A higher selectivity for high molecules weight hydrocarbons was about 73.03% detected at lower reaction temperature (250 °C) when a promotion catalyst was used.

Keywords: GTL, Iron catalyst, promotion, FTR, Liquid fuels.

1. Introduction

Natural gas was deliberated as one of the cleanest and abundant fossil fuels, that can be converted to liquid fuels form to be more economical, have lower environmental harm through transportation and uses [1], 40 to 60 % of the world's confirmed natural gas reservoirs are distant or stranded, thus transporting of natural gas from the reservoir to the users by pipeline is costly and difficult [2]. Liquefied of natural gas (LNG) is a present solution for transporting a natural gas, but rigorous transportation demand, energy safety of supply and environmental interest create a requirement search to alternate ways to profit natural gas resource [3].

Gas-to-Liquids (GTL) technology has been confirmed to be a promising method for the exploitation of a natural gas [4]. In the GTL process, the methane from a natural gas firstly convert to synthesis gas (syngas) by many methods such as partial oxidation [5], reforming [6] or auto-thermal reforming [7] which is then converted catalytically by Fischer-Tropsch synthesis (FTS) technology to synthetic crude that contained a different fraction of beneficial hydrocarbon which can be upgraded and separated into suitable liquid transportation fuels such as (gasoline and diesel) [8].



Increasing the high molecular weight hydrocarbons products are the main objective of FTS reaction [9]. So, selecting an appropriate catalyst and reaction conditions are actually significant in the FTS [10].

Iron-based catalysts were utilized as commercial catalysts for the production of a high molecular weight hydrocarbon at different reaction temperature [11, 12]. On the way to increase the activity and selectivity of iron- catalysts towards C_{5+} contents, recently various studies have recognized by the addition of different promoters, Mangaloğlu et al., 2018[13] found the addition of alkali promoters namely potassium, copper, and manganese to iron catalysts increases the amount of total produced liquid fuel from 48% to 64-79%, Beasley et al., 2018[14], showed that gallium addition to iron catalysts affected the reduction of Fe_3O_4 to metallic iron and the reactant conversions were reduced by an increase of gallium content in Fe catalysts, Park et al., 2018[15], presented the high catalytic activity and product selectivity for (C_{5+}) under the optimum FTS reaction, based on the well-dispersed of iron-carbide surface with potassium promoter, the CO conversion was about 94.1% and the products selectivities were (41.5, 7.6, 15.6 and 35.3%) for CO_2 , CH_4 , C_2-C_4 and C_{5+} respectively they were noted at GHSV = $14\text{ NL}\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$, 15 bar, 340 °C, and $H_2/CO = 1$, Li et al., 2019[16], observed that the addition of manganese promoter into the iron based catalyst has a great effect on the products distribution and a higher selectivity for long-chain hydrocarbons (C_{5+}) was about 63.9 % they were obtained when 10 wt% of Mg was used.

There were limited studies in the literature that focus on the low loaded iron-based catalysts promoted with cerium to enhance the FTS product selectivity towards the high molecular hydrocarbon. Accordingly, the main objective of the present work is to find the effects of cerium addition as the promoter on the structure and activity of iron-based catalysts besides the range of reaction temperature.

2. Experimental Work

2.1. Catalysts preparation

$\gamma\text{-Al}_2\text{O}_3$ (Axens) was used as a support after thermal treatment under air flow at 500 for 4 h, the iron-based catalyst was prepared by incipient wetness impregnation methods through the following steps, firstly, the treated $\gamma\text{-Al}_2\text{O}_3$ was impregnated in calculated amount of aqueous solutions of iron nitrate $Fe(NO_3)_3\cdot 9H_2O$ (Sigma-Aldrich, $\geq 99.95\%$ purity), with continuous mixing by a magnetic stir bar at room temperature until 20 wt.% of Fe was loaded, followed by drying overnight at 110 °C, subsequent the dried catalyst was calcined under air flow at 550 °C for 4 h with heating ramp 0.5 °C/min [17], to achieve 20Fe/ $\gamma\text{-Al}_2\text{O}_3$ catalyst after reduction.

In the cases of promotion, some of the dried catalyst before the calcination was promoted with 5wt. % of Ce by the co-impregnation of dried 20Fe/ $\gamma\text{-Al}_2\text{O}_3$ in an aqueous solution of $Ce(NO_3)_2\cdot 6H_2O$ (Merck), then the promoted catalyst was dried and calcined by following the same above procedure.

2.2. Catalyst characterization

Temperature programmed reduction (TPR) of the calcined promoted and unpromoted catalysts were recorded by using TP-5000 analyzer equipped with a quartz tube reactor and thermal conductivity detector, in the first 100 mg of each sample was charged into quartz tube and heated under an argon flow to 400 °C for 2 h to eliminate the water, followed by cooling to room temperature, then the TPR program test was started by flowing 5 vol% H_2/Ar gas mixture at a flow rate of 30 mL/min with heating from room temperature to about 850 °C with heating ramp 10 °C/min for 12 h.

BET surface area and porosity characteristics of calcined promoted and unpromoted catalysts were measured by N_2 adsorption-desorption isotherms at -196 °C by using the Micrometrics ASAP- 2020 system. Before accomplishment the test, the temperature was slowly ramped to 200 °C and the sample was evacuated at this temperature for 10 hours to about 0.07 bar, then the BET surface area, pore volume, and an average pore radius were obtained for each sample.

2.3. Fischer-Tropsch reaction

The catalyst tests for converting a syngas to liquid fuels (high molecular weight hydrocarbons) were carried out in a single stainless steel fixed bed reactor (ID: 10mm and L= 900 mm) as shown a schematic diagram in (Figure1). Firstly 5 grams of calcined catalysts were loaded in a middle of the reactor and surrounded by two quartz beds, the reactor was heated by electrical furnace.

The flow rates of the reactant ($H_2 > 99.5\%$ purity, $CO > 99.3\%$ purity, and inert gas (Ar) $\geq 99.999\%$ purity) and the reduction/reaction temperatures were controlled by a separate electronic mass flow controller and a proportional integral derivative controller respectively. Prior to Fischer–Tropsch reaction, the promoted and unpromoted iron catalysts were reduced in-suites by 5 % H_2/Ar . at flow rate 30 mL/min for 12 hours, Later on in-suites reduction the temperature was down gradually to the ambient temperature in the same gas mixture and with the same under reduction gas flow, after that the reactor was heated and pressured to the reaction temperature and pressure under inert gas (Ar) flow with heating ramp 5 °C/min, then followed by syngas mixture flow. The FTR was carried out at optimum reaction conditions pressure 20 bar, space velocity 1400 h^{-1} , $H_2/CO=2$ [18], and four different temperatures (250, 275, 300 and 325 °C). Every temperature was keep for 24 hours and then changed using the same ramp rate.

The products stream was removed continuously and reduced to atmospheric pressure by a back pressure regulator, then passed through hot and cold traps at 100 and 0 °C respectively, the compositions of gas has were analyzed on-line gas chromatograph (GC) Shimadzu-2014 fitted with a GS-GASPRO capillary column connected with flame-ionization detector (FID) for analysis of light hydrocarbons and Carboxen-1000 packed column connected with thermal conductivity detector (TCD) for the analysis of CO_2 , H_2 , and CH_4 , however the compositions of liquid phase were collected in the two traps and analyzed off-line by using Varian CP 3800 Gas Chromatograph fitted with (FID).

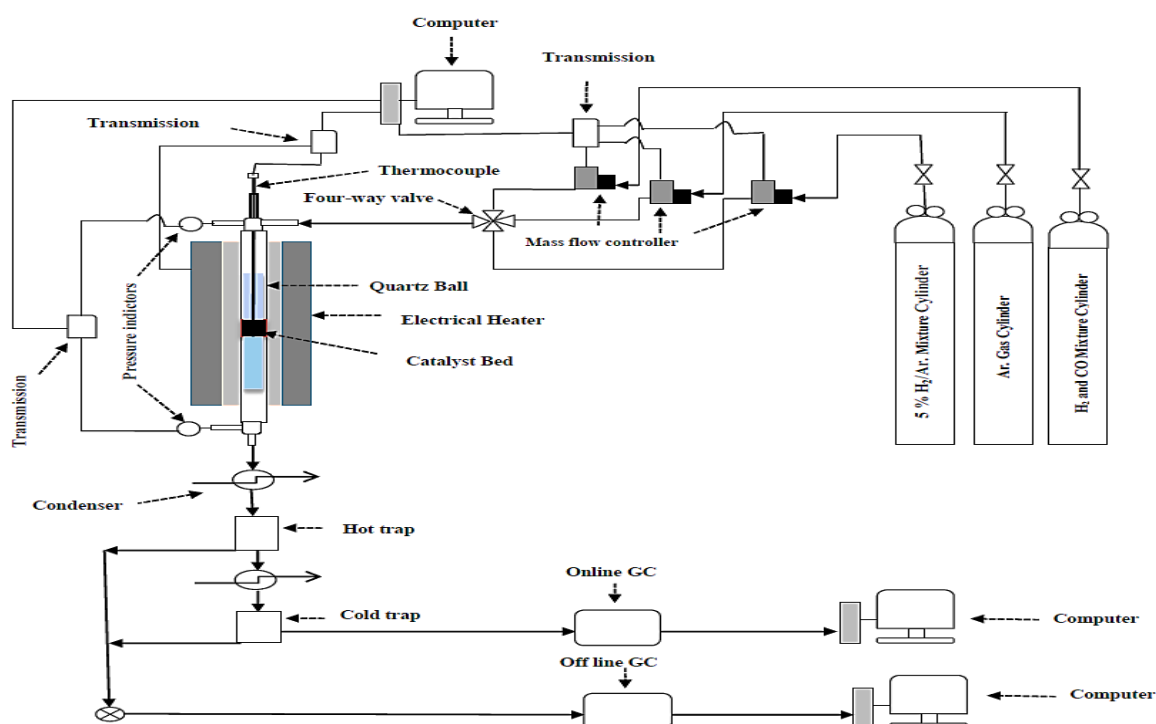


Figure 1. Schematic diagram of Fischer – Tropsch reaction system on single stainless steel fixed bed reactor.

3. Results and Discussion

3.1. Catalyst characterization

H₂-TPR profiles of the calcined (20% Fe/ γ -Al₂O₃) and (5%Ce-20% Fe/ γ -Al₂O₃) catalysts are presented in (Figure 2). Two hydrogen reduction peaks were observed for reduction of iron oxides. In the first peak, Fe₂O₃ was reduced to Fe₃O₄ and the second peak assigned to the reduction of Fe₃O₄ to FeO which was subsequently reduced to Fe. For the (20% Fe/ γ -Al₂O₃) catalyst, reduction of Fe₂O₃ to Fe₃O₄ occurred at 450°C, and then consequently followed by the reduction of Fe₃O₄ to Fe at 625°C. The promoting of iron-catalyst with 5% Ce has strongly affected on the TPR profile (demonstrated in Figure 2), shifted to lower reduction temperature where the first reduction peak shifted to 310°C although the second peak reduced to 460°C. The similar trend has also been stated in the literature by Beasley et al., 2018 [14]. Moreover, the TPR results assured that the chosen parameters (5 % H₂/Ar gas mixture with the flow rate of 30 mL/min for 12 h) were suitable for reducing the Fe₂O₃ to Fe in-suite reactor before starting the reaction.

BET surface area, single point pore volume and single point average pore radius measurements for calcined support (γ -Al₂O₃), iron-based catalyst (20% Fe/ γ -Al₂O₃) and cerium promoted iron-based catalysts (5%Ce-20% Fe/ γ -Al₂O₃) are listed in (Table 1). The surface area of support was 145 m²/g which plunged to 98.8 m²/g for the unpromoted catalyst, and then little decreases was observed when the catalyst was promoted with 5wt. % of Ce.

The single point pore volume and single point average pore radius for the support were 0.542 cm³/g and 6.8 nm respectively that decreases to 0.312 cm³/g and 5.2 nm after the support was loaded with 20 wt. % of Fe, whereas the addition 5 % of promoting resulting smaller reductions in a single point pore volume and single point average pore radius of the catalyst, the reduction of pore volume and average pore radius values as the metal loading, indicates that Fe and Ce were effectively introduced into the catalysts porous structure [19], the similar tendency was observed by Peña et al., 2018 [20].

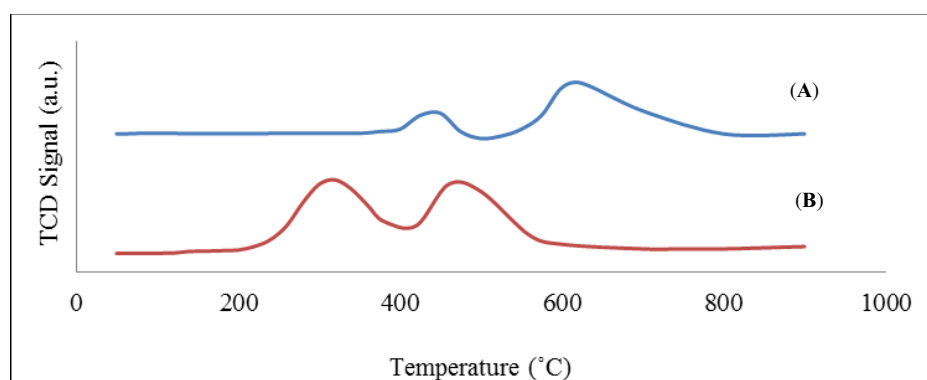


Figure 2.TPR profiles for unpromoted (20%Fe/ γ -Al₂O₃) and promoted (5%Ce-20Fe / γ -Al₂O₃) calcined catalysts, where (A) and (B) for unpromoted and promoted catalysts respectively.

Table 1. BET surface area and pore volume.

Catalyst	BET SA (m ² /g)	Single point pore volume (cm ³ /g)	Single point average pore radius (nm)
γ -Al ₂ O ₃	145	0.542	6.8
Fe	98.8	0.312	5.2
Ce-Fe	95.3	0.297	4.9

3.2. Effect of reaction temperature on catalyst activity and products selectivity

To investigate the effect of reaction temperature on the activity of catalysts, and the selectivity towards liquid fuels production, several experiments were done at pressure 20 bar, space velocity 1400 h⁻¹,

$H_2/CO=2$ and different reaction temperature.

The results obtained for the catalysts activity and products selectivity were considered when steady-state conditions were reached, presented in (Figure 3) and (Figures 4a, b, c, and d). The results shown an increase reaction temperature from 250 to 325 °C the conversion of CO for both catalysts were gradually increased, this indicated that the reaction temperature is affecting an activity of iron catalysts [18]. Moreover, it can be seen, at increases reaction temperature the selectivity of light hydrocarbons (CH_4 and C_2-C_4), and CO_2 was increased. Consequently, lead to a decreases in the selectivity of desired products (C_{5+}), since the higher reaction temperature is favoured for the chain termination essential to produce low molecular weight hydrocarbons, whereas a low reaction temperature was favoured for chain growth and production of high molecular weight hydrocarbons [21]. From results, it can be noted that the promoted catalyst was found to be affected by reaction temperature at a lowered level than unprompted one, because of the promoter addition increase the dispersion of the active FTS metal according to the metal-support interaction [22], for that reason, the addition of cerium to the iron-based catalyst increased the forming of high molecular weight hydrocarbons, the similar trends were obtained in other studies using iron-based catalysts promoted with another promoter Peña et al., 2018[20], Feyzi et al., 2013 [23], Chernavskii et al., 2017[24], Comazzi et al., 2017 [25], Nikbakht et al.,2018[26].

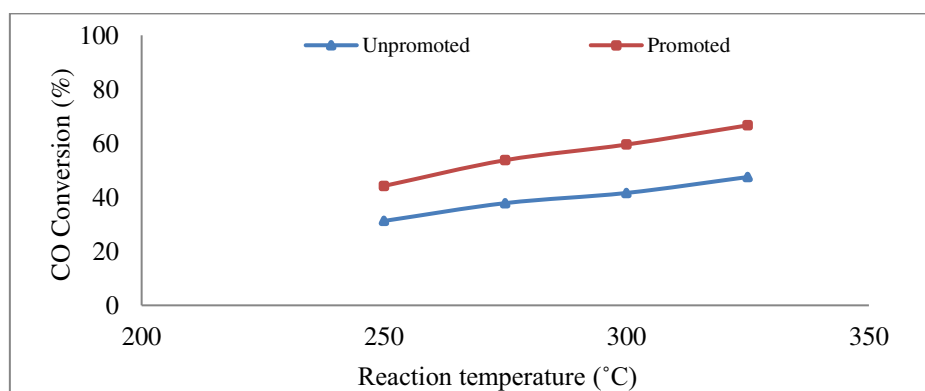


Figure3. Effect of reaction temperatures on carbon monoxide conversion for unpromoted and Ce-promoted iron based catalysts at $P = 20$ bar, $SV = 1400\ h^{-1}$ and $H_2/CO = 2$.

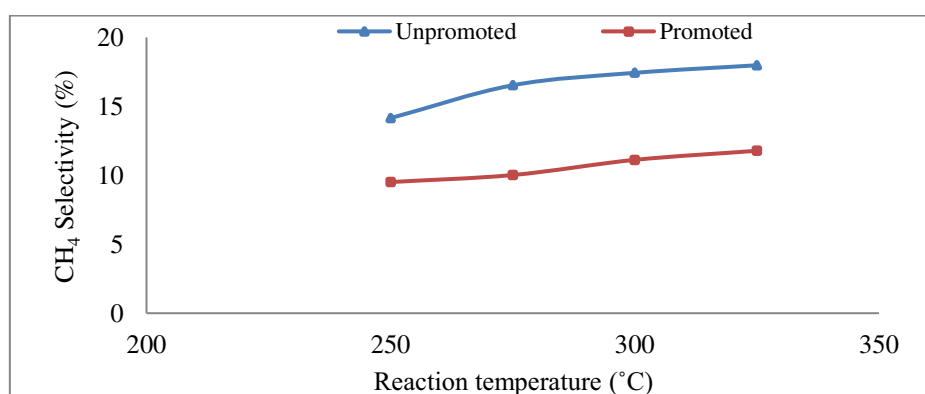


Figure 4a. Effect of reaction temperatures on CH_4 selectivity for unpromoted and Ce-promoted iron based catalysts at $P = 20$ bar, $SV = 1400\ h^{-1}$ and $H_2/CO = 2$.

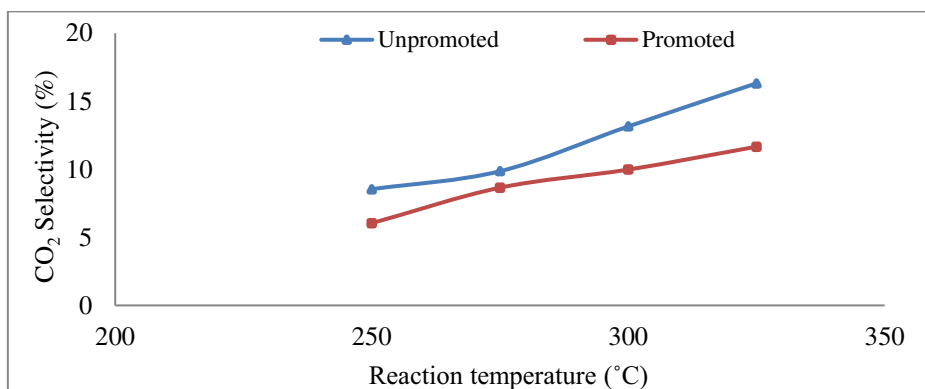


Figure 4b. Effect of reaction temperatures on CO₂ selectivity for unpromoted and Ce-promoted iron based catalysts at P = 20 bar, SV= 1400 h⁻¹ and H₂/CO= 2.

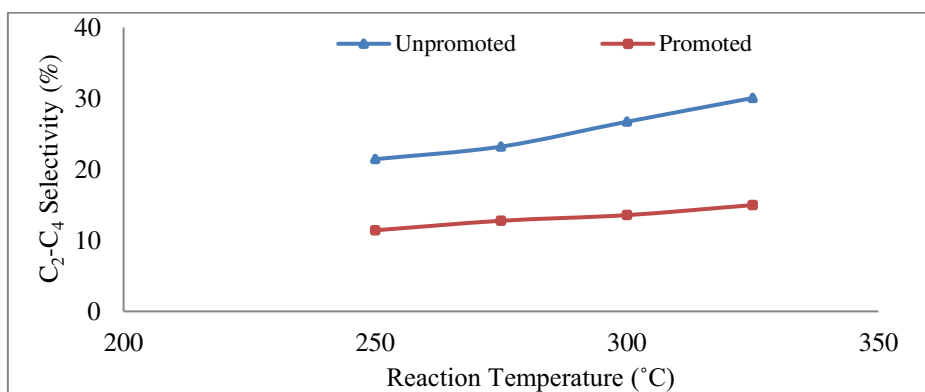


Figure 4c. Effect of reaction temperatures on C₂-C₄ selectivity for unpromoted and Ce-promoted iron based catalysts at P = 20 bar, SV= 1400 h⁻¹ and H₂/CO= 2.

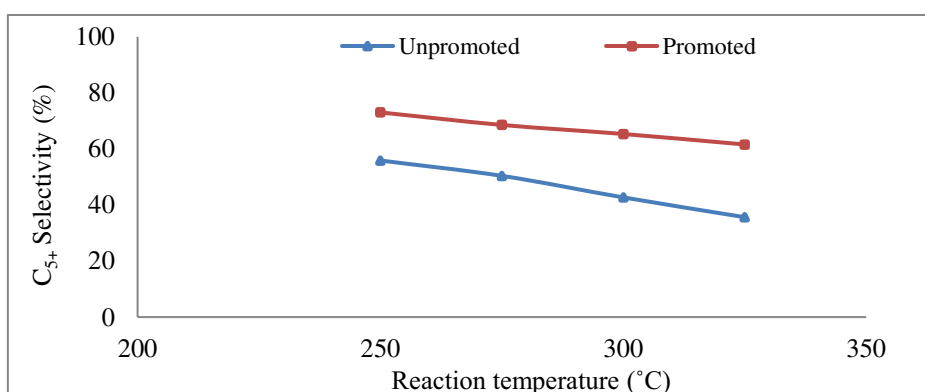


Figure 4 d. Effect of reaction temperatures on C₅₊ selectivity for unpromoted and Ce-promoted iron based catalysts at P = 20 bar, SV= 1400 h⁻¹ and H₂/CO= 2.

4. Conclusions

The FTS of syngas derived from a natural gas was studied using an iron-based catalyst prepared by incipient wetness impregnation methods and promoted with cerium in order to synthesize liquid fuels. The prepared catalysts were characterized by TPR and N₂ adsorption-desorption isotherms. The results shown the addition of cerium to iron-based catalyst enhanced the reducibility of Fe₂O₃ through a shift down in reduction temperature from 450 to 310°C and from 625 to 460°C for reduction of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to FeO respectively. The FTS reaction was carried out in a fixed bed reactor under range of temperatures (250- 325 °C), pressure 20 bar, space velocity 1400 h⁻¹ and H₂/CO=2, for both catalysts, the results show that the conversion of CO and selectivity of light hydrocarbon products (C₁-C₄) and CO₂ increased but, the selectivity of desired products (C₅+) was decreased with an increase in a reaction temperature, the higher selectivity for the liquid product was about 73 % obtained at lowered reaction temperature (250 °C) when promotion catalyst was used.

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