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Ms. Cathy Yang
Assistant Editor,
Special Issue " Nickel-Based Catalysts for Hydrocarbon Fuel Reforming"
Catalysts
December 8th, 2020

Dear Ms. Cathy Yang,

We are grateful for your feedback and for the reviewers' comments on our manuscript entitled, "The effects of Co and CeO₂ doping on the properties and the performance of the Ni/Al₂O₃-MgO catalyst for the combined steam and CO₂ reforming of methane using ultra-low steam to carbon ratio" (ID catalysts-1024099). Each comment and suggestion were enhancing the quality of our paper. We have carefully responded to all comments as well as have revised the manuscript according to the comments and suggestions. We have studied these comments and have carefully responded to all points as well as have revised the manuscript accordingly.

The main purpose of our study was the effects of CeO₂ and Co doping on the physicochemical properties of the Ni/Al₂O₃-MgO catalyst for hydrogen production via combined steam and CO₂ reforming of methane with the low S/C ratio. Therefore, this manuscript presents the effects of Co and CeO₂ doping on the physicochemical properties of the Ni/Al₂O₃-MgO catalyst as well as combined steam and CO₂ reforming of methane with the low S/C ratio.

Our research presented the effects of Co and CeO₂ adding on the Ni/Al₂O₃-MgO catalyst. The behavior of each promoter (CeO₂ and Co) attracted the different co-oxidant (H₂O and CO₂) absorption which affected the H₂/CO ratio in the combined steam and CO₂ reforming of methane using ultra-low steam to carbon ratio. The pathway of CeO₂ on the Ni/Al₂O₃-MgO catalyst improved the water adsorption and dissociation that booted the increasing H₂/CO ratio via oxygen vacancies. Meanwhile, the CO₂ adsorption and dissociation were promoted that decreased the H₂/CO ratio by the redox potential in the Co on the Ni/Al₂O₃-MgO catalyst. The appearance of CeO₂ and Co on the Ni/Al₂O₃-MgO catalyst enhanced the oxygen species at the surface that inhibited the coke deposits.

We believe our findings are important for publication in the special issue " Nickel-Based Catalysts for Hydrocarbon Fuel Reforming ", Journal of Catalysts because the effects of Co and CeO₂ over Ni/Al₂O₃-MgO catalyst affected the syngas and hydrogen production. The information of research supports the selective catalytic for each reforming. Thus, our work is significant for both general

knowledge in the area of heterogeneous catalyst and reforming reaction for syngas and hydrogen production.

We hope that we will meet with your approval. The changes in the revised manuscript are written in red. The responses to the reviewers' comments are provided in a separate file.

We would like to express our great appreciation to you and the reviewers for the comments on our paper. If you have any further suggestions, please do not hesitate to contact us.

Sincerely,

A handwritten signature in blue ink that reads "M. Phongakorn." with a period at the end.

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Response to Reviewer 2 Comments

Point 1: The authors, starting from the title, propose to discuss the role of CeO₂ and Co in the catalysts prepared in the reaction of steam and CO₂ reforming. However, this fact is not sufficiently emphasized in the text. The authors should accompany the reader in understanding the effect of these two metals in the reaction mechanism, justifying the results obtained in the light of the results of the characterizations.

Response 1: We thank very much for your suggestions that truly improve our article. We have added the simplified reaction mechanism and also discussed how the mechanism relates with the results of the characterizations. The additional discussion in the revised manuscript at the results and discussion section after the TGA part (after line 212) would accompany the reader in understanding the effect of these two metals in the reaction mechanism.

Revise

line 219-237: A simplified reaction mechanism of CSCRm to produce synthesis gas on a Ni-based catalyst consists of three element reactions: CH₄ dissociation/decomposition (Eq. 7), H₂O activation-dissociation (Eq. 8) and CO₂ activation-dissociation (Eq. 9). CH₄ dissociation/decomposition produces carbon surface (C*) and H₂. CO₂ and H₂O activation-dissociation generate oxygen surface (O*) with CO and H₂, respectively. The C* on surface can be then removed by reacting with the O* surface to form CO (Eq. 10). Therefore, the catalytic behavior of the catalyst for the reaction steps can be tentatively evaluated by conversions of reactants, H₂/CO ratio, and the quantity of coke formation. The activity toward CH₄ dissociation/decomposition step directly relates to CH₄ conversion. The H₂O and CO₂ activation-dissociation can be preliminary predicted using H₂/CO ratio with the amount of coke. If the high H₂/CO ratio with low carbon accumulation are occurred, the catalyst is selective for H₂O activation-dissociation. Likewise, the catalyst is selective for CO₂ activation-dissociation when the low H₂/CO ratio and low carbon accumulation are founded. According to the results under the low S/C ratio condition of CSCRm process, it suggested that 10Ni/MA is the most active catalyst for CH₄ dissociation/decomposition. CeO₂ in 5Ni5Ce/MA and Co in 5Ni5Co/MA boots the H₂O and CO₂ activation-dissociation, respectively.



Point 2: Regarding with the synthesis of the catalysts, the sol-gel method was used for the supports and impregnation for the final catalysts. However, the description of the procedures followed to obtain supports and catalysts is somewhat incomplete, the authors should enrich this part with more details.

Response 2: We thank for your comment. We have added more details for a better procedure of the catalyst synthesis to provide as seen in the catalyst preparation part (line 214-220).

Revise

line 240-248: The Al₂O₃-MgO (MA) was synthesized by the sol-gel method. The mixture of aluminium isopropoxide (Acros OrganicsTM 98%), nitric acid (CARLO ERBA Reagents 65%), magnesium ethoxide (Sigma-Aldrich 98%) and distilled water were refluxed at 80°C for 20 h. The resulting gel was dried at 60°C for 24 h and calcined at 800°C for 6 h. The MA support was crushed and sieved to 355-710 µm. The 10 wt% Ni/Al₂O₃-MgO (10Ni/MA), 5 wt% Ni-5 wt% Ce/Al₂O₃-MgO (5Ni5Ce/MA) and 5 wt% Ni-5 wt% Co/Al₂O₃-MgO (5Ni5Co/MA) catalyst were prepared by the incipient wetness impregnation of the MA support with a solution of nitrates. Precursors included Ni(NO₃)₂·6H₂O (Merck 99%), Ce(NO₃)₃·6H₂O (Honeywell FlukaTM 99%) and Co(NO₃)₃·6H₂O (Sigma-Aldrich 99%). Then, the wet solid cake was dried at 60°C for 24 h and calcination at 650°C for 5 h

Point 3: The authors state that catalysts with CeO₂ and Co are characterized by a higher specific area and better dispersion, compared to the catalyst without. But between these three systems there is a difference in the Ni content. For a complete picture the authors should also indicate the dopant-free solid with the same Ni content.

Response 3: We thank you for this point of suggestion. In this research article, we compare all catalysts in the case of similarly total metal content (10Ni/MA, 5Ni5Ce/MA, and 5Ni5Co/MA). It would have been interesting to compare the dopant-free solid with the same Ni content. We understand your concern. However, we apologize indeed that we cannot complete experiments of the 5Ni/MA catalyst within four days according to the time for catalyst preparation and the different experiments.

Point 4: An important aspect in this reaction concerns the deactivation by the Coke. The authors report TGA values to discuss carbon deposits, but it is unclear whether the proposed catalysts are stable or not.

Response 4: This suggestion helps to improve our article. We also understand this reaction concerning. Therefore, we rewrote the TGA part to relate the results with the deactivation by the coke. This revision should clarify that the CeO₂ and Co promoters enhance the carbon tolerance of Ni/MA catalyst (line 198-209)

Revise

line 203-216: The quantity and the types of carbon deposition on the spent catalysts were elucidated using the TGA results (Figure 7). The percentage of weight loss directly relates to the amount of carbon deposition. TGA profiles of the spent catalysts represented the physically adsorbed water and amorphous carbon (≤ 250°C), the graphitic carbon (250°C - 450°C) and the carbon filament (≥ 450°C) on the surface [18,52–54]. The last two types, which are not easily oxidizable, have been considered as the major reason for the catalyst deactivation. The total weight loss of spent 10Ni/MA, 5Ni5Ce/MA and

5Ni5Co/MA catalysts were 17%, 11% and 12%, respectively. Although the main type of coke in all catalysts was the graphitic carbon, the highest temperature of carbon removal was found from the spent 10Ni/MA catalyst. It implied that carbon deposition was formed more easily via the CH₄ dissociation/decomposition on the Ni/MA catalyst. The coke deposited can be deduced by the oxygen intermediate in H₂O activation-dissociation for 5Ni5Ce/MA and oxygen intermediates in CO₂ activation-dissociation for 5Ni5Co/MA. Consequently, with Ce and Co promoters, the carbon tolerance of Ni/MA catalyst was improved, requiring only small amount of steam added in the feed of the methane reforming in order to prevent carbon deposition [55-57]

Point 5: The relative errors related to conversion values and characterization measures of catalysts are missing. These data are important to understand the scattering of some results reported in the tables and figures.

Response 5: We thank for your comment. The systematic error of N₂ adsorption-desorption is about $\pm 5\%$. As the TPD and TPR techniques are tested in the same instrument, the systematic error is about $\pm 1\%$ for temperature and about $\pm 8\%$ for the quantity of gaseous substances. For the relative errors of conversion values is about $\pm 3\%$. We have added the systematic error under Table 1 and Figure 6, respectively.

Revise (line127-129)

Table 1. The properties of 10Ni/MA, 5Ni5Ce/MA and 5Ni5Co/MA catalysts.

Catalyst	N ₂ adsorption-desorption ^a		H ₂ -TPR ^b	Deconvolution of the CO ₂ -TPD ^b (mmol/g _{cat})			
	Surface area (m ² /g)	Total pore volume (cm ³ /g)		Weak	Medium	Strong	Total basicity
10Ni/MA	97	0.20	11.9	0.04	0.02	0.13	0.19
5Ni5Ce/MA	111	0.24	4.3	0.02	0.03	0.17	0.22
5Ni5Co/MA	108	0.22	10.8	0.03	0.03	0.10	0.16

^a The systematic error of N₂ adsorption-desorption is $\pm 5\%$

^b The systematic error is $\pm 1\%$ for temperature and $\pm 8\%$ for the quantity of gaseous substances.

(line201-202)

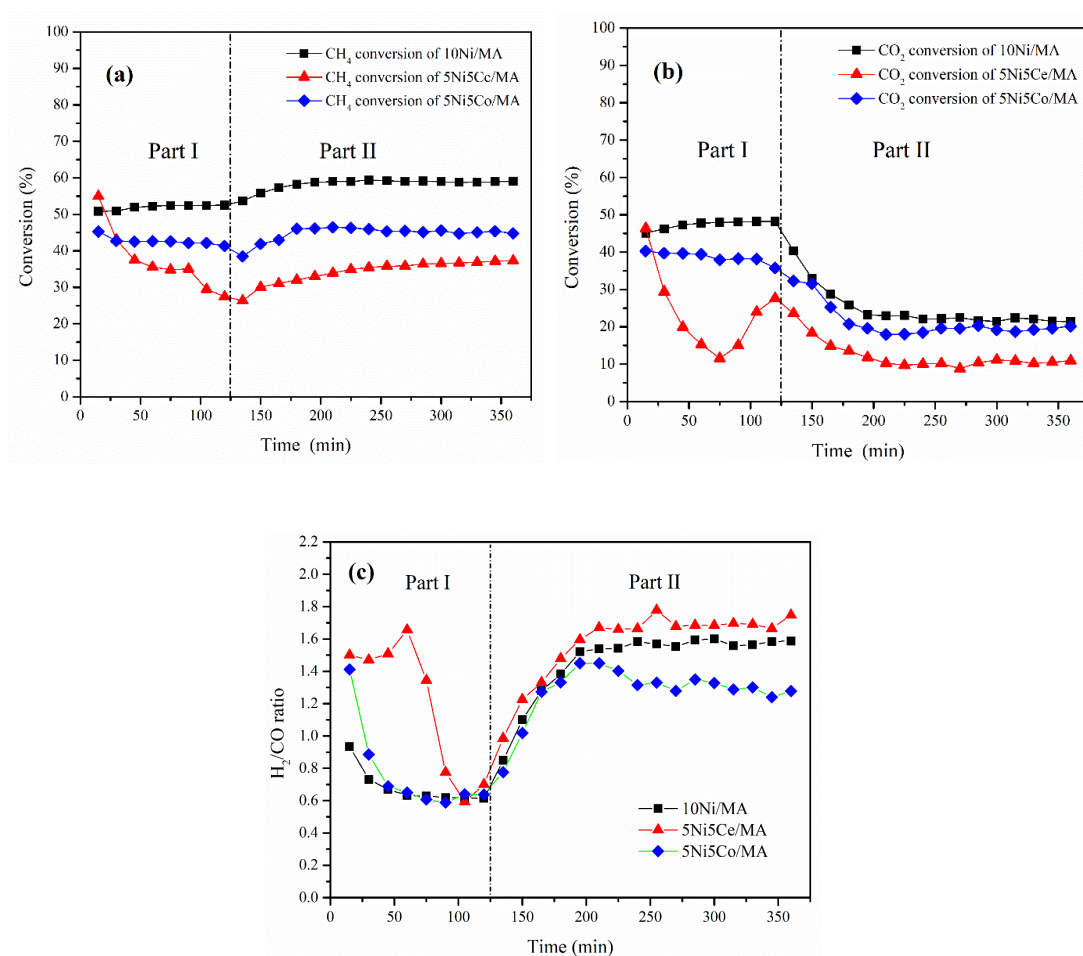


Figure 6. The CH₄ (a) and CO₂ conversions (b) for CSCRM and H₂/CO ratios (c) of 10Ni/MA, 5Ni5Ce(T)/MA, 5Ni5Ce/MA catalysts at 620°C under ambient pressure (the relative error is 3%)