CO_2 REFORMING OF METHANE ON $LaA'Ru_{0.8}Ni_{0.2}O_3$ (A'= Sm, Nd, Ca) PEROVSKITES AS CATALYSTS PRECURSORS IN PRESENCE AND ABSENCE OF O_2

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Introduction

Over the past years, the CO_2 reforming of methane yielding synthesis gas has been the subject of numerous studies. The objective is to find a suitable material that allows the reaction to proceed at low temperature with a minimum of carbon production. Among these material, the perovskites like oxides ABO_3, in which A-site cation is a rare earth and/or alkaline earth and B-site cation is a transition metal has drawn a lot of attention. The reason for this is because by a careful reduction of the perovskites, the B-site cations will remain distributed in the structure, producing a well dispersed and stable metal particle inhibiting coke formation. Although many previous investigations of the CO_2 reforming of methane were performed over transition metals supported on alumina, silica and magnesia, the use of perovskite has been less studied. The performance of these solids for the CO_2 reforming of CH_4 in the presence (combine) and absence (dry) of O_2 was investigated. The use of oxygen as co-reactant could allow the reaction to proceed at lower temperatures due to its exothermic character.

Experimental

Four Ru-Ni based perovskite type oxides were synthesized by the citrate sol gel method based on the Pechini type reaction route. La in the A-site position was partially replaced by Sm, Nd and Ca to produce $LaRu_{0.8}Ni_{0.2}O_3$, $La_{0.8}Sm_{0.2}Ru_{0.8}Ni_{0.2}O_3$, $La_{0.8}Nd_{0.2}Ru_{0.8}Ni_{0.2}O_3$, and $La_{0.8}Ca_{0.2}Ru_{0.8}Ni_{0.2}O_3$. The procedure has been published elsewhere [1]. The homogeneity and structure of the obtained powders have been investigated before and after reduction and after reaction by ICP, IR, BET surface areas, XRD, TPR and XPS analysis. Catalytic tests were performed in a continuous flow system an integral reactor at atmospheric pressure.

Results and Discussion

The XRD patterns of the as synthesized solids at room temperature revealed that the perovskite structure was the main phase detected for all solids. All perovskites could be indexed with an orthorhombic or cubic symmetry of the ABO_3 type. The ICP analysis showed a close agreement between experimental and theoretical values corroborating the advantage of the sol-gel method. The TPR shows that the perovskite reduction proceeds in two steps. The XRD in situ reduction results seems to indicate, that the first peak of reduction at ~ 400 °C could be attributed to weakly bound Ru-Ni cations and to residues of the precursors. The second peak could be attributed to a simultaneously Ru and Ni reduction to produces Ru^0 and Ni^0 probably with an alloy formation. For all solids, the observed phases after reduction at 700ºC were: Ru metal (alone or allied with Ni), La_2O_3 and CaO, Sm_2O_3 and Nd_2O_3 depending on the composition of the starting perovskite. However, changes in the reducibility pattern were introduced due to the difference in ionic radii of the substituting cations. XRD analysis was also used to determine the metal particles size of the reducible species. It is interesting to point out that the metallic particle sizes were in the order of 10-34 nm as determined by the Scherrer equation [2]. Peaks correspond mainly to Ru (44,37°, 2θ) slightly shifted, due to the presence of Ni.

The experimental results of the methane reforming show high methane conversions both in presence and absence of O_2 (Table 1). However, higher ratios H_2/CO were obtained for the combined reaction. For this reaction, CO_2 conversion was also lower (30%) than that of methane due to the fact that the CO_2 is being generated as a product of the methane combustion in the presence of O_2 [3].

On Sm and Nd containing solids, a great improvement on the H_2/CO ratios was observed for the combine reaction compared to the dry reaction, while the substitution of La by Ca increases the activity and selectivity, as shown in table 1. On this solid, for the dry reaction, the CO_2 conversion is higher than that of CH_4 due to the reverse water gas shift reaction.

The simultaneous oxidative and CO_2 reforming reaction of methane notably diminished coke formation, increasing the syngas production. The addition of oxygen to the CH_4 + CO_2 system decreases the reaction temperature and energy consumption, indicating that the partial oxidation (exothermic) reaction promotes the dry (endothermic) reaction, in agreement with Tomishige et al. result for Ni/Al_2O_3 and Pt/Al_2O_3 catalysts [4].

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References

(1) Pietri, E.; Barrios, A.; Gonzalez, O.; Goldwasser, M.R.; Pérez-Zurita, M.J.; Cubeiro, M.L.; Goldwasser, J.; Leclercq, L.; Leclercq, G. *Stud. Surf. Sci. Catal.*,**2001**, *136*, 381.
(2) Bradford, M.C.J. and Vannice, M.A. *Appl. Catal. A: Gen.* **1996**, *142*,73.
(3) Ruckenstein, E. and Wang, H.Y. *Catal. Lett.* **2001**, *73*, 2.
(4) Tomishige, K.; Kanazawa, S.; Suzuki, K.; Asadullah, M.; Sato, M.; Ikushima, K. and Kunimori, K. *Appl. Catal. A:Gen.* **2002**, *233*, 35.

Table 1. CO_2 Reforming of Methane in the Presence and Absence of O_2

SOLIDS	DRY			COMBINE		
	XCH_4	XCO_2	H_2/CO	XCH_4	XCO_2	H_2/CO
$LaRu_{0.8}Ni_{0.2}O_3$	79.0	81.0	0.94	87.0	47.0	1.18
$La_{0.8}Sm_{0.2}Ru_{0.8}Ni_{0.2}O_3$	84.4	67.4	0.75	89.7	39.7	1.04
$La_{0.8}Nd_{0.2}Ru_{0.8}Ni_{0.2}O_3$	83.5	63.8	0.66	81.3	32.3	1.02
$La_{0.8}Ca_{0.2}Ru_{0.8}Ni_{0.2}O_3$	67.9	85.3	0.86	85.0	50.0	1.18

tr =24 h, WHSV =24L/ h.g, CH_4/CO_2 =1, CH_4/O_2=2, W = 200 mg, Tred =700ºC/ 8h, Treac. = 700ºC