Dry Reforming of Methane and Carbon Dioxide over a Rh(2wt.%)/CeO_2 Catalyst

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Abstract

Methane reforming of carbon dioxide over Rh(2wt.%)/CeO_2 was studied by using a microactivity reference unit reactor at 500-680°C and a micromeritics autochem pyrex reactor at 200 to 800°C with existence of a mass spectrophotometer. For this purpose, different types of CuO/CeO_2 catalysts were used, initially, but lower catalyst activities and lower hydrogen yields have been found for different feed ratios of methane and carbon dioxide. Then, a Rh(2 wt.%)/CeO_2 catalyst has been prepared and by loading different quantities of this catalyst into the both reactors, the kinetic measurements of dry reforming of methane and carbon dioxide were conducted, successfully. By selecting Rh as an active metal, meaningful hydrogen yields have been found at the exit of both reactors. So the selected metal type(Rh) for the prepared catalyst is one of the best metal for this particular reaction. The consumptions of CH_4 and CO_2 with first order reaction has started approximately at 400 °C, but it was speeded up at 550°C. Determined activation energies of CH_4 and CO_2 reaction at 550-680ºC were 89.4424 and 61.9309 kJ/mol, respectively.

Key Words : Dry reforming of CH_4 and CO_2, catalyst preparation, catalyst reduction, activity tests of catalysts, hydrogen production

1. Introduction

Dry reforming of CH_4 and CO_2 is one of the most important reaction to study, recently. Because, CO_2 emission of the world is continously increasing and resulting to temperature rises and climate changes in different parts of the world[1] . Development of ultra-stable Ni catalysts for CO_2 reforming of CH_4 was studied by Tomishige and co-workers [2]. They have reported the most serious problem in CO_2 reforming of CH_4 is destruction and deactivation of catalysts caused by carbon deposition[2].

CO_2 reforming of CH_4 into syngas over Ni/γ-Al_2O_3 catalysts was studied by Wang, et.al.[3]. The activation energy for CO production in this reaction amounted to 80 kJ/mol[3]. Portugal and co-workers[4], have reported a study which is related to CH_4 and CO_2 reforming over Rh catalyst with different supports. They had found that support material type has some important effects on

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catalyst activity. Reforming of CH_4 with CO_2 over supported platinum catalysts were carried out by Souza, et.al. [5]. Verykios[6] has investigated mechanistic view of CO_2 reforming of CH_4 over a Rh/Al_2O_3 catalyst. He had concluded that origin of carbon formation is coming, basically from CO_2. The CH_4-CO_2 reforming activities of Ni-based catalysts under fixed and fluidized bed operations were studied by Chen and co-workers[7].

CH_4 and CO_2 reforming reaction has been carried out over Rh/Al_2O_3 catalyst by Nagai and others[8]. They have concluded that activity of Rh/CeO_2 catalyst is less than activity of Rh/Al_2O_3 catalyst. Dry reforming of methane and carbon dioxide was studied by Donazzi et.al.[9] over Rh(4%)/α-Al_2O_3 catalyst. They have investigated kinetics of CH_4 and CO_2 over Rh(4%)/α-Al_2O_3 at 300-800 °C. Li and co-workers[10], have investigated the effects of Rh loadings on perormance of Rh/ Al_2O_3 catalyst for partial oxidation of methane to produce synthesis gas.

Ni catalysts supported on different ceramic oxides (Al_2O_3, CeO_2, La_2O_3, ZrO_2) were prepared with wet impregnation method by Barroso-Quiroga, et,al.[11]. They were reported that CeO_2 has a relatively good activity[11]. A combination of experiment and modeling was used by McGuire and co-workers[12] for catalytic dry reforming of CH_4 and CO_2 in a flow reactor.

A few 3% Ru-Al_2O_3 and 2wt.% Rh-CeO_2 catalysts were synthesized and tested by Djinovic et al.[13]. They concluded that H_2/CO molar ratio in produced syngas can be increased either by operating at higher temperatures, or by using a feed stream with higher CH_4/CO_2 ratios[13]. Additionally, Rh–CeO_2 catalyst was synthesized and characterized by means of N_2 ads./desorp.[14]. The CuO/CeO_2 catalysts have not shown convenient activity levels, therefore, a new catalyst(Rh(2 wt.%)/CeO_2) has been synthesised for the purposed reaction[15].

2. Experimental

2.1. Method of feed flow measurements, catalyst activity studies within microactivity reference unit, and micromeritics autochem pyrex glass reactors, and gas analysis

For CH_4 and CO_2 dry reforming reaction and catalyst activity tests, a computer controlled microactivite reference unit reactor has been used at temperature range of 20-700 °C and pressure range of 0-100 bars. The microactivite reference unit reactor of NIC has been developed recently, by PID eng. and technology company in Spain[15]. Reaction measurements of dry reforming of CH_4 and CO_2 and activity tests of synthesised catalysts(different types of CuO/CeO_2) have been carried out[15]. Product mixtures were observed continously, and reactor effluent gas mixtures were analyzed by an Agilent model gas chromatography[15].

The catalyst was loaded into the reactor before catalyst conditioning measurements. Then, reactor has replaced, by adjusting the appropriate feed flowrates, experimental measurements were realized. Due to existed reversible water-gas shift reaction over CuCe15 and CuCe20-impregnated catalysts at desired study conditions, and because the bad activity of these catalysts for CH_4+CO_2 reaction, were caused for us to try using CuCe10-co-precipitated catalyst in

CH_4+CO_2 reaction. With different feed flowrates to the system at 450°C-680°C, any H_2 values were not determined in the exit gas composition[15]. For investigation of catalyst activities at 300-800 °C, an online mass spectophotometer was connected to the exit of the system for purposed reaction. Reaction products were analysed via this mass spectophotometer[15].

2.2. Synthesis method, TPR and TPD analysis of Rh(2wt%)/CeO2 catalyst

Appropriate quantity of commercial ($Rh(NO_3)_3.H_2O$) (~36% Rhodium based) aqueous solution was added into 25 ml of ethanol. This commercial Rh based solution was added slowly into 3.08 grms. CeO_2, completely. The mixture was stirred at 400 rpm and at room temp. for a duration of 1 hour. Obtained catalyst pre-substance was kept at 400°C for three hours[16]. With this procedure, Rh(2wt.%)/CeO_2 catalyst was produced by the "**wet impregnation method"**[15].

Temperature programmed reduction(TPR) and temperature programmed desorption(TPD) experiments for Rh(2wt.%)/CeO_2 catalyst were performed[15] within micromeritics autochem equipment. By setting total flowrate of both gases to 25 ml/min and programming temperature to 500°C, reduction experiments were continued for 2 hours. We have started up this process by loading 104.5 mg impregnated catalyst(Rh(2wt.%)/CeO_2) into autochem glass reactor with accompaniment of cold trap[15].

2.3. XRD analysis, The method of BET and carbon analysis of remainder catalyst

XRD analysis of Rh(2 wt.%)/CeO_2 catalyst was carried out at room temperature with an XRD equipment(PANalytical X'Pert PRO). BET surface area of 0.2384 g. powder Rh(2 wt.%)/CeO_2 catalyst has been determined with a micromeritics surface measurement equipment. TOC analyser has an IR detector which was operated at 680°C for determination of carbon in the remainder Rh(2 wt.%)/CeO_2 catalyst sample. By using TOC analysis method, first of all, sample was preheated up to 800°C. Then, temperature of TOC was reduced gradually to room temperature[15].

3. Results, discussions and interpretations

In this study, the reaction of dry reforming of CH_4 with CO_2, different forms of CuO/CeO_2 catalysts and a Rh(2 wt.%)/CeO_2 catalyst were used. In conducted experiments of dry reforming of CH_4 and CO_2 with different types of CuO/CeO_2 catalysts, the lower activity values have been found. With different feed flowrates, significant H_2 percentages were not found in the exit of microactivite reference unit reactor[15]. Different carrier gas compositions (5% H_2/He, 5% CO/He, 10% CO/Ar), have been used at different temperatures (400-680°C) during the reduction process. Some formed oxides were not possible to remove, on catalyst surfaces in spite of higher temperatures [15]. As a consequence of lower activities of above catalysis(CuO/CeO_2), the synthesis of a Rh(2 wt.%)/CeO_2 catalyst was performed[15].

3.1. Results and discussions of XRD, BET area and TOC analysis of Rh/CeO$_2$ catalyst

Fresh catalyst has very low rhodium metal percentage in a possible oxide form of RhO_2/CeO_2, so that absolute quantity of rhodium was not seen, exactly. But, some higher piks of CeO_2 were determined at different 2θ angles of XRD equipment [15]. In consequence of fact that conducted analysis with micromeritics surface measurement equipment, determined BET surface area of the latest prepared Rh(2 wt.%)/CeO_2 catalyst was 121.378 m^2/gr[15]. This surface area of catalyst has been confirmed well with similar catalyst studies of literature[9].

3.2. Results and discussions of autochem pyrex glass and microactivity ref. unit reactor

In completed experiments of TPR, prepared new Rh(2wt.%)/CeO_2 catalyst was reduced completely within autochem equipment at 280°C within first 75 minutes (fig. 1). TPR experiments with accompaniment of cold trap were realized by setting up the system to 500°C, initially(fig. 1).

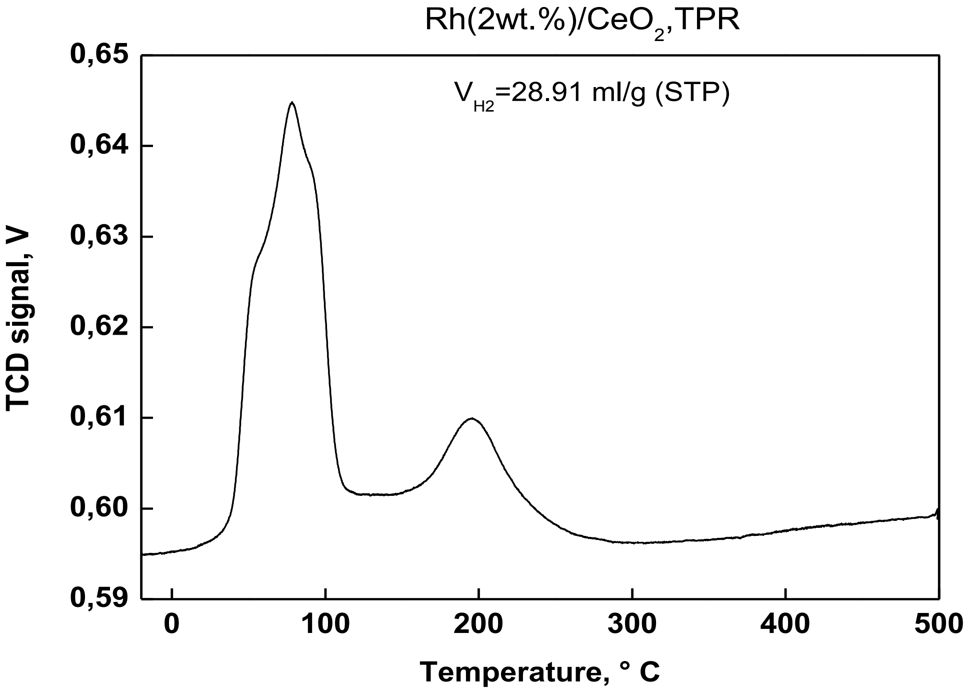

Fig.1. TPR analysis at different temperatures against TCD signal for Rh(2wt.%)/CeO_2 catalyst with autochem equipment

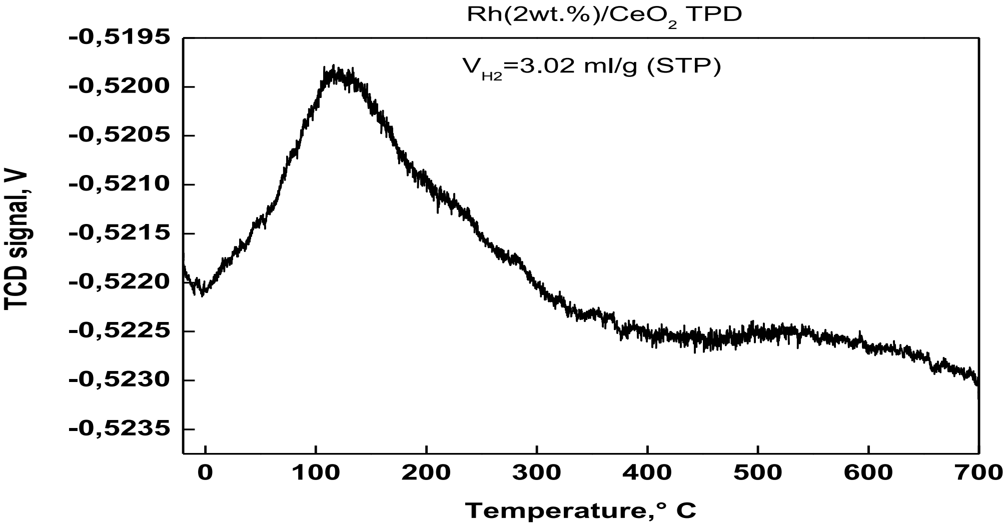

Fig.2. TPD analysis at different temperatures against TCD signal for Rh(2 wt.%)/CeO_2 catalyst with autochem equipment

In conducted TPD experiment, desorption procedure of Rh(2 wt.%)/CeO_2 catalyst was realized with pure argon gas by adjusting system to 700°C, initially(fig.2). TPR experiments were completed approximately within 2 hours and TPD experiments were completed approximately with in four hours[15]. Automatically, by increasing temperature step by step from 25°C to 200°C, MS signal levels of standart gas mixture (contained CO, CH_4, CO_2, H_2) against time were drawn in Fig. 3 [15].

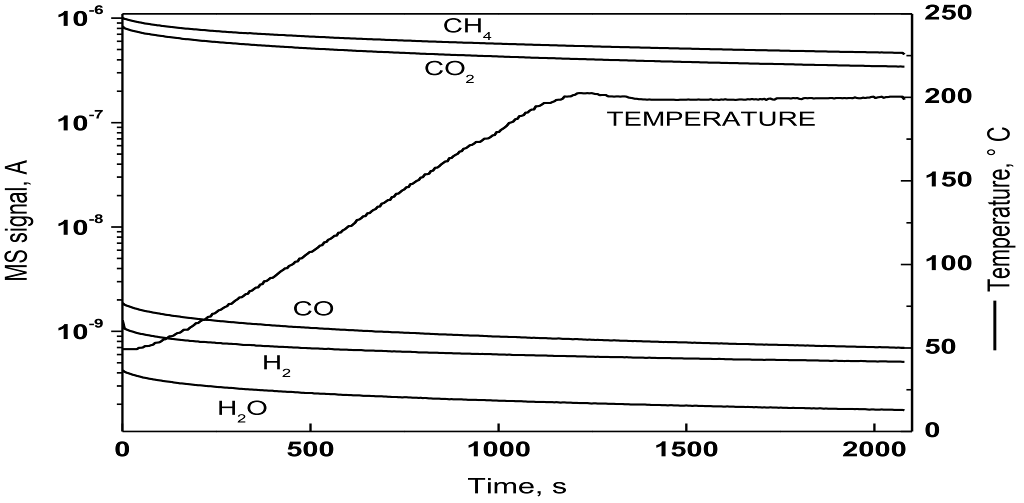

Fig.3. MS signal of standart gas mixtures against time at lower temperatures(35-200°C) with autochem equipment.

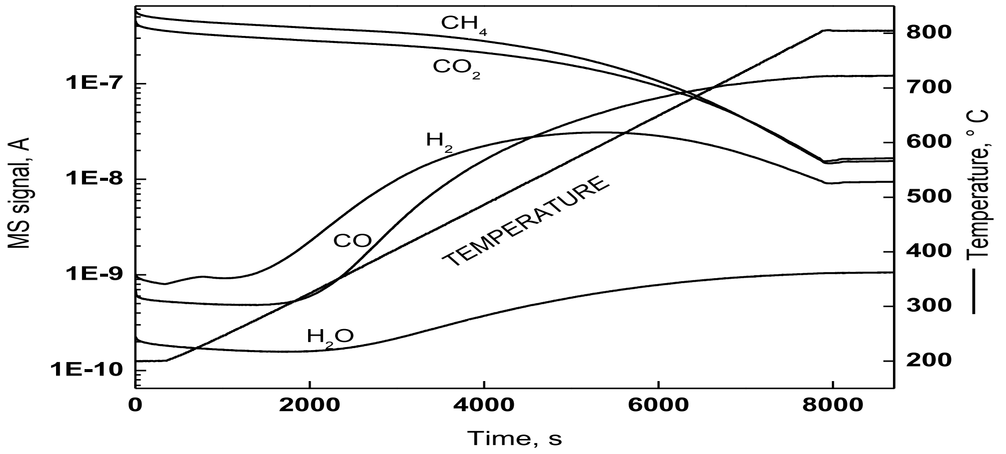

Fig. 4. MS signal against time on stream over Rh(2 wt.%)/CeO_2 catalyst during dry reforming of methane and carbon dioxide reaction with micromeritics autochem equipment.

According to conducted TPR and TPD experiments, CeO_2 surface was decreased 30.1% around 500°C-600°C temperatures in autochem equipment. In fact, to study with CeO_2 support material will not be convenient at very high temperatures(600-800°C)(see fig. 4)[15]. Graphs of catalyst testing and reaction studies of autochem system were presented on figs.3-4[15]. A graph of time, MS signals and temp. related to reaction studies within autochem equipment has presented on fig. 4. Temp. was increased linearly from 200°C to 800°C. CH_4 and CO_2 compositions were reduced, continously, but then, H_2 was raised to a significant value, then it was decreased evidently, because, decomposition rate of CeO_2 surface was effective at higher temps. above 500°C. The greatest increases in CO and H_2 quantities were found, in a temp. range of 200-800°C[15].

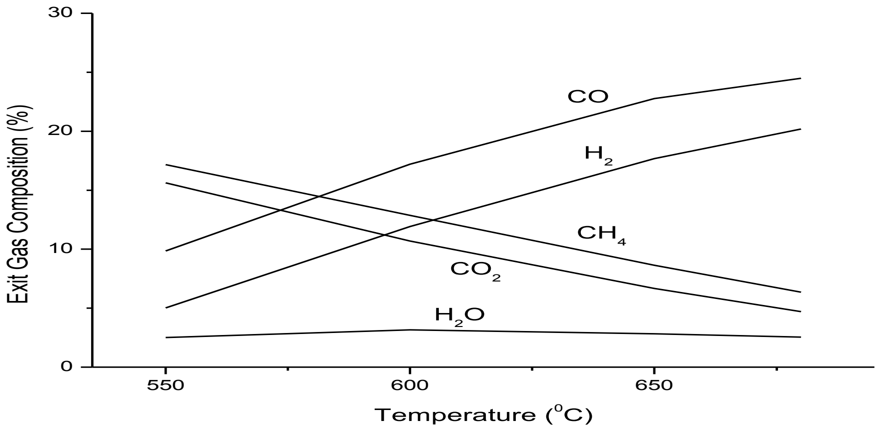

Fig.5. Gas composition percentage(%) at the exit of reactor against different temperatures during CH_4+CO_2 reaction with microactivity reference unit reactor.

Reactor exit gas compositions against temp. was presented in fig.5. H_2 compositions were increased with temp. in the studied temp. range. Gas compositions of CH_4 and CO_2 in fig. 5 were decreased, gradually. This result is a valuable indication which shows that newly synthesised catalyst has a good activity. In conducted dry reforming of CH_4 and CO_2 reaction with 50% CH_4+CO_2 and 50% He feed flowrates over Rh(2 wt.%)/CeO_2 catalyst at 680°C, measured quantity of H_2 was 20.19%(see fig.5). When, feed gas flowrates have increased gradually, slight decreases in H_2 and CO ratios(~4%) have recorded in exit gas composition[15].

Because of these lower values of activation energies, we may say that dry reforming of CH_4 and CO_2 reaction is chemical reaction controlled and it is first order on the basis of CH_4 and CO_2 consumptions and H_2 formation rates. The calculated activation energies and activation energies of similar studies in literature have good agreement [3].

Conclusions

Reaction studies with autochem equipment have cofirmed this fact, but, different types CuO/CeO_2 catalysts have not shown appropriate activities for this reaction at studied temp. range from 400°C up to 680°C. Contribution of Rh(2wt.%)/CeO_2 catalyst on produced H_2 and synthesis gas was investigated, the obtained H_2 and synthesis gas ratios were high enough in studied temp. range and thus, the activity of new catalyst was found to be better for the purposed reaction. In the case of using Al_2O_3 as a support material for Rh catalyst at higher temperatures, then, higher ratios of synthesis gas will be produced. Obtained activtion energies show that CH4+CO2 reaction is first order and chemical reaction step has some influences on the overal reaction rate.

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