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Modification of catalytic performances due to the co-feeding of hydrogen or carbon dioxide in the partial oxidation of methane over a NiO/γ-Al_2O_3 catalyst

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Abstract

The influence of the addition of 1–10 vol.% of hydrogen or carbon dioxide to the feed during the partial oxidation of methane was studied over a NiO/γ-Al_2O_3 catalyst. The addition of H_2 decreases the conversion and syngas selectivity. This decrease of performance seems to be related to a higher reduction of the catalyst due to the H_2 co-feeding. The addition of CO_2 also appears unfavorable to the production of hydrogen but increases the CO yield. A combination of the dry reforming and the reverse water gas shift reactions is suggested to explain the observed modifications in the product yields.

Keywords: Partial oxidation of methane; Syngas; NiO/γ-Al_2O_3; CO_2 and H_2 co-feeding

1. Introduction

The production of hydrogen is now receiving growing attention because its utilization in fuel cells is expected to increase in the future. The catalytic partial oxidation of methane (POM) to produce hydrogen is currently investigated. Among the different catalysts tested for this reaction, NiO/γ-Al_2O_3 is one of the most frequently studied. The mechanism of POM over Ni catalysts is still debated and two mechanisms have been suggested: (i) the direct oxidation mechanism—by which hydrogen is directly produced from the dissociation of CH_4 and CO is formed from the reaction between surface oxygen and surface carbon species originating from the CH_4 decomposition [1–3] and (ii) the indirect oxidation mechanism—which involves the complete oxidation of methane to CO_2 and H_2O followed by reforming of methane, with CO_2 and H_2O formed during the first step of the reaction [1,4,5]. In the direct mechanism, metallic Ni would be the active component, while in the second mechanism, NiO would be required for the combustion step, and metallic Ni for the reforming step [6,7].

The addition of gaseous promoters in the reaction gas feed is a new promising approach to understand dynamic processes on the surface of catalysts and to mastering the selectivity and/or activity of catalysts at work, in particular to stabilize the superficial atoms in their most efficient state. It has been reported that the addition of gaseous promoters (CO_2 and H_2) into the feed during catalytic combustion of methane improves the performances of Pd/Ce-Zr-O or Pd/γ-Al_2O_3 catalysts. Indeed, the oxidation state of the active sites can be carefully tuned via the use of gaseous promoters [8].

The objective of this work is to investigate the effect of co-feeding gaseous promoters (H_2 and CO_2) on the partial oxidation of methane into syngas. As metallic Ni species are necessary for the reaction, the addition of H_2 has been considered because it could help maintain a high concentration of metallic Ni at the surface. The addition of CO_2 has been studied because it is a powerful oxidant, modifying the oxidation state of surface atoms [8], CO_2 can be produced in the reaction, and it can participate to the reforming reaction and water gas shift reaction.

2. Experimental

2.1. Preparation of NiO (10 wt% Ni)/γ-Al_2O_3

The nickel was deposited on commercial γ-Al_2O_3 from an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ by a conventional

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wet impregnation method. The final catalyst ($S_{BET} = 53\ m^2/g$) was obtained after drying at 110 °C for 15 h and calcination at 700 °C for 5 h.

2.2. Catalytic tests

The standard test conditions (in absence of H_2 or CO_2) use a 5 vol.% CH_4, 2.5 vol.% O_2 and 92.5 vol.% N_2 gaseous mixture. The tests with the H_2 or CO_2 as co-feeding were performed by adding 1, 2, 5 or 10 vol.% of H_2 or CO_2 to the feed. In all cases, the space velocity was maintained constant by balancing with N_2 (total flow always equal to 100 ml/min over 100 mg of catalyst (sieved between 200 and 315 μm)). The catalyst was pretreated in situ under a pure H_2 flow at 700 °C for 1 h. The catalytic activity was measured between 400 and 700 °C in increasing then decreasing steps of temperature. The catalyst was cooled down under the reaction conditions. The products and reactants were quantified using a VARIAN gas chromatograph (two thermal conductivity detectors and five columns). The relative error on the measurements of conversions and yields was inferior to 5%. The introduced quantities were removed in calculating the yields of H_2 and CO_2 presented in the figures.

2.3. Characterization techniques

XRD was performed on a Siemens D5000 diffractometer using Kα radiation of Cu (λ = 1.5418 Å). The 2θ range between 15° and 90° was scanned at a rate of $0.00033\ ^\circ\ s^{-1}$. Identification of the phases was carried out by using JCPDS database. XPS analyses were performed using a SSI X-Probe (SSX-100/206) spectrometer from Surface Science Instrument (Fisons) working with a monochromatic Al Kα radiation (10 kV, 22 mA). Charge neutralization was achieved using an electron flood gun adjusted at 8 eV and placing a nickel grid 3.0 mm above the sample. Pass energy of the analyzer was 50 eV and the spot size was 1000 μm in diameter, corresponding to a full width at half maximum (FWHM) of 1.1 eV for the Au $4f_{7/2}$ band of a gold standard. For these measurements, Ni 2p, Al 2p, O 1s and C 1s bands were recorded. The binding energies were calibrated by fixing the center of the Al 2p signal coming from the Al_2O_3 support at 74.3 eV. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

3. Results

3.1. Catalytic performances

3.1.1. Addition of H_2 to the feed

From Fig. 1, it is observed that the introduction of hydrogen at 600 °C into the feed results in: (i) a decrease in the conversion of CH_4 proportional to the amount of hydrogen added to the feed, (ii) a decrease in the yields of H_2 and CO and (iii) a modification of the CO_2 yield that shows a maximum and then decreases when the addition of H_2 is too high. Similar trends are observed at other tested temperatures.

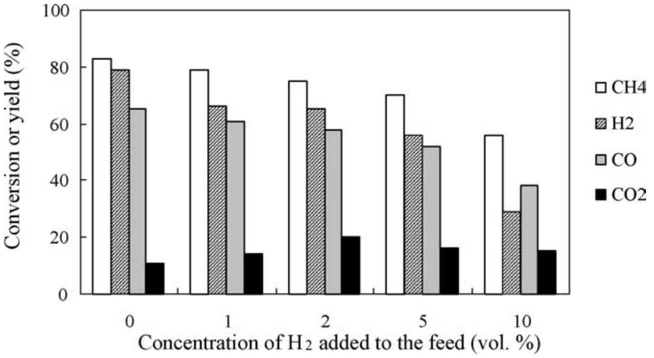

Fig. 1. Conversion of CH_4 and yields of H_2, CO and CO_2, measured at 600 °C over Ni/γ-Al_2O_3 as a function of the H_2 concentration added to the feed.

3.1.2. Addition of CO_2 to the feed

Fig. 2 shows that the introduction of CO_2 at 600 °C into the feed results in: (i) a slight decrease in the production of H_2, (ii) a significant increase in the yield of CO and (iii) a significant increase in the CO_2 yield at low amounts of CO_2 added in the feed, then the yield passes through a maximum, decreases and becomes negative with further increases in CO_2 addition. Only a slight increase in CH_4 conversion is observed with high CO_2 amounts.

3.2. Characterization of samples

3.2.1. XPS results

Table 1 presents the XPS Ni/Al, O/Al and C/Al atomic ratios measured over the catalyst before and after the tests in various conditions. The presence of carbon coming from the usual organic contamination of the catalyst was detected over all samples. However, no increase in the C/Al ratio was observed after standard reaction, and the addition of H_2 or CO_2 to the reaction feed did not change that ratio. These results suggest that no coke deposition occurs with the different sets of conditions. A decrease of the Ni/Al ratio is observed after pretreatment of the catalyst. This decrease could be due to a sintering of the nickel particles during this step or to the embedding of nickel particles in the γ-Al_2O_3 support. An increase in the Ni/Al ratio is observed after test in standard conditions, indicating a migration of Ni on the surface of the

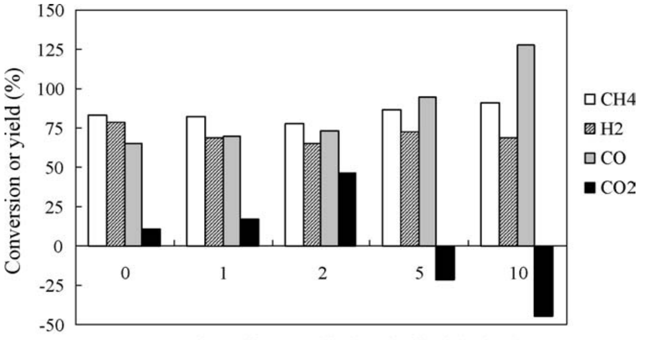

Fig. 2. Conversion of CH_4 and yields of H_2, CO and CO_2, measured at 600 °C over Ni/γ-Al_2O_3 as a function of the CO_2 concentration added to the feed.

Table 1
XPS and XRD analysis results of Ni/γ-Al_2O_3 catalyst before test, after pretreatment or after catalytic tests in absence or in presence of H_2 or CO_2

Operational conditions	XPS (atomic ratios)			XRD		
	Ni/Al	O/Al	C/Al	Detected phases	Intensity ratio	
					NiO/Al_2O_3	Ni/Al_2O_3
Before test	0.12	1.7	0.5	NiO, γ-Al_2O_3	33.7	n.d.
After H_2 pretreatment (700 °C/H_2)	0.08	1.6	0.6	Ni, γ-Al_2O_3	n.d.	35.2
After test in absence of H_2 or CO_2	0.10	1.6	0.4	NiO, γ-Al_2O_3	34.5	n.d.
After test in presence of 1% H_2	0.08	1.5	0.4	NiO, γ-Al_2O_3	32.0	n.d.
After test in presence of 2% H_2	0.08	1.5	0.5	NiO, γ-Al_2O_3	30.4	n.d.
After test in presence of 5% H_2	0.08	1.5	0.4	NiO, Ni, γ-Al_2O_3	22.8	22.7
After test in presence of 10% H_2	0.07	1.5	0.5	NiO, Ni, γ-Al_2O_3	22.0	28.6
After test in presence of 1% CO_2	0.08	1.5	0.5	NiO, Ni, γ-Al_2O_3	27.4	15.7
After test in presence of 2% CO_2	0.13	2.0	0.5	NiO, Ni, γ-Al_2O_3	27.2	15.2
After test in presence of 5% CO_2	0.11	1.9	0.5	NiO, Ni, γ-Al_2O_3	24.6	16.9
After test in presence of 10% CO_2	0.13	2.0	0.5	NiO, Ni, γ-Al_2O_3	31.1	14.8

2θ position of the band taken for each phase: NiO (62.9°); γ-Al_2O_3 (66.9°); Ni (51.8°); n.d.: not detected.

support. After reactions in presence of H_2, the Ni/Al ratios values remain the same as after the reductive pretreatment. In contrast, the addition of more than 1% of CO_2 to the feed increases the Ni/Al ratio compared to the sample analyzed after the H_2 pretreatment. The decomposition of Ni 2p in two different components corresponding to Ni^{2+} and Ni^0 species was not possible because of the presence of many satellites in addition to the doublet peaks in this region. Superimposition of the peaks recorded over the same catalyst submitted to different conditions of reaction or pretreatment is shown in Fig. 3. A broadening and a shoulder of the Ni 2p peak is observed after pretreatment of the catalyst under pure hydrogen at 700 °C. This broadening can be assigned to the presence of metallic Ni^0 at lower binding energies coming from the reduction of Ni^{2+} (NiO). After standard reaction, the catalyst is in an intermediate oxidation state between the fresh NiO/γ-Al_2O_3 and the pre-reduced catalysts. The broadening of the Ni 2p peak towards the lower binding energies observed over the catalysts recovered after test in presence of H_2 in the feed indicates that the introduction of H_2 in the feed maintains the surface Ni species in a slightly more reduced state than after the test in standard conditions (no H_2 or CO_2 added). The broadening and the associated reduction also increase with the amount of H_2 introduced in the feed. The addition of CO_2 does not significantly modify the peak shape. In all cases, the catalysts are in an intermediate oxidation state between fresh NiO/γ-Al_2O_3 and the pre-reduced catalyst.

3.2.2. XRD results

The phases detected over the catalysts after XRD and the relative intensity of these phases to the support are given in Table 1. A decrease of the NiO (51.8°) band intensity is observed when H_2 or CO_2 is introduced in the feed, compared to the test without gaseous promoters. Moreover, a metallic Ni (62.9°) phase is clearly detected over all catalysts recovered after reactions performed in presence of CO_2, or with high concentrations of added H_2 (5 or 10 vol.%). A reduction of the NiO phase and a detection of metallic Ni are also observed on the catalyst submitted to the hydrogen pretreatment only. The measurement of the size of the nickel particle by the Scherrer equation was not possible because an overlapping by a band of the γ-Al_2O_3 support made it difficult to measure the full width at half maximum height of the NiO main band.

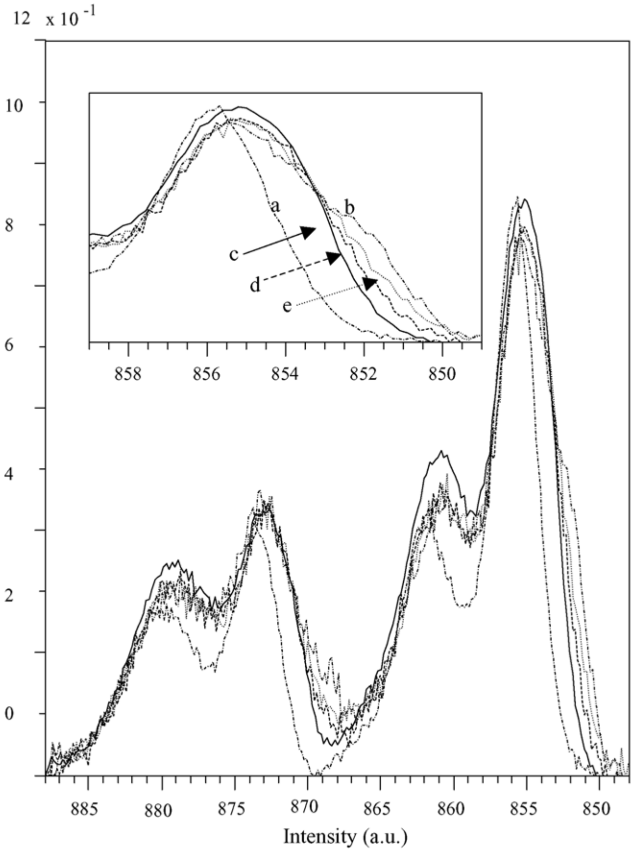

Fig. 3. Normalized XPS Ni 2p peaks of: (a) fresh Ni/Al_2O_3, (b) Ni/Al_2O_3 after pretreatment at 700 °C for 1 h under pure hydrogen, (c) Ni/Al_2O_3 after the POM reaction in standard conditions, (d) Ni/Al_2O_3 after the POM reaction in presence of 5% H_2 in the feed and (e) Ni/Al_2O_3 after the POM reaction in presence of 10% H_2 in the feed.

4. Discussion

An important observation is that the introduction of H_2 or CO_2 to the feed drastically modifies the catalytic performances in POM. H_2 is the most selective product produced by POM. This strongly suggests that, due to the H_2 produced in the reaction, the Ni/γ-Al_2O_3 catalyst may not work in optimal conditions. Explanations of the results are discussed in relation to the involvement of other reactions and the solid state modifications.

4.1. Involvement of other reactions

It is well known that in the same ranges of temperature, concentrations, and space velocity, dry (DR) and steam (STR) reforming of methane as well as (reverse) water gas shift (RWGS) and total oxidation of methane (TOM) reactions are simultaneously involved in the partial oxidation of methane (POM) over Ni/Al_2O_3 [9,10]. A thermodynamic calculation taking into account all the species involved in the reaction has been performed elsewhere [11]. The conclusion of this study was that thermodynamics could not fully explain the observed change in the performances due to the addition of H_2 or CO_2. The explanation resides in the modifications in the solid state properties of the catalysts.

The increase in CO_2 production when a low amount of CO_2 is added to the feed indicates that the catalyst promotes TOM. Furthermore, the water produced in this reaction could promote the STR. The apparent negative CO_2 yield at high concentration of added CO_2 indicates that CO_2 is consumed during reaction. An increase of the H_2 production should be expected with the addition of CO_2 thanks to the occurrence of the DR. The decrease of the H_2 yield, the increase in the CO yields and the increase in the conversion observed with increasing CO_2 amounts support the fact that the RWGS and the DR reactions are favored when CO_2 is added to the feed. These observations are also in agreement with the kinetic model for the CO_2–CH_4 reforming reaction [12], which states that the RWGS reaction is involved in the mechanism. In the case of H_2 addition, it seems that the main consequence is a decrease of all products, except for CO_2 which goes through a maximum at 2% hydrogen addition. This small increase in the CO_2 yield could be explained by a modification of the kinetics of the reverse water gas shift reaction. No other reaction seems to be favored when H_2 is introduced into the feed.

4.2. Solid state modifications

A decrease in activity and syngas selectivity observed for the reactions performed with H_2 and CO_2 addition to the feed could be explained by a deposition of coke on the surface. The kinetic predictions developed by De Groote and Froment [9] showed that the addition of CO_2 reduces the formation of coke while H_2 does not. Furthermore, Liu et al. [13] experimentally evidenced over a LiLaNiO/γ-Al_2O_3 that the addition of CO_2 to POM prevent the carbon deposition [13]. In the present work, the sensitive XPS analysis used to characterize the modifications of surface composition does not evidence any increasing coke deposition on the samples after standard test or in presence of CO_2 or H_2.

The reduction of Ni (XRD and XPS) could explain changes in the activity of the catalyst. Catalysts are reoxidized after standard conditions. H_2 and CO_2 promote the reduction of the catalysts (decrease of the NiO). In the case of H_2 addition, it seems that the main consequence is a decrease of all products except CO_2 production due to a diminution in the total number of active sites able to perform POM, because of a deeper reduction of the catalyst. A reduction of the NiO/γ-Al_2O_3 catalyst is required to activate the catalyst [14]. It is suggested that during the reaction, the catalysts work in an accurate oxidation state: oxidized and reduced species should coexist. An optimum ratio of oxidized and reduced nickel exists. A too high amount of metallic Ni does not seem adequate for the partial oxidation of methane. Surprisingly, a reduction of the catalyst bulk is also observed when CO_2 is added to the feed. However, the test performed in these conditions did not show significant changes in the activity or an important decrease in the H_2 yield. Only important changes in the CO and CO_2 yields are observed. Moreover, the surface Ni oxidation state is similar to that of the test in standard conditions. These observations suggest that factors other than catalyst reduction influence the activity and selectivity of the catalyst when CO_2 is added to the feed.

5. Conclusions

The co-feeding of H_2 or CO_2 to POM changes catalytic performances. Co-feed is not favorable to the production of hydrogen. Changes in performances are explained principally by a modification in the oxidation state of the catalysts due to the addition of H_2 or CO_2. Results are explained considering the total scheme of reactions (DR, RWS and TOM) happening under stoichiometric conditions for POM, which depend of the oxidation state of Ni.

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