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Catalysis Today 106 (2005) 47–51

CATALYSIS TODAY

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Influence of the co-feeding of CO, H_2, CO_2 or H_2O in the partial oxidation of methane over Ni and Rh supported catalysts

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Abstract

The influence of the addition of 5 vol.% of carbon monoxide, hydrogen, carbon dioxide or water to the feed of partial oxidation of methane was investigated over Ni/γ-Al_2O_3 and Rh/γ-Al_2O_3 catalysts. In addition to catalytic tests, thermodynamic calculations were performed to predict the effect of these gas co-feeds. Compared to the thermodynamic trends, differences in the influence of the co-feeding on catalytic performances were observed between both catalysts. Co-feeding of CO, H_2, CO_2 or H_2O can modify the oxidation state and dispersion of the metal component of the catalysts during reaction, and as a consequence, their performances. Changes in catalysts can be due to dynamic processes occurring during reaction. It is suggested to take these processes into account in a more complex kinetic equation for the reactions involved.

Keywords: Rh/Al_2O_3 catalyst; Ni/Al_2O_3 catalyst; Gas dopes; Dynamic processes

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1. Introduction

Due to the increasing demand for hydrogen and clean fuels, the partial oxidation of methane into syngas is receiving growing attention. Nickel- and rhodium-based catalysts are usually reported as very active and selective catalysts to perform this reaction [1].

It is well recognized that dynamic processes occur on catalysts during catalytic reactions [2]. Under reaction conditions, the catalysts can be modified in many different ways: active sites are created and/or regenerated, oxide-reduction cycles are involved, mobile chemical species are formed which can migrate from one site (phase) to another, active new phases are developed, eventually the catalyst is deactivated, etc. The improvement of performances and selectivity and the control of deactivation of catalysts require the knowledge of the effects induced by these dynamic processes on the architecture of the catalyst active sites during the reaction. A promising approach to study these dynamic phenomena, at the surface of oxides at work, consists in the addition of gaseous promoters in the reaction feed [3–6]. The addition of gas co-feeds allows to tune the activity and/or selectivity of the catalyst at work and also provide a new tool to master "in situ" the dynamic phenomena occurring at the surface of catalysts. In particular, it appears as a potential means to stabilize the superficial atoms in their most efficient state and, coupled with thermodynamic calculations, allow to study dynamic processes involved during reaction. In addition, this method is very attractive as it can be applied directly under operating conditions.

This work investigates the influence of the co-feeding of CO, H_2, CO_2 and H_2O to the partial oxidation of methane (POM) on Rh/γ-Al_2O_3 and Ni/γ-Al_2O_3 catalysts. Preliminary explanations based on the comparison of the results with thermodynamic predictions and catalyst characterizations are proposed.

2. Experimental

2.1. Catalyst preparation

Ni/γ-Al_2O_3 (10 wt% Ni; 48 m^2/g) and Rh/γ-Al_2O_3 (1 wt% Rh; 64 m^2/g) were prepared by the conventional

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2005.07.151

wet impregnation method using $Ni(NO_3)_2{\cdot}6H_2O$ or $(NH_4)_3RhCl_6{\cdot}3H_2O$ precursors and commercial γ-Al_2O_3 (Alfa Aesar). After impregnation, both catalysts were dried at 110 °C for 15 h and calcined at 700 °C for 5 h.

2.2. Catalytic tests

All the reactions were carried out at atmospheric pressure in a conventional fixed bed reactor. The total flow and catalyst weight were kept constant for each test (1000 ml/(min $g_{catalyst}$)). The reactor consisted of a quartz U-tube of 8 mm internal diameter into which the catalyst (100 mg) was deposited. Catalysts were pressed, then slightly fragmented and sieved between 200 and 315 μm. The volume of the catalytic bed was about 0.1 ml. The temperature of the catalysts was monitored with a PI temperature regulator coupled with a thermocouple, which was introduced in a sheath in tight contact with the catalysts placed in the middle of the small catalytic bed. Prior to the reaction, the catalysts were reduced in situ under a pure H_2 flow at 700 °C for 1 h then cooled at 400 °C. The catalytic activity was measured between 400 and 700 °C in increasing then decreasing steps of temperature (50 °C). The catalyst was cooled down under the reaction conditions. The standard POM feed was composed of 5 vol.% CH_4 and 2.5 vol.% O_2 diluted in N_2. The tests with H_2, CO, H_2O or CO_2 as co-feed were performed by adding one of each co-feed at a concentration of 5 vol.%. 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). The products and reactants were quantified using a VARIAN gas chromatograph equipped with two thermal conductivity detectors and a flame ionization detector, and five columns. The yields and selectivities presented in the figures below correspond to the amount of CO or H_2 actually produced. Indeed, they were calculated taking into account the difference between the measured and introduced quantities. External mass transfer and diffusion limitations. Experiments were performed at constant space velocity but varying the amount of catalysts (50, 100 or 200 mg) and the flow rates of identical feed composition under standard POM conditions. Conversion of methane CO and H_2 yields remained unchanged at all gas flow rates, indicating that gas film resistance does not influence the rate of reaction. Tests of POM were performed with catalyst particles of different size ranges (100–200, 200–315 and 315–500 μm). Conversion of methane and yields of CO and H_2 remained unchanged for all ranges of particle sizes indicating that the resistance to pore diffusion was negligible.

2.3. Characterization techniques

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 FWHM (Full Width at half maximum) 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 C–(C, H) contribution of the C 1s adventitious carbon at 284.8 eV. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

XRD was performed on a Siemens D5000 diffractometer using Kα radiation of Cu ($\lambda = 1.5418$ Å). Over Ni/Al_2O_3 samples, the 2θ range between 47 and 70° was scanned at a rate of $0.001^\circ\ s^{-1}$. Identification of the phases was carried out by using JCPDS database.

3. Results and discussion

3.1. Catalytic performances

Fig. 1 presents the variations induced on the CH_4 conversion and CO and H_2 yields and selectivities when CO, H_2, CO_2 or H_2O are added individually to the feed over Rh/γ-Al_2O_3. Similarly, Fig. 2 presents the trends observed in the same conditions over the Ni/γ-Al_2O_3 catalyst. In absence of co-feeding, the comparison of Figs. 1 and 2 show that both catalysts have more or less the same levels of activity and selectivities: Ni/γ-Al_2O_3 is slightly more active (higher CH_4 conversion) than Rh/γ-Al_2O_3, but Rh/γ-Al_2O_3 presents a slightly higher selectivity towards CO and H_2.

It can be observed that the co-feeding of CO, H_2, CO_2 or H_2O to the partial oxidation of methane induces the same following overall effects on the conversion, yields and selectivities over both catalysts:

- The introduction of CO to the feed causes a strong decrease in the methane conversion, the yield and selectivity towards CO and a slight increase in the selectivity towards H_2.

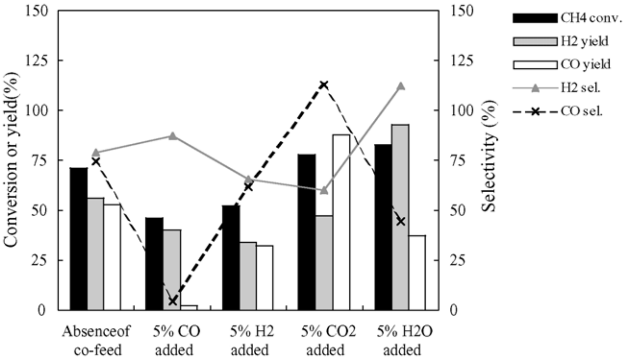

Fig. 1. Influence of CO, H_2, CO_2 and H_2O co-feeding in the POM on the conversion of methane and selectivities in hydrogen and carbon monoxide measured at 600 °C over Rh/γ-Al_2O_3.

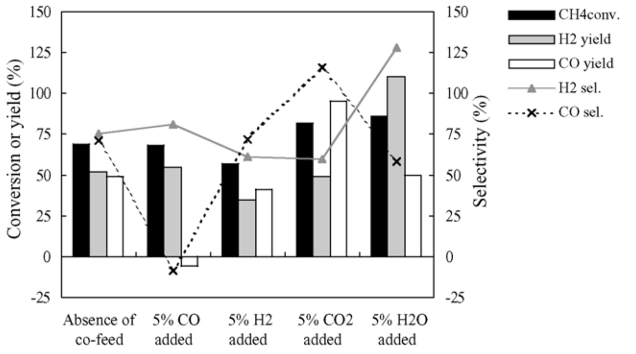

Fig. 2. Influence of CO, H_2, CO_2 and H_2O co-feeding in the POM on the conversion of CH_4 and selectivities in H_2 and CO measured at 600 °C over Ni/γ-Al_2O_3.

- H_2 addition reduces the CH_4 conversion and the yields of H_2 and CO. The selectivity towards H_2 is also diminished over both catalysts.
- When CO_2 is co-fed, the conversion of CH_4 as well as the yield and selectivity versus CO increase, whereas yield and selectivity towards H_2 decrease.
- The co-feeding of water improves the conversion of methane, the yield and selectivity towards H_2 and diminishes the yield and selectivity towards CO.

In addition to these common features, some differences can also be observed between both catalysts. The proportions in which conversions, yields and selectivities change often differ from one catalyst to another. For example, the introduction of CO to the POM feed is unfavorable to the conversion of methane and H_2 productivity over Rh/γ-Al_2O_3, while it slightly promotes the H_2 yield over Ni/γ-Al_2O_3 and has no significant effect on the conversion. Furthermore, some differences in the trends of the yields or selectivities caused by the co-feeding of products can also be noticed. In presence of H_2 added to the feed, the selectivity towards CO decreases compared to that measured with the standard feed over the Rh-based catalyst, while it is slightly increased over the Ni catalyst. The main differences between Rh and Ni catalysts are observed when CO or H_2 are added to the feed.

A straightforward explanation of these trends when CO, H_2, CO_2 or H_2O are added to the feed is to consider that other reactions are involved simultaneously. Indeed, in the same ranges of temperature, concentrations and space velocity, dry (DR) and steam reforming (STR) as well as water gas-shift (WGS) and total combustion (TC) reactions occur over the Rh/γ-Al_2O_3 and Ni/γ-Al_2O_3 catalysts.

3.2. Thermodynamic calculations

Thermodynamic calculations for the conditions of our experiments to determine the equilibrium levels that can be predicted when co-feeds are added were performed using Outokumpu HSC thermodynamic software. For these calculations, only enthalpy, entropy and heat capacity data for all prevailing compounds is needed [7]. The program calculates the amounts of products at equilibrium in isothermal and isobaric conditions. The substances to be taken into account in the calculations (CH_4, CO, H_2, CO_2, H_2O), the amounts of reactants, the potentially stable phases (gas phase), as well as temperature of raw materials were specified as input. The activity coefficient of species in the gas mixture was selected as unity (Raoultian activity). The equilibrium composition is calculated by the Gibbs energy minimization method (GIBBS solvers), which takes into account the different reactions and gaseous species that could be involved in the different sets of reaction conditions considered and introduced as starting data. The GIBBS program finds the most stable phase combination and seeks the phase composition where the Gibbs energy for the system reaches its minimum at constant pressure and temperature.

Fig. 3 gives the thermodynamic equilibrium results calculated for the addition of 5 vol.% of CO, H_2, CO_2 or H_2O to the POM feed. The comparison of this figure with the results measured over Rh and Ni catalysts in Figs. 1 and 2 show that discrepancies exist between the predicted thermodynamics and experimental data. The most obvious differences concern the co-feeding of CO, H_2 or CO_2:

- The CO co-feeding causes a very strong decrease in CO production over both catalysts, but not predicted by the thermodynamics. Moreover, the experimentally measured selectivity towards H_2 increases compared to standard conditions while they are expected to slightly decrease according to the thermodynamic trends. Over Rh/Al_2O_3, the methane conversion is strongly reduced compared to thermodynamic data.
- Over both catalysts, the addition of H_2 to the feed causes a stronger decrease of activity compared to the low diminution predicted by the thermodynamic calculations. Moreover, the increase of CO selectivity observed over Ni/Al_2O_3 also differs from the thermodynamically expected decreasing trend.
- In the presence of CO_2 in the feed, the H_2 yields and selectivities over both catalysts are more strongly reduced than thermodynamically expected. The increase in CO

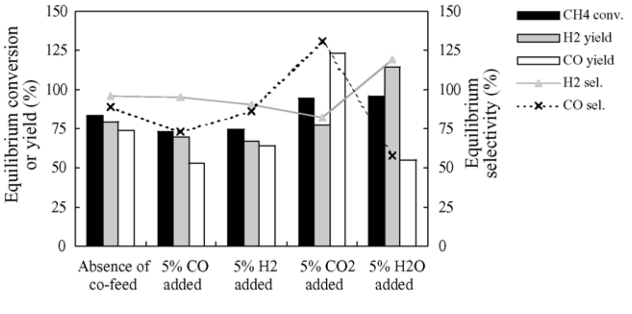

Fig. 3. Thermodynamic equilibrium results in function of the different co-feeds introduced in the partial oxidation of methane at 600 °C [2].

yield and selectivity is also smaller than in the thermodynamic calculations.

It could be argued that due to exothermic reactions some temperature deviations could develop and that the small catalyst bed is not really isothermal. However, we have also made some calculations at 650 and 700 °C. These results show that the trends observed at these temperatures are the same as those shown in Fig. 3 at 600 °C. This indicates that the discrepancies between the observed results and the thermodynamics could not be explained by variations of the catalyst bed temperature. Discrepancies observed between experimental and thermodynamic results can have two explanations: (i) a modification of the dynamic phenomena occurring on the catalyst surface and (ii) a change in the kinetics of the POM and the different reactions (DR, STR, WGS, TC, etc.) which can be involved simultaneously with POM. It is shown in the literature that the addition of water and CO_2 can produce such modifications [8]. Similarly, the partial pressures of CO and H_2 also play a role in the kinetics of POM and of the simultaneous reactions [8]. However, it must be pointed out that these two explanations are coupled: the addition of these co-feeds must change the state of the catalyst active sites, consequently modifying the kinetics of the catalytic reactions involved. In this work we focus our attention on the study of the modifications encountered by the catalysts.

3.3. Characterizations

XPS, a very sensitive surface technique, was used to analyse catalysts before and after catalytic tests, to study any change in the surface composition and in the oxidation state of the catalysts due to the introduction of the gaseous co-feeds. Table 1 summarizes the XPS results measured on the $Rh/\gamma\text{-}Al_2O_3$ samples. The reductive pretreatment performed before starting the reaction leads to an increase of the Rh/Al atomic ratio as well as a shift of the Rh 3d5 towards lower binding energies. The pretreatment under H_2 thus causes a reduction of the Rh and a higher dispersion of Rh at the catalyst surface. But, during the standard POM test, the rhodium undergoes a partial reoxidation and aggregates compared to the H_2 pretreated sample.

The addition of gaseous dopes induces some modifications of the Rh/γ-Al atomic ratio and of the position of the Rh 3d5 band compared to the standard test. In contrast, the XPS C/Al atomic ratio remains unchanged, indicating that no significant coke deposition is caused by the co-feeding of the reaction products to the POM. Compared to the catalyst recovered after the POM test in standard conditions, the following effects of the introduction of the co-feeds are observed:

- increase of XPS Rh/Al atomic ratio and higher reduction of the catalyst in presence of CO;
- increase of XPS Rh/Al atomic ratio when H_2 is added to the feed;
- increase of XPS Rh/Al atomic ratio and slight reoxidation of the catalyst in presence of CO_2;
- slight reoxidation of the catalyst in presence of H_2O.

These results evidence that the atmosphere of reaction plays an important role on the catalyst state: the oxidation state and dispersion of the Rh at the surface are modified by the reaction conditions.

Since decomposition of the Ni 2p band recorded by XPS was not possible due to the presence of satellites, XRD was also used to study possible variations in Ni oxidation state through the measurement of the peak intensity of Ni and NiO phases. The results of the XPS and XRD characterizations measured over $Ni/\gamma\text{-}Al_2O_3$ samples are presented in Table 2.

The H_2 pretreatment decreases the XPS Ni/Al atomic ratio and increases the amount of metallic Ni particles. During the reaction, a reoxidation of the Ni is evidenced, as shown by the decrease in the ratio of the intensities of the ray of Ni over that of NiO. But the reaction does not change the dispersion of Ni at the catalyst surface. As observed over the $Rh/\gamma\text{-}Al_2O_3$ samples, the addition of dopes to the reaction feed induces modifications of the catalyst. Compared to

Table 1
XPS characterizations of $Rh/\gamma\text{-}Al_2O_3$ before test and after pretreatment and tests in absence or presence of CO, H_2, CO_2 or H_2O added to the feed

Test conditions	XPS atomic ratios		XPS Rh 3d5 binding energies (eV)
	Rh 3d/Al 2p(10^{-2})	C 1s/Al 2p	
Fresh	0.8	0.2	309.5
H_2 pretreatment	1.1	0.3	307.3
Standard POM	0.8	0.3	308.2
POM + 5% CO	1.3	0.3	307.7
POM + 5% H_2	(1.3)[a]	(0.3)[a]	–
POM + 5% CO_2	1.5	0.3	308.5
POM + 5% HO	0.8	0.2	308.6

[a] Not measured over this sample, but the indicated values were recorded over three other samples recovered after POM reaction in presence of 1, 2 or 10% H_2.

Table 2
XPS and XRD characterizations of $Ni/\gamma\text{-}Al_2O_3$ before test and after pretreatment and tests in absence or presence of CO, H_2, CO_2 or H_2O or added to the feed

Test conditions	XPS atomic ratios		XRD ratio of Ni/NiO rays intensities
	Ni 2p/Al 2p	C 1s/Al 2p	
Fresh	0.23	0.44	0.4
Pretreated	0.15	0.37	0.4
Standard POM	0.15	0.57	0.6
POM + 5% CO	0.13	5.07	1.4
POM + 5% H_2	0.24	0.22	1.1
POM + 5% CO_2	0.19	0.24	0.7
POM + 5% H_2O	0.13	0.42	0.8

catalysts after standard POM, the main modifications undergone by the catalyst due to the addition of co-feed are the following:

- strong increase of the XPS C/Al atomic ratio and catalyst reduction when CO is introduced in the feed;
- high increase of the XPS Ni/Al atomic ratio and reduction in presence of H_2;
- increase of the XPS Ni/Al atomic ratio when CO_2 is added;
- slight reduction of the sample in presence of H_2O.

As for Rh/Al_2O_3, the conditions of the reaction change the oxidation state and dispersion of Ni. Moreover, the presence of a great concentration of CO in the feed also causes an important deposition of coke at the catalyst surface. The coke deposition, often reported over Ni alumina catalysts, could result from the methane cracking [9] and the Boudouard reaction ($2CO \rightarrow C + CO_2$). This last reaction and principally WGS could play an important role in the negative yield of CO observed in Fig. 2.

Over both catalysts, the addition of water to the feed induces only very small modifications of the catalyst compared to the sample recovered after the test in standard POM conditions. Moreover, the trends predicted by the thermodynamics and experimental observations show a very good agreement. However, the most important differences between thermodynamic and experimental observations were noticed when CO, H_2 or CO_2 were added to the feed. The characterizations of the $Rh/\gamma\text{-}Al_2O_3$ and $Ni/\gamma\text{-}Al_2O_3$ catalysts after these tests show more significant modifications of oxidation state and dispersion than the samples recovered after a test in standard conditions.

The differences observed between experimental and thermodynamic trends are thus explained by the modifications of the catalyst during reaction. But any change in the catalyst can lead to changes in kinetics and/or in the reaction mechanism of the simultaneous reactions involved. An important insight of these results is that in the kinetic equations, a term which takes into account any change of the catalysts as the reaction proceeds, must be included. Per reaction, a two-term kinetic equation can be suggested, one term taking into account the mechanism by which the active site operates (reflected by Langmuir–Hinshelwood, Mars van Krevelen kinetic equations, etc.), and the other giving the number of these active sites which are present as the reaction proceeds, where the reaction mechanism operates. This second term depends on the dynamic processes occurring on the catalysts, and could change as the reaction proceeds. It also depends on the operational conditions. The present results add a complication to the kinetic equation, but give a physical meaning to changes in kinetics and mechanisms. This type of equation can be very useful to explain catalytic performances and deactivation.

4. Conclusions and perspectives

Results obtained on the co-feeding of the reaction products to the POM show that the addition of gas co-feeds modifies the performances of Rh/Al_2O_3 and Ni/Al_2O_3 catalysts. Over both catalysts, the H_2 selectivity could be enhanced by the addition of H_2O or CO to the feed. In contrast, the presence of CO_2 and H_2 is not favorable for the production of hydrogen. In the presence of both, the catalyst works may not work in optimal conditions. These results provide important characteristics of the POM reaction that can be useful to improve its technology. For example, enhanced performances could be obtained if some reaction products (H_2 and CO_2) were continuously evacuated from the reactors as soon they are produced. Addition of CO inhibits production of CO. The H_2/CO production ratio could be modulated by CO injection.

Furthermore, this contribution evidences that the co-feeding of reaction products modifies the dynamic pheno mena occurring during the reaction. Further investigations are however required to identify the correlations existing between the variations of oxidation state and dispersion and the modifications of conversion and selectivities induce by the co-feeding.

Acknowledgements

The authors gratefully acknowledge the “Direction Générale des Technologies, de la Recherche et de l’Energie (DGTRE)” of the “Région Wallonne” (Belgium) and the “Fonds National de la Recherche Scientifique (FNRS)” of Belgium for their financial support. The involvement in the Coordinated Action “CONCORDE” and in the Network of Excellence “FAME” of the EU Sixth FP, in the IUAP network: “Supramolecularity” sustained by the “Service public fédéral de programmation politique scientifique” (Belgium) is acknowledged.

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