

Oxidative transformation of methane over nickel catalysts supported on rare-earth metal oxides

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Abstract

The oxidative transformation of methane over Ni catalysts supported on La, Sm and Ce oxides was investigated at atmospheric pressure, $T=723\text{--}923\text{ K}$ and $\text{CH}_4/\text{O}_2=1\text{--}10$. The BET surface areas were low ($3\text{--}22\text{ m}^2\text{ g}^{-1}$) and decreased strongly after reaction (down to $0.5\text{ m}^2\text{ g}^{-1}$). Carbonate species, Ni_2O_3 and supported oxides were identified by XRD or IR spectroscopy studies in both the fresh and used catalysts. The Ni° phase was also probably formed as amorphous phase. The oxidative coupling of methane route passed through a minimum as a function of the Ni percentage and was favored by the Ce or Sm oxide support, Li additive and low reaction temperature. High selectivities (60–90%) and good yields (about 15%) in C_2 hydrocarbons with low carbon balance (0–10%) were obtained at 823 K. La supported oxide, Ba additive and high reaction temperature favored the partial oxidation of methane. The obtained results were discussed in the light of the reducibility and acid–base properties of the catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Partial oxidation; Oxidative coupling; Ni; Rare-earth oxides

1. Introduction

Due to the growing interest in natural gas upgrading [1,2], numerous studies have been devoted to the oxidative transformation of methane (OTM) either toward the partial oxidation of methane (POM) [3–10] or the oxidative coupling of methane (OCM) [11–19]. The POM reaction was notably carried out with Ni dispersed on different supports [3–10]. For the OCM route, the catalysts are mainly composed with irreducible oxides [11–19]. A close inspection of the literature data and preliminary results in our laboratory [20] showed that OTM on supported nickel catalysts should be directed toward OCM or POM

according to the nature of the support, the presence of metal additive or the reaction conditions. In the present paper we report results obtained in the OTM reaction at atmospheric pressure over nickel catalysts supported on rare-earth oxides. The active phase was modified by varying the nickel loading (5–20%) or nature of the support (La, Sm or Ce oxides) or by Li or Ba additives. The catalysts were characterized by their BET surface areas, IR and XRD spectra.

2. Experimental

2.1. Catalysts preparation and characterization

The catalysts were prepared by conventional impregnation of Ni carbonate on the support then calcination was done at 873 K/air/12 h. The modified

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catalysts were prepared by impregnation of Li or Ba carbonates on the 10%Ni/Sm₂O₃ catalyst then calcination was done as above. The specific areas, XRD and IR spectra were performed on a BET Coultronics 2100D, Phillips 1710 diffractometer and Phillips 9800 IR device, respectively.

2.2. Catalytic testings

The catalytic performances were carried out in a fixed-bed quartz tubular reactor with 0.5 g samples at atmospheric pressure at a total flow rate of 21 h⁻¹. The steady-state activities were determined by crossing the reaction temperature. The reactants and products (Air Liquide) were analyzed on line using Delsi 121 ML FID and TCD GC equipped with porapak (C₁–C₂ analysis) and carbosieve (C₁, CO, CO₂, H₂, air analysis) columns, respectively. The catalytic activity was determined at steady state.

3. Results and discussion

3.1. Characteristics of the catalysts

The BET surface area for the fresh Ni/Sm₂O₃ catalysts decreased with the nickel loading (from 22 to 7 m² g⁻¹) or in the presence of Li or Ba additives (from 13 to 10 or 3 m² g⁻¹). In contrast, for the corresponding used catalysts, the specific surface area strongly decreased (down to 1 m² g⁻¹). In the case of the fresh La and Ce supported catalysts, the BET area (9 and

7 m² g⁻¹, respectively) remained unchanged after reaction.

The XRD studies of the 10%Ni/Sm₂O₃ and 10%Ni/La₂O₃ catalysts showed sharp bands of well crystallized solids. Besides NiO and NiCO₃ common phases, Ni₂O₃ and LaNiO₃, La₂NiO₃ and La₂O₃CO₃ phases were observed for the Sm and La supported catalysts, respectively. In the used catalysts, only the NiO phase disappeared in both catalysts whereas the Ni₂O₃ phase appeared for the 10%Ni/La₂O₃. The Ni⁰ phase was not observed in the used catalyst, probably as an effect of its redispersion in the reaction conditions whereas oxidized nickel phase were still present.

The IR spectroscopy studies of both La and Sm supported catalysts mainly confirmed the presence of carbonate species with their characteristic bands in the 800–900 cm⁻¹ (sharp bands) and 1300–1600 cm⁻¹ (large bands) regions, respectively. These bands were observed in both the fresh and used catalyst.

3.2. Catalytic activity

Testing experiments are reported in Tables 1–5. They showed that the POM relative to OCM activity depended on the chemical composition of the catalysts, nature of the support and reaction conditions. Steady-state activity in the CH₄/O₂ reaction was reached within about 1 h.

3.2.1. Influence of the reaction conditions

Raising the reaction temperature led to an increase of the conversion of methane and coke deposit (as calculated from carbon balance) in the case of the La and

Table 1
Influence of the reaction temperature in OTM for the 10%Ni rare-earth supported catalysts (CH₄/O₂=5; F=41 h⁻¹)

Catalyst	T (K)	CH ₄ conversion (%)	Selectivity (%)			H ₂ /CO	Carbon balance (%)
			C ₂	CO	CO ₂		
10%Ni/LaO ₃	723	0.1	0	0	100	–	0
	823	25	0	55	45	3.0	2
	923	42	0	84	16	3.5	25
10%Ni/Sm ₂ O ₃	723	9	17	0	83	–	8
	823	6	58	0	42	–	4
	923	94	0	64	36	–	75
10%Ni/CeO ₂	723	10	0	0	100	–	0
	823	25	62	0	38	–	0
	923	8	0	8	92	1.8	0

Table 2
Influence of the CH₄/O₂ ratio in OTM for the 10%Ni/Sm₂O₃ catalyst (reaction temperature=923 K)

	CH ₄ /O ₂ ratio			
	1	2	5	10
CH ₄ conversion (%)	63	63	94	99
C ₂ selectivity (%)	0	0	0	0
CO selectivity (%)	31	74	64	66
CO ₂ selectivity (%)	69	26	36	34
Carbon balance (%)	9	22	75	90

Sm supported catalysts, whereas for the Ce supported catalyst, methane conversion passed through a maximum at 823 K and no carbon was deposited (Table 1). The OCM selectivity is favored at low temperature (about 60% at 823 K) whereas POM or combustion mainly occurs at high reaction temperature (up to 84 and 92% at 923 K for CO and CO₂ selectivity, respectively, Table 1).

When the CH₄/O₂ ratio was varied from 1 to 10 and at the reaction temperature of 923 K, the 10%Ni/Sm₂O₃ catalyst led to an increase of the conversion of methane from 63 to 99%, mostly as a result of carbon deposit (carbon balance reached from 9 to 90%, Table 2). No C₂ hydrocarbons were detected

and the selectivity to POM passed through a maximum then a plateau for CH₄/O₂>2. A minimum is observed for the combustion of methane due to the limiting effect of the dioxygen reactant (Table 2).

3.2.2. Effect of the catalyst pre-treatment

The effect of the catalyst pre-treatment was studied with the 10%Ni/Sm₂O₃ catalyst with CH₄/O₂ ratio of 2 at the temperature of the reaction of 923 K. For the non-reduced catalyst, the obtained results (Table 3) showed no great influence of the temperature of calcination on the activity: methane conversion (about 50%) and CO and CO₂ selectivities (about 70 and 30%, respectively) were not changed whereas no hydrocarbon formation was observed. For the pre-reduced catalyst, significant change was observed since conversion of methane and POM selectivity decreased from 63 to 45% and 74 to 60%, respectively (Table 3). The reaction conditions of Table 3 correspond to the total consumption of dioxygen, also the change in selectivity from OPM to combustion resulted in a sensible change in conversion. Although the temperature of H₂ pre-treatment is not high enough to reduce the supported nickel oxide precursor and whatever the nature of this pre-treatment, it has induced changes in the reaction course. Further

Table 3
Influence of the pre-treatment on the catalytic performances of 10%Ni/Sm₂O₃ in OTM (reaction temperature=923 K, F=41 h⁻¹, CH₄/O₂=2)

Calcination, T (K)	Reduction, T (K)	CH ₄ conversion (%)	Selectivity (%)			H ₂ /CO	Carbon balance (%)
			C ₂	CO	CO ₂		
473	No reduction	50	0	71	29	2.6	17
673	No reduction	63	0	74	26	2.2	22
673	673	45	0	59	41	3.0	24
873	No reduction	57	0	72	28	3.6	26

Table 4
Effect of the nickel loading on the catalytic performances of 10%Ni/Sm₂O₃ in OTM (reaction temperature=923 K; W/F=CH₄/O₂=2)

	Catalyst			
	5%Ni/Sm ₂ O ₃	10%Ni/Sm ₂ O ₃	15%Ni/Sm ₂ O ₃	20%Ni/Sm ₂ O ₃
CH ₄ conversion (%)	22	63	18	28
C ₂ selectivity (%)	83	0	41	63
CO selectivity (%)	1	74	7	0
CO ₂ selectivity (%)	16	26	52	37
H ₂ /CO	–	2.2	–	–
Carbon balance (%)	9	22	14	22

Table 5
Effect of Li and Ba on the performances of the 10%Ni/Sm₂O₃ catalyst in OTM (reaction temperature=923 K, CH₄/O₂=2)

	Catalyst		
	10%Ni/Sm ₂ O ₃	10%Ni–2%Li/Sm ₂ O ₃	10%Ni–2%Ba/Sm ₂ O ₃
CH ₄ conversion (%)	63.0	24	52
C ₂ selectivity (%)	0	89	0
CO selectivity (%)	74	0	67
CO ₂ selectivity (%)	26	11	33
H ₂ /CO	2.2	–	2.7
Carbon balance (%)	22	7	4

work has to be planned to confirm and explain the phenomenon.

3.2.3. Influence of the support

The pure rare-earth oxides were not active in the OTM reaction in our conditions (conversion <10% at 923 K for La₂O₃), but as supports, they strongly influenced the activity of the nickel phase as it can be shown in Table 1. At 823 K, the Ce supported catalyst was OCM selective (15% of yield) whereas the La supported catalyst was rather POM selective (13% of yield). In the same conditions the samarium supported catalyst was little active mainly produced C₂ hydrocarbons (58% of selectivity at 6% of conversion). At 923 K, the cerium supported catalyst became highly combustion selective (92%) and little active (8% of conversion). This low activity is attributable to the limiting effect of the dioxygen reactant in the used conditions. At the same reaction temperature, for both the La and Sm supported catalysts, the POM production (14 and 13% of yield, respectively) and carbon balance (25 and 75%, respectively) increased.

Whatever the OTM route, it necessarily needs H atom abstraction from methane, also acid–base properties of the catalysts ought to play an important role as reported by several workers [12–14]. The study of metal additive effect on the activity of the present catalysts confirms this point (see below) as also did preliminary results of surface acidity measurements [22]. However, at high temperature, the nickel phase should be reduced in the reaction conditions and then conversion and carbon yield may be related to the reducibility of the catalysts. In such a case, the obtained orders of conversion and coking (Ni–Sm>Ni–La>Ni–Ce) may reflect to some extent the order of reducibility of the catalysts. This conclusion is in good agreement with

the standard redox potential E_0 of Sm, Ce and La oxides [21]. Further, in the used catalysts, an oxidized nickel phase has been detected by XRD and the Ni⁰ phase is also probably present; then both reduced and oxidized metal phase is needed in the OTM reaction course [4,13].

3.2.4. Influence of the nickel composition

The 5–20%Ni/Sm₂O₃ catalysts were tested at the reaction temperature of 923 K and CH₄/O₂ ratio of 2. The obtained results (Table 4) showed that the samarium supported catalysts gave interesting yield of C₂ hydrocarbons (up to 11%), important combustion selectivity (up to 52%) and low carbon balance (<10%) except for the 10%Ni composition which led to a maximum of conversion (63%) and carbon balance (22%). Nickel thus played an important role in the OTM reaction for the samarium supported catalysts. Calculations showed that this effect (Table 4) cannot be attributed only to changes in the BET surface area as a function of the nickel composition but rather to changes in the catalysts chemical surface structure. Further investigations are needed for a better understanding of the nature of these changes.

3.2.5. Influence of the metal additives

The surface composition of the 10%Ni/Sm₂O₃ catalyst was modified by Li or Ba additives (Table 5). The main result was the strong increase of the C₂ hydrocarbons selectivity in the exit gas (from 0 to 89%) for the catalyst promoted by 2% Li. It also produced CO₂ (11% of selectivity) but not CO and low level of carbon yield (7%). The conversion was diminished from 63 to 24% by the Li additive but the obtained OCM yield was substantial (15%). As to the Ba additive, it decreased the conversion of methane to a lesser extent

(from 63 to 52%) but yielded high POM selectivity to CO (67%). In the mean time, it decreased sharply carbon balance (4%).

The decrease of the conversion of methane for both metal additives should probably be due to the embedding of part of the active nickel sites [12–14]. In connection, the higher effect of the Li additive (24 against 52%) can be ascribed to a stronger interaction with the nickel active phase. The metal additives also decreased coke formation (4–7% for carbon balance) as an effect of their base properties [12–14]. On the other hand, the good yield (15%) of OCM with the Li additive is in agreement with the literature data [12]. Indeed, it is well known that, through H abstraction of methane, Li favored the production of high concentrations of methyl radicals, the intermediate precursors of the C₂ hydrocarbon products [12]. Similar behavior should hold for our catalysts, at least partly. Further, it is worth noting that the more basic Ba additive enhanced POM (32% of yield). Also, it is tempting to infer that, as far as H atom abstraction from the methane molecule is concerned, strong base properties rather favor the POM process. However, the Li or Ba additives should have induced changes but only in the nickel active phase and, consequently, changes in methane activation. Such a structural effect on the metal properties of nickel should occur at high reaction temperature as suggested above.

4. Conclusions

Our results show that several factors influence the OTM reaction course on nickel based catalysts, among them the reaction conditions, the nature of the support, the nickel composition and the presence of metal additives. The OCM route was favored by Ce and Sm supports, low nickel composition, Li additive and low reaction temperature, whereas La support, Ba additive and high reaction temperature enhanced the POM activity. These effects were attributed

to modifications of the reducibility or acid–base surface properties by changes in the surface chemical composition of the catalyst or reactive atmosphere. Further investigations (reducibility and acid–base measurements, particle size determination, etc.) are needed to assess these conclusions and for a better understanding of our results.

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