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Non-stationary catalytic cracking of methane over ceria-based catalysts: Mechanistic approach and catalyst optimization

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Abstract

The non-stationary cracking of methane over various noble metal/CeO_2-doped catalysts at 400 and 600 °C was followed by DRIFT spectroscopy and on the basis of the identified elementary steps a simplified kinetic modeling is proposed. The production of H_2 by direct decomposition of CH_4 on the noble metal is improved by the capacity of ceria to store carbonaceous surface species thanks to: (i) the spillover of carbonyls from noble metal particles towards basic hydroxyls formed on partially reduced Ce sites and (ii) the reverse spillover of ceria oxygen towards metal to oxidize the carbon issued from methane cracking. The resulting formate adspecies are in turn oxidized into carbon dioxide during the regeneration step. Doping the ceria with basic lanthanide oxides and replacing Pt by more efficient and eventually better dispersed metals for methane decomposition like Rh and Ir lead to significant improvements in the hydrogen productivity.

Keywords: Methane cracking to hydrogen; Noble metals supported on ceria, Pt, Ir, Rh; Ceria doping; Transient kinetic modeling; In situ DRIFT; Non stationary processes

1. Introduction

Within the perspective of sustainable hydrogen production for feeding fuel cells and/or generating synthetic fuels, new catalytic processes have to be designed for meeting non-stationary conditions imposed by the targeted application. For example, frequent start-up and shutdown operations have to be foreseen for any domestic stationary or on-board reformers. Non-steady-state processes can also be considered as an alternative to conventional continuous ones, being designed specifically to take advantages of transient operations. Recently, a novel process for hydrogen production with purity higher than 90% was proposed by sorption-enhanced steam methane reforming reactions in two parallel fixed bed reactors operated in a cyclic manner. First, through addition of a CO_2 sorbent into a reforming reactor, the reactions of reforming, water–gas shift and CO_2 sorption were combined, and more CH_4 was expected to convert H_2 in one reactor. Second, regeneration of the sorbent was carried out in the other reactor. The hydrogen production and sorbent regeneration processes were carried out simultaneously in the two fixed bed reactors, operated in a cyclic manner by switching a methane/steam feed and an Ar-containing feed between the two reactors at a fixed feed switchover time [1].

On a similar basis, other promising non-stationary processes were proposed years ago, like the cyclic two-step reforming which combines a step of hydrocarbon cracking into hydrogen and carbon deposits followed by a step of catalyst regeneration, as proposed in Refs. [2–4] for the case of natural gas conversion:

$$\text{step I } CH_4 \rightarrow C_{\text{deposited on catalyst}} + 2H_2$$
$$\text{step II } C_{\text{deposited on catalyst}} + O_2 \rightarrow CO_2$$

For this case, both the oxygen and the carbon storage capacity of the catalytic systems have to be considered as key factors for ensuring proper operations control. As a matter of fact, oxygen stored on the catalyst may partly oxidize the hydrogen formed during step I, but also favors the reoxidation in step II. In turn, a high capacity of C storage associated with fast dynamics appears as a prerequisite for such a transient process. In turn, the capacity to store carbon deposits during the

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cracking step is essential for avoiding a fast deactivation of the catalyst but also for allowing a fast and controlled regeneration that is not detrimental for the catalyst structure.

At variance with Ni based systems that may store carbon as carbide and graphite at high temperature (700–800 °C), supported noble metals, which operate at lower temperature, require C storage assistance from the support. For this case, a low temperature process is expected to be more efficient since the rate of adspecies diffusion on the support has to be comparable with the rate of carbon formation on metal during the cracking step.

When associated to oxygen storing materials like CeO_2 and doped CeO_2 solid solutions, noble metals were already recognized as effective catalysts for the partial oxidation of methane (POM), water gas shift (WGS) equilibration and selective oxidation of CO (SELOX) [5–7]. Their potential for being operated under transient conditions has already been successfully demonstrated in our group by considering the model catalyst Pt/CeO_2, investigated by means of in situ IR studies [8], mechanistic and kinetic modeling [4]. The exact and respective role of the metal and the support remains however a key question, which has to be answered in order to design improved materials able to meet the requirements of these relatively low temperature transient operating conditions.

As a continuation of our previous studies, this paper will first give an overview of the main findings on this model catalyst and then present new results on a series of noble metals supported on doped ceria, aiming at: (i) improving the catalysts performances and (ii) gaining a better understanding of the dynamic processes of this two-step process.

2. Experimental

2.1. Materials

High surface area ceria powder used either pure or modified by La and Pr oxides doping (210–180 m^2/g) (provided by Rhodia) were first calcined at 600 °C, then impregnated with an aqueous solution of $Me(OH)_2(NH_3)_4$ salts (Me = Pt, Rh and Ir) at various contents. Precursors were calcined at 500 °C for 8 h, reduced in a hydrogen flow at 300 °C for 15 h and then kept under inert gas (Ar) before reaction. A commercial 0.5% $Pt/\gamma Al_2O_3$ catalyst was used as reference. The composition of all ceria-based catalysts after calcination is reported in Table 1.

2.2. Catalysts characterization

The specific surface area of the samples was calculated from the N_2 adsorption–desorption at −196 °C by using the BET method, after desorption under vacuum for 3 h at 300 °C.

Noble metal dispersion was evaluated for some cases by the method of temperature-programmed reduction (TPR) over used samples. Its principle, well adapted to the case of noble metals supported on redox supports like ceria, consists in a TPD measurement carried out in the presence of hydrogen in the sweep gas [9]. Typically, the sample is first re-reduced at 400 °C in H_2 flux for 4 h, then cooled down and heated under a flux of 4 vol% H_2 in Ar from 25 to 800 °C with a ramp of 10 °C/min. By integrating the low temperature peak of hydrogen desorption (at ca. 120 °C), an evaluation of the noble metal dispersion was obtained.

2.3. Testing procedure

The reaction was carried out at 400 °C under atmospheric pressure either in fixed bed reactor (4 mm i.d.) or in an in situ DRIFT cell (SPECTRATECH, 5 mm i.d.) [4,8]. Experiments consisted in flowing alternatively 20–50% CH_4 in inert gas (during 1 min), then pure inert gas (as a flush) and finally 20% O_2 in inert gas (as long as necessary to eliminate all the reversible C stored), all mixtures with a total flow rate of 20 ml/min (STP). The gas concentration at the reactor outlet was continuously monitored by on line mass spectrometry. For the case of DRIFT experiments, infrared spectra were recorded

Table 1
Catalysts composition and performance (GHSV = 3400 h^{-1})

Me	Catalysts		Temperature (°C)	Conversion%	S_{H_2} %	Y_{H_2} %	$[CO]_{max}$ (%)	H_2 prodced (ml/min)	C storage ($\mu g\ C/g_{cat}$)
	Loading (wt.%)	Ceria doping							
Pt	0.8	Undoped	400	8.6	39.5	3.4	0.2	0.7	138
Pt	5	Undoped	400	15.6	37	5.7	0.1	1.1	nd
Pt	5	23.7% Pr_6O_{11}	400	14.2	39.8	5.6	0.2	1.2	228
Ir	0.5	10.0% La_2O_3	400	12.5	47.0	5.9	0.2	1.3	464
Ir	0.5	Undoped	400	18.9	39.2	7.4	0.2	1.6	187
Ir	0.5	23.7% Pr_6O_{11}	400	22.7	32.9	7.5	1.5	1.6	902
Rh	0.5	Undoped	400	13.7	64.6	8.8	0.3	1.9	597
Pt	5	14.5% ZrO_2	600	38.2	75.0	28.7	14.0	6.1	217
Ir	0.5	Undoped	600	36.7	81.6	29.9	8.9	6.4	235
Pt	5	Undoped	600	36.7	83.7	30.7	9.0	6.6	585
Ir	0.5	23.7% Pr_6O_{11}	600	33.6	92.9	31.2	8.7	6.7	377
Rh	0.5	Undoped	600	34.1	92.9	31.7	10.8	6.8	361
Pt	5	10.0% La_2O_3	600	32.6	97.6	31.8	9.0	6.8	461
Pt	5	23.7% Pr_6O_{11}	600	38.5	84.2	32.4	9.5	6.9	228
Ir	0.5	10.0% La_2O_3	600	36.2	94.6	34.3	9.5	7.3	414

The catalysts are listed and ranked according to increasing hydrogen yield.