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Investigation by high throughput experimentation of ceria based catalysts for H₂ purification and CO₂ reforming of CH₄.

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1. Introduction

High-Throughput Experimentation (HTE) aims at i) increasing the probability for new materials discovery, ii) increasing speed and efficiency for process development and optimisation (faster access to optimised operating conditions through the development of micro-pilot technologies), iii) improving safety and environmental aspects (reduced reactor volumes and integrated mass and heat transfer improving the overall energy balance) [1,2].

Testing and comparing different catalytic compositions belonging to a given library, the HTE strategy is generally restricted to evaluate at simplified standard conditions as rapidly as possible catalytic performances such as reaction yield towards desired products. However, this fast testing procedure may eliminate good candidates which could have been revealed under more appropriate operating conditions, or select false hits which will turn out to be inactive after longer time on stream.

Parallel reactors when operated for fast primary screening can hardly be used for solving the above mentioned issues. However, in addition to primary information upon catalysts ranking, various ways exist to capture the essence of catalysts instability, improving considerably the selection process. Indeed catalysts instability in general refers to activation/deactivation processes occurring during steady-state operations. It also relates to catalyst behaviour under transient operating conditions which may correspond to permanently unsteady processes employing moving or fluidized bed, post-combustion, reverse flow reactors, domestic applications, etc.

In addition to using parallel reactors, an elegant and efficient way to have access to catalyst instability is to perform fast kinetic measurements under transient conditions, which may indeed add a leap in the acceleration of the investigation process [3].

This paper aims at illustrating how catalyst instability can be captured by HTE in the domain of natural gas conversion and hydrogen production. The first case study deals with the discovery of new ceria based material for hydrogen purification. Here, already published data are reinvestigated by focusing on the transient measurements of OSC and the use of parallel reactor for selecting performing new materials. New perspectives on this domain of HTE investigation of adsorption phenomena like the fast measurements of CO₂ adsorption are also presented. The second case study deals with the instability of Pt/doped ceria catalysts for CO₂ reforming of methane and unpublished results of an on-going HTE investigation are presented.

2. HTE for investigating OSC of new ceria based material for hydrogen purification. Perspectives for HT investigation of adsorption phenomena

Context. Ceria-based mixed oxides (Ce_xM_{1-x}O_y) are versatile solid oxygen exchangers. At high temperatures (400–800°C) the redox cycle $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+} + e^-$ facilitates oxygen storage and release from the bulk fluorite lattice. This makes them ideal candidates for catalytic oxidation applications such as the above mentioned hydrogen purification methods [5]. However, the *surface* redox chemistry of ceria is sensitive even at low temperatures to crystal structure defects, which can be tuned by substituting some of the Ce cations with ions of different size and/or charge [6,7].

In this first case study, the effects of doping the ceria support of platinum catalysts for the close reactions of SelOx, WGS and reverse water-gas shift (RWGS) are investigated using parallel synthesis and testing reactors, aiming at discovering new materials especially under dynamic conditions (start-up and shut-down) [8].

Methodology and results. A set of 12 catalysts containing 2 wt% Pt on Ce_{0.9}M_{0.1}O_x was prepared (where M = Pb, Bi, Zr, V, W, Mo, Y, La, In, Sn, and two combinations of Zr/Bi, respectively) by impregnating platinum on various doped ceria supports. Details on this catalysts library and their characterization are given in [8]. Despite their nearly identical X-ray crystal structures, these catalysts were shown to display diverse redox/acidic/basic properties and different selectivities in the three test reactions. The best SelOx catalysts were also found to be the most active for WGS/RWGS equilibration. In addition to these conventional catalytic properties under steady-state regime, a major descriptor of these materials within the perspective of a domestic application is the oxygen storage capacity (OSC). The latter is involved during all the transient procedures of the targeted process, i.e. start-up and shut down of the hydrogen generator, according to the users needs. The OSC which controls the behaviour of the ceria based material under instable process conditions was evaluated by adapting a 16 channel parallel reactor to capture the breakthrough curves by admitting a mixture H₂/Ar = 10/90 after catalyst oxidation. OSC was

derived from the H_2 consumption of available oxygen of the ceria to form H_2O (Fig.1).

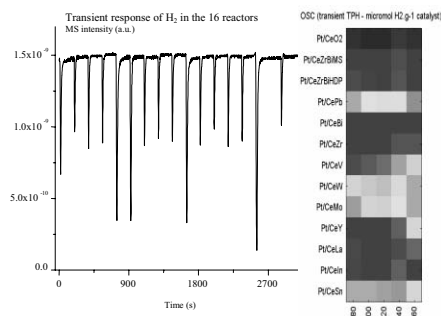


Figure 1: Evaluation of Oxygen Storage Capacity of catalysts (OSC) in transient mode for one generation of ceria based catalysts [8]

A 4.75 wt% Pt on high surface ceria catalyst was used as reference, displaying a very high OSC whatever the temperature. In contrast, 2% wt%Pt doped samples prepared for this study showed in general a lower OSC. Nevertheless, among 13 ceria additives, 4 (Pb, W, Mo and Sn) lead to increase the OSC by factors of 2 to 3 independently of the temperature. In contrast, V-doped ceria showed a continuous increase of the OSC with the temperature to attain an OSC of 120 micromols per gram of catalyst. Correlation between OSC and CO oxidation results were observed and discussed elsewhere [8].

As a general trend, it was found that the most performing samples exhibited the poorest OSC, indicating that excess of oxygen delivered by the system is quite detrimental for the selective oxidation of CO in the presence of hydrogen.

From a technical point of view, this method of transient OSC measurement at iso-temperature was proved to be efficient for assessing key features of 16 oxygen storing and oxygen conducting materials within a few hours.

Thus, by combining the information get from the HT measurements of OSC and the known effects of doping ceria with various heterovalent atoms [6], explanation of doped systems can be provided.

Perspectives for HT investigation of adsorption phenomena. Recently we extended this HTE facility to capture other types of adsorption phenomena. As such, isotherms of pure component and gas mixtures can be measured by means of parallel breakthrough curve experimentation. The capabilities of the testing units were demonstrated for the HT CO_2 adsorption on microporous materials [13]. As an example, Figure 2 presents the isotherms of CO_2 adsorption over a series of microporous materials acquired in a 16 channels parallel reactor. By using Langmuir models, the adsorption parameters were calculated. Thus, we found activation energy of 20 kJ/mol for the reference 13X zeolite in good agreement with literature data.

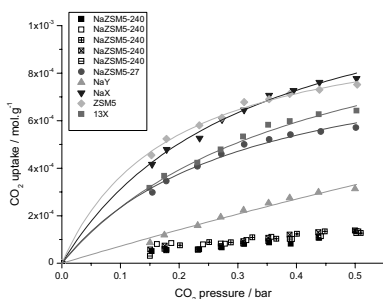


Figure 2: CO₂ adsorption isotherms at 120°C from a mixture N₂/CO₂/He on zeolites. For the sample NaZSM5-240, five replicates have been studied [13].

3. Instability of Pt/doped ceria catalysts for CO₂ reforming of methane

Context. Crude natural gas may contain, in addition to methane, light alkanes and moisture, up to 30 vol. % of carbon dioxide, and up to 50% for the case of bio-gas. In order to convert these mixtures into syngas for a Gas-To-Liquid (GTL) process without prior separation, high performance catalysts for CH₄ and higher alkanes dry reforming are required, with a high activity and selectivity towards CO and H₂. Suitable catalysts are generally achieved with most group VIII based materials, but materials require also a high stability on stream ensured by a low coke formation, as coking constitutes the main drawback of the dry reforming process [9].

Accelerating this search of performing systems, HTE was recently implemented according different strategies. Maier et al. [10] used high-throughput synthesis and primary screening techniques for discovering and optimizing new formulas of catalysts able to be self reduced by the reacting feed of methane dry reforming. Several larges libraries have been synthesized with sol-gel methods using a synthesis robot and library design software. Those catalyst libraries were screened for catalytic activity and stability at 600°C in a simple high-throughput reactor system with micro-GC analysis. From several generations of catalysts, the best performing stable systems were found to be Ni on ceria doped with Al and Zr. The interest of the work lies in the fast access to catalyst instability in HTE, where either initial activation (linked to the in situ reduction of the active phases) or deactivation processes (related to carbon deposits and/or metal sintering) are revealed. However, only further conventional studies on selected formulas permitted a better understanding of these processes [10].

Methodology and results. In our laboratory, an on going medium throughput strategy was chosen to test rapidly the aging testing sequences for long period on stream with the fast characterization of carbon deposits by sequential H₂ and O₂ TPR sequences, able to rapidly elucidate the content and variety of coke deposits. Data may then be inserted into kinetic models designed to predict

ageing processes, in view of foreseeing the state of the catalyst after virtual long term ageing experiments. A realistic ranking may thus be proposed in order to proceed towards a next generation of samples. In this paper, only results on HTE investigation of dry reforming aging are presented, the sequential H_2 and O_2 TPR measurements being kept for a full forthcoming paper.

Figures 3 and 4 illustrate how a series of Pt/ceria based catalysts tested in parallel reactors for the dry reforming of methane behaves as fresh and used systems, and the ranking which may be derived as a function of the dopant added to ceria, respectively.

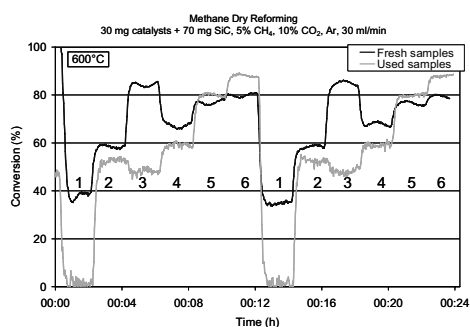


Figure 3: Time dependence of the methane dry reforming activity for a series of 6 Pt/ceria doped catalysts tested as fresh or used systems over series of 20 experimental cycles.

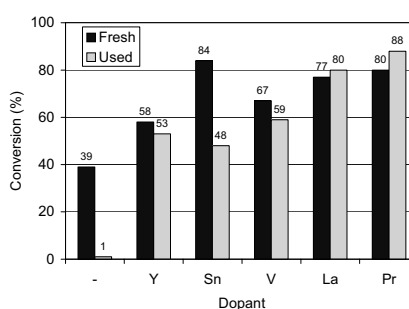


Figure 4 : Catalyst ranking according to the nature of ceria dopant and the resistance to aging.

From these data it comes that the best resistance to coking was obtained for lanthanum and praseodymium doped materials, showing even a slight improvement in activity after aging cycles, while significantly lower performances and stability were observed for Y, Sn or V doped materials.

Referring to an advanced in situ characterization of lanthana doped Ni catalysts during methane dry reforming [11], it can be assessed that the specific role of the lanthanide additives is to protect the Ni particles with a layer of carbonates from emitting encapsulating carbon. This layer was shown to be built progressively with time on stream, which accounts for the improvement of performances upon aging. These carbonates in equilibrium with gas phase CO_2 act also as a continuous source of oxygen at Ni/ceria interface for oxidizing selectively into CO the CH_x fragments arising from methane decomposition [9,11]. For the case of V doped material, an increase in support acidity resulting from a spreading of V_2O_5 over the ceria surface (as shown for the close system VMgO [12]) might explain lesser performances, since the bi-functionality ensured by surface basicity is no more operating for this case. Finally, when an

easily alloying element like Sn is added to ceria, its likely migration onto the Ni particles might lead to a poisoning of the Ni phase since Sn is inactive for methane dissociation.

4. Conclusion

Through studies related to hydrogen purification and methane dry reforming, it is shown that high or medium throughput techniques can be adapted to capture unsteady processes in heterogeneous catalysis like ageing and dynamics of oxygen storage and CO₂ adsorption. However, a compromise has to be searched between fast screening of process parameters and deep understanding of the observed phenomena. The choice of the test reactions is therefore crucial. One option, as shown here, is to test sets of diverse catalyst formulations combined with real-time performance analysis and modeling, adapted to process instability.

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