TAP study on the active oxygen species in the total oxidation of propane over a CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst

V. Balcaen[a], R. Roelant[a], H. Poelman[a], D. Poelman[b], G.B. Marin[a],*

[a] Laboratory for Chemical Technology, Department of Chemical Engineering, Ghent University, Krijgslaan 281, S5, B-9000 Ghent, Belgium
[b] Department of Solid State Sciences, Ghent University, Krijgslaan 281, S1, B-9000 Ghent, Belgium

ARTICLE INFO

ABSTRACT

The activation of propane both in the absence and presence of gas-phase O$_2$ or CO$_2$ over a CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst is investigated in a TAP reactor between 623 and 873 K. Two different types of oxygen species are involved dependent on the mixture introduced: (1) lattice oxygen from the surface and bulk of the catalyst and (2) weakly adsorbed oxygen species produced either from gas-phase O$_2$ or CO$_2$. Both types of oxygen species participate in the total oxidation of propane. If pulses of pure propane are admitted, lattice oxygen from CuO and CeO$_2$ is consumed, reducing these oxides to a certain extent. Apart from surface lattice oxygen from CuO and CeO$_2$, also bulk lattice oxygen is involved in the activation of propane, demonstrating the high O mobility within the lattice of these metal oxides. Lattice oxygen of alumina is not available for reaction with propane. Introduction of O$_2$ reoxidizes the reduced sites on CuO and CeO$_2$, as expected for a Mars–van Krevelen mechanism. Also CO$_2$ can replenish O vacancies in the active phase by dissociative adsorption on alumina and ceria. The adsorption on alumina is followed by reverse spillover of reactive O species to the active phase. The second type of oxygen consists of weakly adsorbed oxygen species, produced either from O$_2$ on both CuO and CeO$_2$, or from CO$_2$ on CeO$_2$, and enhances strongly the catalytic activity. In the presence of both O$_2$ and CO$_2$ in the propane feed, the predominant reaction pathways will only involve the two types of active species produced from O$_2$, and not from CO$_2$.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Due to environmental concerns, a major challenge is to reduce the emission levels of detrimental waste gases like volatile organic compounds (VOCs) in the atmosphere. A potential solution is to adopt the catalytic oxidation process to oxidize the VOCs, often present in rather small amounts in air, to mainly CO$_2$ and water [1]. Metal oxide catalysts are interesting candidates for the total oxidation process, because of their lower costs compared to noble metals and their higher stability. Exhibiting unique redox features, CuO–CeO$_2$/γ-Al$_2$O$_3$ is a very promising catalyst among these metal oxides [2]. A full insight in the important fingerprints of this catalyst enables to predict its performance in diverse operating conditions and, if necessary, to optimize the catalyst formulation for various applications. More specifically, the type of the active oxygen species is crucial in the activation of propane and determines the ease with which propane can be destroyed.

Although the total oxidation process is a combination of two processes, i.e. reduction of the catalyst by propane and simultaneous reoxidation of the catalyst by O$_2$ present in the feed, in this

work these two processes are decoupled by feeding propane or dioxygen separately. Hence, the interaction of these two gases with the catalyst in a certain state can be investigated. Apart from the interaction of the catalyst with the reactants, also the interaction of the products (H$_2$O and CO$_2$) can be of interest while unraveling the different important steps in the reaction mechanism. Although in literature, quite some attention has been paid to the influence of the reaction products, the exact role of CO$_2$ is still a point of discussion [3].

In this study, a Temporal Analysis of Products (TAP) reactor is applied as a unique transient tool to investigate the activation of propane in the total oxidation reaction over a CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst.

2. Experimental

The TAP reactor system developed by Gleaves et al. [4–6] is a catalyst characterization and evaluation set-up, in which a quartz micro-reactor is encased within a high vacuum chamber (10^{-4} to 10^{-5} Pa). A simplified scheme of the TAP-1 reactor system used in this work can be found in [4]. Using two high speed pulse valves, small amounts of gaseous reactants, typically 10^{14} to 10^{15} molecules/pulse, are introduced into the reactor, while

---

* Corresponding author. Tel.: +32 9 264 4516; fax: +32 9 264 4999.
E-mail address: Guy.Marin@Ugent.be (G.B. Marin).

monitoring both reactants and products at the exit of the reactor with a UTI 100C quadrupole mass spectrometer, located in the analysis chamber of the set-up. The inlet pulse size is usually limited to some 10^{14} to 10^{15} molecules, ensuring a Knudsen flow regime throughout the experiment. Indeed, for the pulse size limit mentioned, Gleaves et al. [6] reported a molecule mean free path of 4000 μm, significantly higher than the mean diameter of the interstitial voids, estimated at 300 μm for the present reactor configuration. Moreover, the validity of the Knudsen flow regime was verified experimentally by performing pulse experiments with varying pulse intensity over a bed of quartz particles with the same size as the catalytic ones. It was observed that within the range of the present experiments, the shape of the pulse responses was independent of the pulse size.

Three types of pulse experiments can be performed: single-pulse, multi-pulse and alternating pulse experiments. Single-pulse experiments are used to study the interaction of several reactants with the catalyst at a predetermined state of the latter. In contrast, multi-pulse experiments are executed to alter the state of the catalyst and are often followed by a single-pulse experiment to redefine its state. In alternating pulse experiments, two different reactants are pulsed from both pulse valves with a certain delay in between the two pulses. That way, intermediates formed on the first pulse by introduction of a pump molecule can be probed on the second pulse with a suitable probe molecule. By varying the time interval between the pump and probe molecule, the life time of the intermediates can be established. Next to pulse experiments, scan experiments are performed in order to screen the background in the vacuum chamber and thus detect possible desorption of products.

The CuO–CeO$_2$/γ-Al$_2$O$_3$ catalyst is a commercial mixed metal oxide known as highly active for total oxidation [2]. The BET surface area of the catalyst amounts to 156 m^2/g. A more detailed characterization of the catalyst is reported in Silversmit et al. [7]. The experiments are typically carried out over 50 mg of catalyst, which corresponds to 7×10^{19} O atoms based on both CuO and CeO$_2$ present in the catalyst (see Table 1). This amount is assumed to be an upper limit for the total number of exchangeable O atoms. Since a maximum inlet pulse intensity of 10^{15} molecules/pulse is applied in all experiments, the number of reactant molecules in a pulse is always 4 orders of magnitude lower than the maximum number of active sites in the reactor. If then a limited amount of pulses, typically 60, is admitted in a single-pulse experiment, the catalyst state should not significantly be altered and an average of the responses can be used to increase the signal-to-noise ratio. However, if the catalyst state is altered by the number of pulses introduced, only the first response of the single-pulse experiment is used, still presenting an acceptable signal-to-noise ratio. In multi-pulse experiments, individual responses were recorded without averaging. Next to the catalyst of interest, two other catalyst samples are tested which contain either only CeO$_2$ or only CuO. Experiments on the alumina supports have also been performed. The most important features of the samples are listed in Table 1.

The catalyst sample is placed between two beds filled with inert quartz, with a particle diameter in the range of 250–500 μm for both catalyst and quartz. The void fraction of the packing amounts to 0.53. The fresh catalyst samples are first heated to reaction temperature with a ramp of 5 K/min under vacuum, during which a background scan identifies the adsorbed species of the fresh catalyst. Subsequently, the catalyst is pretreated with multi-pulses of O$_2$ until a constant level of the oxygen response is obtained.

For the study of the total oxidation of propane, a mixture of C$_3$H$_8$/Kr + O$_2$ with an O$_2$/C$_3$H$_8$ ratio of at least 5 is applied. For the separate study of the reduction and the reoxidation of the catalyst, a C$_3$H$_8$/Kr (90/10), respectively an O$_2$/Ar (50/50) mixture is applied. A CO$_2$/Ar (50/50) mixture and a C$_3$H$_8$/Kr + CO$_2$ mixture with a CO$_2$/C$_3$H$_8$ ratio of 5 are also used as feed in order to study the interaction of CO$_2$ as total oxidation product with the catalyst. Next to CO$_2$, C^{18}O$_2$ is also employed in order to study the interaction of CO$_2$ with the catalyst. Inert gases are applied as internal standard, allowing to monitor any valve variation and/or instability and to calculate conversion and yields. The experiments are carried out at temperatures between 623 and 873 K. For the quantification of each component, the mass spectrometer is focused to a different mass, the selection of which was based on an analysis of the mass spectra of the individual components. Water was chosen to be monitored at 18, CO at 28, C$_3$H$_8$ at 29, O$_2$ at 32, Ar at 40, C$_3$H$_6$ at 41, CO$_2$ at 44, C^{16}O^{18}O at 46, C^{18}O$_2$ at 48 and Kr at 84 AMU. When there was an unavoidable interference by the fragmentation peaks of other gases, a correction was applied to remove their contributions, e.g. CO$_2$ is monitored at 44 AMU, subtracting the contribution of propane, i.e. 27–30% of the peak at 29 AMU.

3. Results and discussion

3.1. Conversion of propane in the presence and absence of O$_2$

The normalized propane responses corresponding to single-pulse experiments with pure C$_3$H$_8$ and with an O$_2$/C$_3$H$_8$ mixture over pretreated catalyst at 623 K, presented in Fig. 1, are compared with the normalized propane response over an inert quartz bed at the same temperature. The shape of the responses to pure C$_3$H$_8$ over pretreated catalyst clearly changed as more pulses were introduced. Such a change was not observed in the responses to an O$_2$/C$_3$H$_8$ mixture. Therefore, in Fig. 1, while the responses to pure C$_3$H$_8$ are simple, the responses to an O$_2$/C$_3$H$_8$ mixture represent an average of a number of replicates. Also, the responses over an inert bed represent an average. As the latter response is indicative for diffusion only, the smaller propane responses over a catalyst bed point to reaction next to diffusion. This is observed both in the presence and absence of gas-phase O$_2$, suggesting that lattice oxygen at the surface, denoted as O$_{L,s}$, is responsible for this propane conversion. However, the conversion with gas-phase O$_2$ present is higher, as shown in Fig. 2, in which the propane conversion is presented

Table 1
Most important features of the different catalyst samples and their supports investigated in this work.

Catalyst sample	BET (m^2/g)	O atoms[a] (10^{19})	Crystallite diameter (nm)		Amount (wt%)	
			CuO	CeO$_2$	CuO	CeO$_2$
CuO–CeO$_2$/γ-Al$_2$O$_3$	156	7	~100	6	12	6
CeO$_2$/γ-Al$_2$O$_3$	143	2	–	9	–	6
CuO/θ-Al$_2$O$_3$	80	5	34	–	13	–
Support						
γ-Al$_2$O$_3$	182	70–80	4		100	
θ-Al$_2$O$_3$	152	70–80	15		100	

[a] For all catalysts (50 mg), the number of O atoms is related to CuO and/or CeO$_2$ and is assumed to be an upper limit for the number of exchangeable O atoms. For the supports, the number of O atoms is related to the Al$_2$O$_3$.