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TAP study on the active oxygen species in the total oxidation of propane over a $CuO–CeO_2/\gamma-Al_2O_3$ catalyst

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ABSTRACT

The activation of propane both in the absence and presence of gas-phase O_2 or CO_2 over a $CuO–CeO_2/\gamma-Al_2O_3$ 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.

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, $CuO–CeO_2/\gamma-Al_2O_3$ 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_2O 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 $CuO–CeO_2/\gamma-Al_2O_3$ 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

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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 $CuO–CeO_2/\gamma$-Al_2O_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 $C_3H_8/Kr + O_2$ with an O_2/C_3H_8 ratio of at least 5 is applied. For the separate study of the reduction and the reoxidation of the catalyst, a C_3H_8/Kr (90/10), respectively an O_2/Ar (50/50) mixture is applied. A CO_2/Ar (50/50) mixture and a $C_3H_8/Kr + CO_2$ mixture with a CO_2/C_3H_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_3H_8 at 29, O_2 at 32, Ar at 40, C_3H_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_3H_8 and with an O_2/C_3H_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_3H_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_3H_8 mixture. Therefore, in Fig. 1, while the responses to pure C_3H_8 are simple, the responses to an O_2/C_3H_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
$CuO–CeO_2/\gamma$-Al_2O_3	156	7	~100	6	12	6
CeO_2/γ-Al_2O_3	143	2	–	9	–	6
CuO/θ-Al_2O_3	80	5	34	–	13	–
Support						
γ-Al_2O_3	182	70–80	4		100	
θ-Al_2O_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_2O_3.

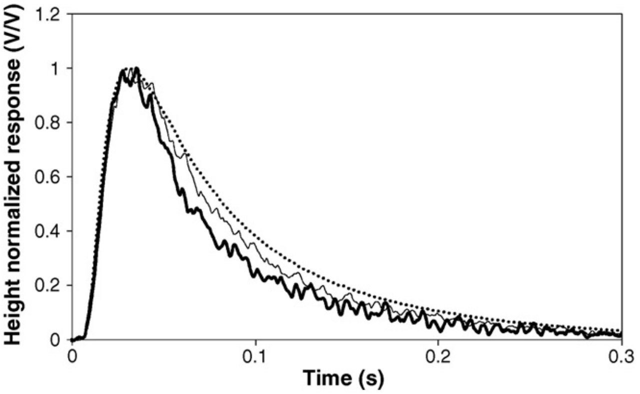

Fig. 1. Height normalized C_3H_8 responses corresponding to single-pulse experiments with pure C_3H_8 (—) and with a C_3H_8/O_2 mixture (**—**, ratio 1:5) over 50 mg pre-oxidized $CuO–CeO_2/\gamma-Al_2O_3$ catalyst at 623 K. The normalized C_3H_8 responses over catalyst are compared with the normalized C_3H_8 response over an inert bed (. . .) at the same temperature.

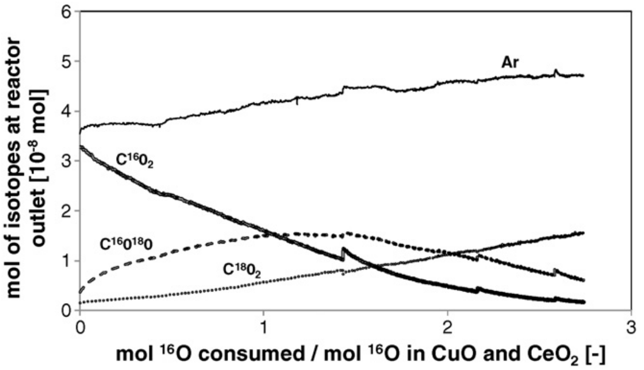

Fig. 3. Molar amount of $C^{18}O_2$ (. . .), $C^{16}O^{18}O$ (- - -) and $C^{16}O_2$ (**—**) corresponding to multi-pulse experiments with a $C^{18}O_2$/Ar mixture over 50 mg pre-oxidized $CuO–CeO_2/\gamma-Al_2O_3$ catalyst at 873 K as a function of the number of ^{16}O atoms that are consumed from the catalyst relative to the ^{16}O atoms originally present in $^{16}O_2$-pretreated CuO and CeO_2. The molar amount of Ar (—) represents the inlet amount of $C^{18}O_2$.

corresponding to several single-pulse experiments performed in a row at 623 K as a function of the ratio between the O consumption in the reaction and the O atoms originally present in CuO and CeO_2 of the pretreated catalyst. When pure propane is pulsed, the conversion amounts to 25% over the pre-oxidized catalyst and decreases rapidly as more propane is introduced into the reactor, indicating that reduction of the catalyst occurs by the consumption of lattice oxygen to form the oxidation products, suggesting a Mars–van Krevelen mechanism [8]. If O_2 is added to the feed, the propane conversion is doubled, see Fig. 2. Clearly, apart from lattice oxygen, weakly adsorbed oxygen species, denoted as O_{ads}, produced from gas-phase O_2 also participate in the activation of propane, pointing towards a combination of a Langmuir–Hinshelwood and Mars–van Krevelen mechanism. After an initial decrease, a conversion level of 30% is maintained, corresponding to the conversion of propane involving lattice oxygen, originated from the bulk of the oxides. Based on these results, it can be concluded that weakly adsorbed oxygen species are mainly produced over pre-oxidized catalyst as is also reported by Pantazidis et al. [9].

If after a treatment with pure propane, the reduced catalyst is kept inside the vacuum for a few hours without intermediate O_2 treatment, a significant increase in the propane conversion is observed, see Fig. 2. Obviously, already at 623 K lattice oxygen has the ability to diffuse from the bulk of the catalyst to the surface, where the bulk lattice oxygen species, denoted as $O_{L,b}$, can be used to convert propane. If higher temperatures are applied, the mobility of lattice oxygen is even more pronounced. This O mobility is confirmed by performing isotopic multi-pulse experiments with $C^{18}O_2$ over the $^{16}O_2$-pretreated catalyst at 873 K. Fig. 3 shows the molar amount of different isotopes detected at the reactor outlet during introduction of $C^{18}O_2$ versus the number of ^{16}O atoms that are consumed from the catalyst, related to the ^{16}O atoms originally present in CuO and CeO_2. It is clear that a large amount of $C^{16}O_2$ is produced from the very beginning of the multi-pulse experiment, indicating that the gas-phase $C^{18}O_2$ undergoes fast isotopic exchange with lattice oxygen. As more ^{16}O atoms from the lattice are consumed, the mixed isotope $C^{16}O^{18}O$ becomes the more predominant product, next to small amounts of $C^{18}O$ and $C^{16}O$ (not shown in Fig. 3). The detection of $C^{16}O_2$ and $C^{16}O^{18}O$ indicates that both simple and multiple exchange occur with the latter mechanism favored over the pretreated catalyst. Since both of the O atoms from $C^{18}O_2$ can easily be exchanged with lattice ^{16}O, these latter O atoms must have a very high mobility within the lattice of the catalyst. As oxygen exchange is still observed after all ^{16}O atoms present in CuO and CeO_2 would have been consumed, also ^{16}O from alumina must be available for exchange, implying a high mobility of these O atoms in the lattice of alumina. This is confirmed by performing multi-pulse experiments with $C^{18}O_2$ over $\gamma-Al_2O_3$ and $\theta-Al_2O_3$ at 873 K obtaining similar results as presented in Fig. 3 for the $CuO–CeO_2/\gamma-Al_2O_3$ catalyst. Martin and Duprez [10] also reported that bulk oxygen diffusion occurs on alumina from 723 K on. However, the support materials $\gamma-Al_2O_3$ and $\theta-Al_2O_3$ showed no activity for the total oxidation, demonstrating that the oxygen species in the lattice of alumina are not available for reaction, despite their high mobility. This can be understood considering that Al^{3+} ions are, in principle, not reducible.

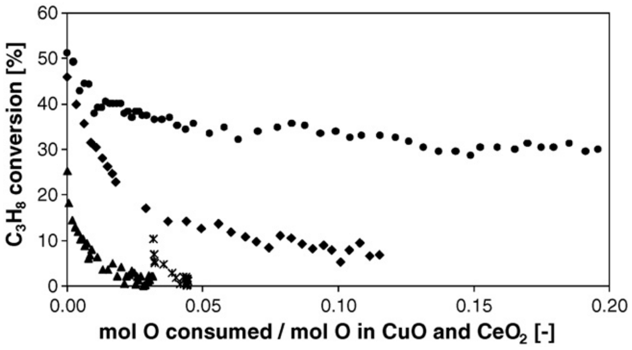

Fig. 2. Propane conversion corresponding to a series of single-pulse experiments over 50 mg pre-oxidized $CuO–CeO_2/\gamma-Al_2O_3$ catalyst at 623 K with pure C_3H_8 (▲, *), C_3H_8/O_2 (●, ratio 1:5) and C_3H_8/CO_2 (♦, ratio 1:5) as a function of the O consumption from the catalyst related to the O atoms originally present in CuO and CeO_2 of the pretreated catalyst. For the experiments with pure propane, a time interval is introduced in between the first (▲) and second (*) series of single-pulse experiments without intermediate O_2 treatment.

The total amount of reactive lattice oxygen, O_L, can be determined based on the propane consumption during multi-pulse experiments with pure propane, assuming that CO_2 and water are the only products and hence that 10 O atoms are needed to convert one propane molecule. This assumption is justified by the very low production of propene and CO as further discussed in Section 3.2. The amount of reactive lattice oxygen is expressed as a function of the maximum amount of exchangeable O atoms originally present in CuO and CeO_2 of the pretreated catalyst. At 623 K, only 5% of the O atoms present in CuO and CeO_2 are easily accessible for interaction with propane; this increases to 15% at 673 K and reaches 50% at 873 K.

3.2. Product formation

The negligible amounts of propene and CO detected at the reactor outlet at all temperatures indicate that total oxidation prevails over partial oxidation, both in the presence and absence of gas-phase O_2. Water cannot be observed as a pulse on the time scale of a single-pulse experiment, but it can be detected as an increase of the 18 AMU signal due to a continuous slow desorption. This water desorption is clearly observed in scan experiments at all temperatures used in this work. Although it is expected, based on the amount of hydroxyl groups on alumina reported by Peri et al. [11,12] at 923 K, i.e. $1.5\ \mathrm{nm}^{-2}$, that hydroxyl groups will be present on the surface of the catalyst, and more specifically on the alumina support at the investigated conditions, the results of the single-pulse experiments are reproducible and thus not significantly influenced by this presence. Moreover, during these single-pulse experiments the HO-coverage is not significantly altered, by limiting the number of admitted reactant molecules related to the number of active sites in the reactor (see Section 2).

The major product detected at the outlet of the reactor is CO_2, whatever be the active species. This implies that both adsorbed and lattice oxygen are non-selective, promoting total oxidation in contrast to the belief of many authors that lattice oxygen accounts for selective oxidation [1]. Moreover, this also demonstrates that only one type of reversibly adsorbed oxygen and one type of lattice oxygen is present on the $CuO–CeO_2/\gamma\text{-}Al_2O_3$ catalyst. The detection of CO_2 is only pronounced at higher temperatures, leading to an unclosed carbon balance at lower temperatures. This suggests a very strong interaction of CO_2 with the catalyst as is demonstrated by very broad CO_2 responses at lower temperatures during single-pulse experiments with pure propane. Even the presence of O_2 in the feed does not improve the desorption of CO_2. Despite this strong adsorption, no long-term loss of activity is observed as several reduction–reoxidation cycles can be performed with stable propane conversion.

3.3. Addition of CO_2 to the feed

Because of the strong CO_2 adsorption on the catalyst, a possible inhibiting effect is to be expected if CO_2 is added to the propane feed. However, Fig. 2 demonstrates that the presence of CO_2 enhances the catalytic activity, especially over the pre-oxidized sample. As more O atoms from the catalyst are consumed, the propane conversion decreases but to a lesser extent compared to when pure propane is introduced. Apparently, the catalyst is able to activate CO_2 and produce O species that participate in the total oxidation reaction. As the conversion level over pre-oxidized sample in the presence of CO_2 is identical to the level in the presence of O_2, it is assumed that like O_2, CO_2 produces both types of oxygen, i.e. very reactive weakly adsorbed species and lattice oxygen species. The activation of CO_2 implies the dissociation to CO and O, although CO was not accurately detected during the single-pulse experiments with the CO_2/C_3H_8 mixture, because of mass overlapping between C_3H_8, CO_2 and CO. However, during multi-pulse experiments with CO_2 after partial reduction of the catalyst with C_3H_8, this CO production is indeed observed. Moreover, during the isotopic exchange experiments with $C^{18}O_2$, the detection of the mixed isotope $C^{16}O^{18}O$ confirms the dissociative adsorption of CO_2 on the catalyst. Although CO_2 is mostly considered as an inert in oxidation reactions, some authors are also convinced of the oxidizing power of CO_2. Dury et al. [13] reported on the active role of CO_2 in oxidation processes in which CO_2 can be added to the feed as promoter, enabling to control the oxidation state of the catalyst and thus the catalytic performance. It is even suggested that CO_2 more efficiently oxidizes the catalyst compared to O_2. This is in contradiction with the observation shown in Fig. 2, where O_2 remains the stronger oxidant as the conversion profile for O_2/C_3H_8 is situated above the profile for CO_2/C_3H_8. Moreover, it is expected that in the presence of both O_2 and CO_2 in the propane feed, the former will mainly provide the oxygen species for activation of propane, diminishing the oxidizing role of CO_2.

3.4. Life time of active oxygen species

As described in the previous sections, two types of oxygen species are present on the $CuO–CeO_2/\gamma\text{-}Al_2O_3$ catalyst: lattice oxygen next to weakly adsorbed oxygen species produced from gas-phase O_2 or CO_2. In order to investigate the life time of the weakly bound oxygen species, alternating pulse experiments are performed in which O_2 is pulsed first, followed by a propane pulse with varying time interval. Fig. 4a shows the outlet flow rates corresponding to an alternating pulse experiment at 723 K, in which a delay of 0.5 s is applied between the oxygen and the propane pulse. Only the first response of the alternating pulse experiment is used for all gases. Clearly, CO_2 is only formed upon the propane pulse, indicating that the catalyst surface does not contain carbon species that can be removed by O_2. In Fig. 4b, the propane conversion at three temperatures corresponding to several alternating pulse experiments with variable time interval are presented. For the lower temperatures (623–673 K), it is obvious that the conversion is higher if the time interval between the oxygen and the propane pulse is equal to or less than 10 ms, indicating that weakly bound oxygen species with a life time $\leq$10 ms are present. The level of propane conversion for a time interval that exceeds 10 ms, corresponds to the level obtained during interaction of pure propane with surface lattice oxygen. At 723 K, the influence of these species can no longer be observed in this kind of experiment because of their even shorter life time at this temperature. As these weakly adsorbed species have such short life time, they

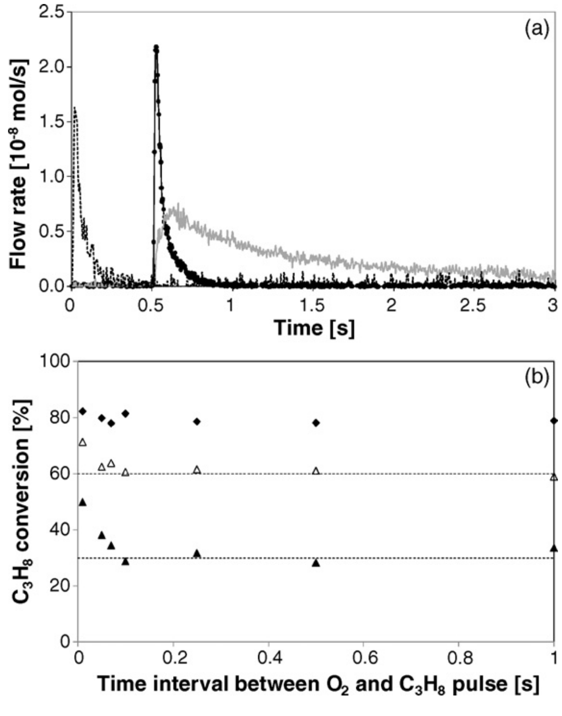

Fig. 4. (a) Outlet flow rates of O_2 (- - -), C_3H_8 (-●-) and CO_2 (—) corresponding to an oxygen/propane alternating pulse experiment over 50 mg pre-oxidized $CuO–CeO_2/\gamma\text{-}Al_2O_3$ at 723 K. The time interval between the oxygen and the propane pulse amounts to 0.5 s. (b) Propane conversion at 623 K (▲), 673 K (△) and 723 K (◆) corresponding to seven oxygen/propane alternating pulse experiments over 50 mg pre-oxidized $CuO–CeO_2/\gamma\text{-}Al_2O_3$ catalyst. The time interval between the oxygen and the propane pulse is respectively 0.01, 0.05, 0.07, 0.1, 0.25, 0.5 and 1 s.

will only contribute to a higher catalytic activity if O_2 is present in the feed.

In the reaction with propane, the surface O atoms will first be consumed, after which O atoms will be provided from the bulk. Important here is to investigate how fast the bulk atoms can diffuse to the surface replenishing it with O atoms, assuming that surface diffusion is considerably faster than oxygen bulk diffusion, as also reported by Martin and Duprez [10]. This is examined by performing single-pulse experiments with pure propane at 623 K using different pulse frequencies. If 1 pulse is introduced per 2.2 s, an increased propane conversion is observed compared to when 1 pulse is introduced every 1.2 s. This indicates that on the time scale of 1 s, lattice oxygen atoms are able to diffuse from the bulk to the surface enhancing the activity. An attempt was made to estimate an average displacement of oxygen atoms in the catalyst lattice, $\bar{x}$, after a given time, t, of 1 s and the corresponding diffusion coefficient, D, using the Einstein relation:

$$\bar{x} = (Dt)^{1/2} \quad (1)$$

Sedmak et al. [14] reported a diffusion coefficient of oxygen species in a bulk $Cu_{0.1}Ce_{0.9}O_{2-y}$ crystallite lattice at 623 K of $10^{-15}\,m^2\,s^{-1}$. Calculation of the corresponding average displacement of oxygen atoms, $\bar{x}$, during 1 s gives 30 nm. Previously reported XRD characterization of $CuO–CeO_2/\gamma\text{-}Al_2O_3$ showed separate CuO and CeO_2 phases [7]. The respective particle diameters are presented in Table 1. Given these values, participation of oxygen atoms of the smaller CeO_2 particles in the redox process on a time scale of 1 s is certainly realistic, but also participation of the O atoms of the larger CuO particles is possible, though not from the core part of the particle. Trovarelli et al. [15] reported much lower diffusion coefficients for ceria and ceria–zirconia crystallites and concluded that the time scale of bulk diffusion on ceria was too high to be of importance. The results reported in this work for the $CuO–CeO_2/\gamma\text{-}Al_2O_3$ catalyst, which are in line with the results from Sedmak et al. [14], clearly demonstrate that the combination of CuO and CeO_2, even though in separate phases, increases the O mobility within the lattice of these oxides. However, the rate of reduction by propane at 623 K must still be quite higher than the rate of surface reoxidation via lattice oxygen migration from the bulk, as indicated by the continuous decrease in activity for both pulse frequencies. If bulk diffusion of O atoms remains the slower step in the mechanism, oxygen vacancies are expected to be replenished through adsorption of gas-phase O_2 under realistic conditions, i.e. if a mixture of propane and O_2 is applied as feed in the total oxidation process. This has been reported by Perez-Ramirez and Kondratenko [16] for the ammonia oxidation over different metal oxides (Fe_2O_3, Cr_2O_3 and CeO_2).

Apart from diffusion throughout the lattice, also desorption of O_2 from the pre-oxidized catalyst is established by performing several O_2 multi-pulse experiments in a row. If in between two subsequent multi-pulses, a time interval of a few minutes is introduced, an increased oxygen consumption was observed at the start of the second multi-pulse experiment, confirming the O_2 desorption during that time interval. This indicates that the oxidized state of the catalyst is not stable, easily releasing its oxygen atoms from the lattice, which is a desired property for a total oxidation catalyst [1].

3.5. Role of the three oxide phases

Pulse experiments with pure propane were performed not only on the catalyst of interest, i.e. the $CuO–CeO_2/\gamma\text{-}Al_2O_3$, but also on $CeO_2/\gamma\text{-}Al_2O_3$ and $CuO/\theta\text{-}Al_2O_3$, see Table 1. At all investigated temperatures, the three samples show significant activity towards the total oxidation reaction introducing pure propane. This indicates that not only the combination of CuO and CeO_2 phases, but also pure CuO and CeO_2 contain active surface lattice O species. Moreover, on all samples the participation of bulk lattice oxygen species is observed by an increased propane conversion after leaving a catalyst, having been exposed to propane, inside the vacuum for a few hours without intermediate O_2 treatment. As mentioned in Section 3.1, the support materials are not active for the total oxidation. Pure propane will thus consume lattice O species present in CuO and CeO_2, creating oxygen vacancies in these metal oxides. These vacancies are replenished either by adsorption of gas-phase O_2, via surface diffusion of oxygen adsorbed on CuO and CeO_2, or via diffusion of oxygen from the bulk lattice. The formation of weakly adsorbed oxygen species is also attributed to the interaction of O_2 with CuO and CeO_2, and not with alumina. It is thus clear that both propane and O_2 adsorb on CuO and CeO_2, which constitute the active phase in the catalyst. In literature, it is often stated that ceria is added to increase metal dispersion, thermal stability or oxygen mobility within a catalyst lattice. In the $CuO–CeO_2/\gamma\text{-}Al_2O_3$ catalyst, the presence of ceria enhances the redox behavior of the copper ions by showing a more stable activity compared to $CuO/\theta\text{-}Al_2O_3$ during single-pulse experiments with pure propane at 623 K. The promoting effect of ceria on copper oxide catalysts supported on alumina in the total oxidation of CO has also been reported by Park and Ledford [17].

As discussed in Section 3.2, CO_2 as product is irreversibly adsorbed on the catalyst during single-pulse experiments in the absence and presence of O_2, but does not block any active sites as no activity decay is observed during reduction–reoxidation cycles. Moreover, in oxygen/propane alternating pulse experiments no CO_2 is desorbed upon the oxygen pulse, despite the very long tail of the former, as demonstrated in Fig. 4a. This indicates that O_2 is adsorbed on other sites than CO_2 is desorbing from. Hence, it is suggested that CO_2, originally produced from propane on CuO and CeO_2 will migrate to the support, i.e. spillover, from which it will partially desorb. This leads to the observed broad CO_2 responses during propane single-pulse experiments in the absence and presence of O_2, especially at the lower temperatures, and to the unclosed carbon balance. The strong adsorption of CO_2 on alumina is confirmed by performing multi-pulse experiments with $C^{18}O_2$ during which not only exchange between gas-phase $C^{18}O_2$ and lattice ^{16}O was observed (see Section 3.1), but also irreversible adsorption of $C^{18}O_2$ occurred as indicated by an unclosed carbon balance during these experiments. Morterra et al. [18] also considered the CO_2 adsorption on transition aluminas, to which both $\gamma\text{-}Al_2O_3$ and $\theta\text{-}Al_2O_3$ belong, and suggested that the interaction is a consequence of the acid–base properties of CO_2 and alumina.

If CO_2 is added to the propane feed, the activity of $CuO–CeO_2/\gamma\text{-}Al_2O_3$ is increased, as described in Section 3.3. The oxidizing effect of CO_2 is also observed on $CeO_2/\gamma\text{-}Al_2O_3$ but not on $CuO/\theta\text{-}Al_2O_3$, indicating that ceria is necessary for the catalyst in order to effectively use the O atoms produced from CO_2. Strong CO_2 adsorption on alumina together with the ability of alumina to dissociatively adsorb $C^{18}O_2$, points to the possible activation of CO_2 to CO and O species on alumina. These species will then be transported to an active phase in the catalyst, in casu only CeO_2, by reverse spillover. The participation of the alumina support in a reaction has been reported by Wang et al. [19] who observed that water adsorbed on the support acted as an oxygen source in the partial oxidation of methane on Rh/Al_2O_3. However, some authors also report that ceria plays an important role in the activating process of CO_2. Demoulin et al. [3] stated that on ceria–zirconia supported catalysts the Ce^{3+} sites would be responsible for this CO_2 activation. Indeed, it is possible that CO_2 is activated on ceria, especially since the oxidizing role of CO_2 is only observed if ceria is present in the sample. Ceria would then be producing weakly adsorbed oxygen species on one hand,

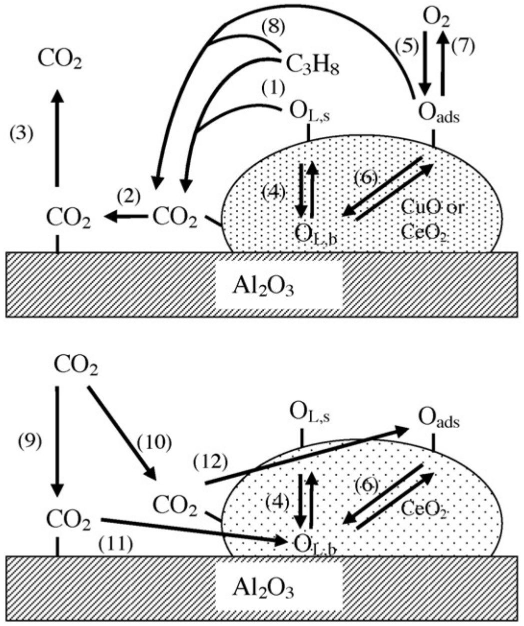

Fig. 5. (a) Schematic representation of the steps in the oxidation of propane over a $CuO–CeO_2/\gamma-Al_2O_3$ catalyst, both in the absence and presence of gas-phase O_2. (b) Schematic representation of the steps in the dissociative adsorption and activation of CO_2 on Al_2O_3 and CeO_2 in a $CuO–CeO_2/\gamma-Al_2O_3$ catalyst.

which are not observed on alumina, and lattice oxygen species on the other hand.

Based on the above analysis, a schematic representation of all the important steps in the oxidation of propane is given in Fig. 5a and b. Fig. 5a presents the steps that are important if propane is introduced both in the absence, steps (1)–(4), as well as in the presence of gas-phase O_2, steps (1)–(8). All steps are identical for both CuO and CeO_2. If instead of O_2, CO_2 is added to the propane feed, the steps involving dissociative adsorption and activation on Al_2O_3 and CeO_2 are presented in Fig. 5b. If both O_2 and CO_2 are added to the propane feed, mostly the steps (1)–(8) presented in Fig. 5a will be occurring.

1. Oxidation of propane by surface lattice oxygen species, $O_{L,s}$ to CO_2.
2. Spillover of CO_2 from CuO and CeO_2 to alumina.
3. Desorption of CO_2 from alumina.
4. Diffusion of bulk lattice oxygen, $O_{L,b}$ to the surface.
5. Production of O_{ads} species by dissociative adsorption of gas-phase O_2.
6. Replenishment of $O_{L,b}$ species from O_{ads} species.
7. Associative desorption of O_{ads} species.
8. Oxidation of propane by weakly adsorbed oxygen species, O_{ads} to CO_2.
9. Dissociative adsorption of CO_2 on alumina.
10. Dissociative adsorption of CO_2 on CeO_2.
11. Reverse spillover of active O species to CeO_2, replenishing $O_{L,b}$ species.
12. Replenishment of active O_{ads} species.

4. Conclusions

Over a $CuO–CeO_2/\gamma-Al_2O_3$ catalyst, propane is activated by two types of active oxygen species dependent on the type of feed. If pure propane is introduced, lattice oxygen from the surface and the bulk is consumed to convert propane to CO_2 and water. The latter oxygen species have a high mobility, allowing to restore at least partially the activity of a catalyst having been exposed to propane. Weakly adsorbed species are formed if O_2 is added to the propane feed, enhancing the catalytic activity. As these species have a life time shorter than 10 ms, their influence will disappear if reduction, by feeding pure propane, and reoxidation, by feeding pure O_2, are decoupled. Apart from weakly adsorbed oxygen species, gas-phase O_2 also produces oxygen species to replenish consumed lattice O. Adding CO_2 rather than O_2 to the propane feed also increases the catalytic activity by producing lattice as well as weakly adsorbed oxygen species. If O_2 and CO_2 are both added to the propane feed, the oxidizing role of CO_2 will be less important as most active species will originate from O_2.

Propane is activated on both CuO and CeO_2 which contain the two types of active O species in the catalyst. The presence of ceria in the catalyst enhances the redox behavior of the copper ions. After consumption of these O species, they can be replenished by gas-phase O_2 adsorbing on the reduced sites on CuO and CeO_2. CO_2 produced on CuO and CeO_2 will spillover from the active phase to the support, from which it will partially desorb. Although the alumina support does not contain active lattice O species nor produces weakly adsorbed O species upon introduction of O_2, it does participate in the total oxidation reaction of propane by CO_2 via the dissociative adsorption of the latter, which acts as an oxygen source. Next to alumina, also ceria plays a key role in the activation of CO_2. Hence, two different routes in this activation are proposed: or the alumina support itself activates CO_2, producing active O species, which can only be used effectively if ceria is present in the catalyst, or it is ceria itself that activates CO_2. In any case, a complex interaction between the active phase of the catalyst and the support is observed consisting of spillover of species from the active phase to the support or vice versa, depending on the reaction conditions.

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