

## PAPER

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13, 1059Gas-phase oxidative dehydrogenation of long  
chain alkenols for the production of key fragrance  
ingredients: from Rosalva isomers to Costenal  
analogues†Jacopo De Maron,<sup>a</sup> Tommaso Tabanelli,<sup>a</sup> Francesca Ospitali,<sup>a</sup>  
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The continuous-flow, gas-phase oxidative dehydrogenation (ODH) of an actual mixture of decen-1-ol isomers ("Isorosolva" alcohol) towards the corresponding mixture of aldehydes ("Costenal" analogues, valuable ingredients in perfumes formulation) is herein reported for the first time over noble metal-free catalysts. In particular, the optimisation of the reaction conditions over a copper ferrite (Cu/Fe/O), as well as dedicated characterizations and comparisons between the fresh, the post-reaction (reduced) and regenerated (re-oxidised) catalytic material, allowed us to underline the key role of well dispersed copper oxide over a Fe-enriched spinel in promoting the selective ODH of Isorosolva alcohol. The superior catalytic activity and selectivity of CuO/γ-Fe<sub>2</sub>O<sub>3</sub> synthesized *ad hoc* were attributed to the very high dispersion of Cu over the support as well as to a cooperative effect between Cu and Fe species in promoting the redox cycle.

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## Introduction

The selective oxidation of complex alcohols (*e.g.*, aromatic, branched or unsaturated fatty alcohols) to the corresponding aldehydes is a fundamental step in the preparation of a wide variety of fragrance ingredients and food additives.<sup>1</sup> Unsaturated fatty aldehydes such as neral, geranial, citronellal and decenal, to cite a few, are among the most important ingredients in perfumery and are used, individually or in combination, in the formulation of most perfume types.<sup>2</sup> Traditionally, the oxidation of fatty alcohols to the corresponding aldehydes has been carried out in high yield using stoichiometric amounts of oxidants such as pyridinium chlorochromate, activated MnO<sub>2</sub>, 2-iodobenzoic acid, the Dess–Martin periodinane or the Swern reagent.<sup>3</sup> Unfortunately, all of these methods present safety/toxicity issues, produce large amounts of waste and have significant scale-up issues; on top of that, their sustainability is further

reduced because apart from Swern-type oxidations that are carried out in dimethyl sulfoxide, the preferred solvent for all the other methods is dichloromethane.

Owing to these limitations of stoichiometric oxidants, significant efforts have been made in the past years to develop the aerobic oxidation of saturated/unsaturated fatty alcohols in the liquid phase: as a result, several homogeneous catalytic systems based on complexes or salts of Cu,<sup>4–6</sup> Ru,<sup>7–12</sup> Pd,<sup>13–15</sup> Au,<sup>16</sup> Fe<sup>17,18</sup> and Co<sup>19</sup> were reported to be active and selective under mild reaction conditions for the oxidation of model substrates such as 1-octanol, 1-decanol, citronellol and geraniol to the corresponding aldehydes. Still, the scale up of these processes remains difficult due to the cost of noble metals, the difficult catalyst recovery and recycle on an industrial scale, the use of non-green solvents (with the only exception of *ref.* 9) and the need for organic co-catalysts (*e.g.* DBAB,<sup>4</sup> TEMPO derivatives,<sup>5,6,10,17–19</sup> hydroquinone,<sup>7</sup> and amines<sup>13–15</sup>). These issues prompted the research towards the development of heterogeneous catalysts containing the same active elements immobilized onto a suitable support: the aerobic oxidation of saturated/unsaturated fatty alcohols has been carried out successfully over a number of supported catalysts based on platinum (Pt and Pt/Bi supported onto Al<sub>2</sub>O<sub>3</sub> and active carbon),<sup>20</sup> on palladium (Pd supported onto hydrotalcite,<sup>21</sup> mesocellular silica foam (MCF),<sup>22</sup> γ-Al<sub>2</sub>O<sub>3</sub> (*ref.* 23) and MgO (*ref.* 24)), on ruthenium (Ru supported onto hydroxyapatite<sup>25</sup> and γ-Al<sub>2</sub>O<sub>3</sub> (*ref.* 26 and 27) or immobilized

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† Electronic supplementary information (ESI) available: Detailed experimental information of catalyst characterisation, namely NH<sub>3</sub> and CO<sub>2</sub>-TPD, TPR, XRD, SEM-EDS and TEM analyses. Additional catalytic tests as well as the reactor scheme and blank runs are also reported. See DOI: <https://doi.org/10.1039/d2cy01836e>

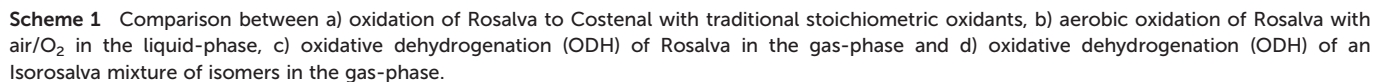
On the other hand, a gas-phase process can be easily carried out continuously and, with catalyst separation being unnecessary, work up operations are extremely simplified. As an example, light alcohols may be converted into the corresponding aldehydes by means of gas-phase dehydrogenation (DH) with a catalyst such as  $\text{MgO}$ ,<sup>39</sup> mixed oxides of Mg and transition metals possessing redox properties ( $\text{Fe}$ ,<sup>40</sup>  $\text{Cr}$ <sup>41</sup> or  $\text{Ga}$ <sup>42,43</sup>), or V-containing oxides<sup>44</sup> such as  $\text{FeVO}_4$  and  $\text{V}_2\text{O}_5$ , to cite a few. Meanwhile, the literature dealing with the gas-phase DH of fatty alcohols is less investigated and focused on the transformation of model substrates such as octanol<sup>45</sup> and decanol.<sup>46</sup> However, DH processes are endothermic and suffer from several limitations, such as the relatively high reaction temperature required to promote dehydrogenations, the presence of a thermodynamic equilibrium that limits the conversion of the substrate and the occurrence of parasitic reactions such as dehydrations<sup>47</sup> and oligomerisations, the latter often leading to catalyst deactivation due to coke formation. Another drawback of DH processes depends on the reaction mechanism, involving the dissociation of the alcohol into a proton ( $\text{H}^+$ ) and an alkoxide anion ( $\text{RO}^-$ ) on the catalyst surface, followed by a hydride ( $\text{H}^-$ ) transfer from the alkoxide anion to the vicinal proton. In fact, since the hydride can be transferred also to another reactive hydrogen acceptor such as a  $\text{C}=\text{C}$  double bond, DH catalysts foster to a certain extent also the so-called catalytic transfer hydrogenation (CHT).<sup>48,49</sup> For this reason, DH is less suited than ODH for the preparation of unsaturated fatty aldehydes. The oxidative dehydrogenation (ODH) of light alcohols in the gas-phase over a catalyst consisting of bulk or supported  $\text{Ag}$ ,<sup>50</sup>  $\text{Fe-Mo}$  mixed oxides,<sup>51</sup>  $\text{FeVO}_4$  and  $\text{V}_2\text{O}_5$  (ref. 44 and 52) is a well-established technology and represents the prevailing method to produce on a large-scale formaldehyde from methanol<sup>53</sup> and, to a lower degree, acetaldehyde from ethanol.<sup>54</sup> However, the applicability of gas-phase ODH is not limited to light alcohols: in fact, the BASF citral process (which involves the ODH of prenol to prenal over  $\text{Au}$ ,  $\text{Ag}$  or  $\text{Cu}$  as a key intermediate step<sup>55</sup>) represents a successful application of ODH to the industrial-scale preparation of a valuable unsaturated fatty aldehyde. The co-feeding of a limited

amount of oxygen, with respect to DH processes, allows the reaction temperature to be lowered by promoting the oxidation of the co-produced hydrogen to water *via* a concerted mechanism, eventually shifting the thermodynamic equilibrium towards the product side. However, despite the potential of gas-phase ODH, this reaction remains very challenging, because of the high reactivity of fatty alcohols and aldehydes at the relatively high temperatures required by their vaporization and reaction. As a consequence, the academic literature available on this topic is narrower than that about liquid-phase oxidations, and deals mostly exclusively with octanol (as a model substrate) and catalytic systems based on either gold (Au/SiO<sub>2</sub>,<sup>56</sup> Au–Ni alloy/SiO<sub>2</sub>,<sup>57</sup> Au/Cu-fibres<sup>58,59</sup> and Au/Ni fibres<sup>60</sup>) or silver (bulk Ag,<sup>61</sup> Ag supported over a zeolite coated Cu grid,<sup>62</sup> Ag/silicon nanowire arrays<sup>63</sup> and Ag–Cu/SiC<sup>64</sup>).

Among fatty aldehydes, the isomers of decenal are notable ingredients in the formulation of perfumes and other personal care products, not only as single isomers (*i.e.*, dec-9-enal, commercial name “Costenal”)<sup>65</sup> but also as a combination of isomers: as an example, mixtures of dec-6-enal, dec-7-enal and dec-8-enal with well-defined compositions were patented as novel ingredients by International Flavors & Fragrances Inc.<sup>66</sup> Despite their relevance, very few catalytic processes have been proposed as alternatives to the traditional oxidation of dec-9-en-1-ol (commercially known as “Rosalba”) with stoichiometric reactants such as pyridinium chlorochromate,<sup>67</sup> Dess–Martin periodinanes,<sup>68</sup> activated  $\text{MnO}_2$ ,<sup>69</sup>  $\text{K}_2\text{S}_2\text{O}_8/\text{NiSO}_4$  in the presence of a base<sup>70</sup> or oxalyl dichloride, DMSO and alkyl amines in Swern-type oxidations),<sup>71</sup> which are not sustainable for large-scale production. To the best of our knowledge, the liquid-phase aerobic oxidation of pure Rosalba to Costenal has been reported only twice: with air and a homogeneous tetrapropylammonium perruthenate catalyst,<sup>12</sup> and with pure  $\text{O}_2$  and a heterogeneous Ru–Co oxide catalyst.<sup>34</sup>

Similarly, also the gas-phase ODH of Rosalva to Costenal was reported only twice, by Gallezot *et al.*<sup>65</sup> over a 4.5% Ag/SiC catalyst charged into a traditional fixed bed reactor and by Cao *et al.*<sup>72</sup> with an Ag/SiO<sub>2</sub> catalyst deposited onto a continuous-flow microreactor. Considering that a pure Rosalva alcohol can be easily isomerised into a selected mixture of its isomers,<sup>66</sup> in this study an actual mixture of decen-1-ols (“Isorosalva” alcohols), produced and supplied by International Flavors & Fragrances Inc., was used as the starting material for the continuous-flow, gas-phase ODH aimed at the production of the corresponding mixture of aldehydes (“Opalene” aldehydes), directly exploitable in fragrance formulation. Moreover, herein we report for the first time this peculiar ODH reaction promoted by a cheap, noble metal-free, non-stoichiometric Cu-ferrite catalyst with a Fe-to-Cu ratio equal to 4 (Cu<sub>0.6</sub>Fe<sub>2.4</sub>O<sub>4.2</sub>) and by a supported copper oxide catalyst (6 wt% CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). The comparison between our synthetic strategy and the alternatives reported in the literature is depicted in Scheme 1. In particular, dedicated catalytic tests showed that our catalyst performs





The XRD powder patterns of all the catalysts were collected using a Bragg–Brentano Philips X’Pert diffractometer and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å, Ni-filtered). The average size of the coherently scattering domain (CSD) of materials was calculated applying the Scherrer equation (eqn (1)):

traps in series: the former was filled with 15 mL of acetonitrile (AcCN, Sigma-Aldrich, 99.8%) and kept at room temperature to absorb the condensable products; the latter was filled with glass spheres and kept at 0 °C by means of an ice bath to condensate the AcCN stripped from the first trap. At regular intervals of time, the reaction mixture was transferred from the first cold trap to a 50 mL flask, together with the AcCN needed to wash the lower portion of the reactor below the catalytic bed and to rinse the cold trap 3 times. Finally, 1 g of dodecane (Sigma-Aldrich, 99%) solution ( $4 \times 10^{-5}$  mol g<sup>-1</sup>) was added as the internal standard. All catalytic tests were carried out for the time required to obtain at least 5 samples (5–6 h) to be analysed by means of GC-FID; the mean values of conversion and selectivities were calculated once steady-state conditions were achieved, usually during the last 3 h of time on stream. The gas mixture exiting the cold traps were driven to an Agilent 8860 GC instrument equipped with an FID and TCD. The quantification of the condensable products was carried out offline with an Agilent HP-5 capillary column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m) connected to the FID. The quantification of the gaseous products (O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>) was carried out online with a set of two parallel columns combining an Agilent CP-Molsieve 5 Å capillary column and an Agilent CP-PoraBOND Q capillary column (“Agilent J&W Select Permanent Gases/CO<sub>2</sub>”) connected to the TCD. An Agilent Technologies 6890 gas chromatograph equipped with an Agilent HP-5 capillary column (30 m  $\times$  250  $\mu$ m  $\times$  1.05  $\mu$ m) and coupled to an Agilent Technologies 5973 mass analyser (GC-MS) was used to identify unknown products; also, the retention times of unknown products were compared to those of purchased standard reference compounds. The following equations were used to calculate Isorosalva Alcohol conversion ( $X_{IRA}$ , eqn (2)), yields ( $Y_i$ , eqn (3)), selectivities ( $S_i$ , eqn (4)), sum of yields (Yield Sum, eqn (5)), and carbon balance (C-balance, eqn (6)). All these parameters were calculated in terms of moles of carbon.

The liquid reactant “Isorosalsa Alcohol” (IRA, mixture of isomers of decen-1-ol provided by Iff) was injected with a KD Scientific Legacy 100 volumetric pump into a thin stainless-steel line (1/16 inches of diameter) and directly driven  $\approx 5$  cm above the catalytic bed with 10 mL min<sup>-1</sup> N<sub>2</sub>. A second flux of pre-heated (250 °C) air diluted with N<sub>2</sub> was driven to the top of the reactor to obtain the desired molar fraction of O<sub>2</sub> and the desired total flux. Usually, the catalyst was flowed with the same air/N<sub>2</sub> mixture to be used during the catalytic test and heated up to reaction temperature at 20 °C min<sup>-1</sup>; the final temperature was kept for 30 min before starting to feed the liquid reactant. The effluent from the reactor was bubbled through two cold

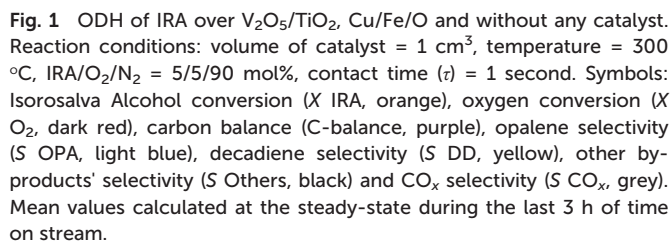
$$\text{C-balance} = (\text{Yield Sum})/(\text{X IRA}) \times 100 \quad (6)$$

The main physico-chemical features of the catalysts are listed in Table 1. CuO/SiO<sub>2</sub> possessed the highest specific surface area (455 m<sup>2</sup> g<sup>-1</sup>) among the materials investigated, followed by the Cu/Fe/O mixed oxide (165 m<sup>2</sup> g<sup>-1</sup>), V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (22 m<sup>2</sup> g<sup>-1</sup>), CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (9 m<sup>2</sup> g<sup>-1</sup>) and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (9 m<sup>2</sup> g<sup>-1</sup>). Apart

|                                                 | SSA <sup>a</sup> [m <sup>2</sup> g <sup>-1</sup> ] | CSD size <sup>b</sup> [nm]                                     | Element or oxide content <sup>c,d</sup> [wt%] |
|-------------------------------------------------|----------------------------------------------------|----------------------------------------------------------------|-----------------------------------------------|
| V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> | 22                                                 | 125 (V <sub>2</sub> O <sub>5</sub> )<br>58 (TiO <sub>2</sub> ) | V <sub>2</sub> O <sub>5</sub> = 6.2 (6)       |
| Cu/Fe/O                                         | 165                                                | 5 (Cu-ferrite)                                                 | Cu = 14.3 (16)<br>Fe = 57.4 (56)              |
| CuO/SiO <sub>2</sub>                            | 455                                                | 35 (CuO)                                                       | CuO = 6.9 (6.1)                               |
| CuO/ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>   | 9                                                  | 81 ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> )                | CuO = 4.8 (6.1)                               |
| $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>        | 9                                                  | 78 ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> )                | —                                             |

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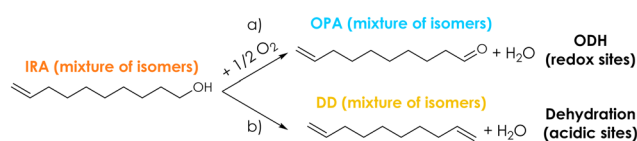
Initially, the ODH of IRA was carried out over Cu/Fe/O,  $V_2O_5/TiO_2$  and without a catalyst (for comparison) at 300 °C temperature,  $\tau = 1$  s and with a feed mixture IRA/O<sub>2</sub>/N<sub>2</sub> = 5/5/90; under these conditions, the O<sub>2</sub> in the feed was two-fold the amount required by the stoichiometry of the desired reaction. The results of these catalytic tests are reported as a bar chart in Fig. 1 in terms of conversion of IRA ( $X_{IRA}$ ), selectivities to products ( $S$ ), and carbon balance (C-balance); these parameters were calculated in terms of moles of carbon. The conversion of IRA at 300 °C was negligible without a catalyst, therefore the occurrence of homogeneous reactions under these conditions can be ruled out. As expected,  $V_2O_5/TiO_2$  was relatively active in the ODH of IRA: the conversion under these conditions was 34% and O<sub>2</sub> was consumed entirely. OPA was the main product in the reaction mixture with a selectivity of 32%, followed by several isomers of decadiene ( $S_{DD} = 20\%$ ) and carbon oxides ( $S_{CO_x} = 18\%$ ),



with CO<sub>2</sub> being largely predominant with respect to CO). Decadienes are likely to be formed by the dehydration of IRA over acidic sites,<sup>78</sup> as shown in Scheme 2 (reaction b), while carbon oxides are formed by the complete combustion of the reactant or products. Apart from CO and CO<sub>2</sub>, all the products found in the reaction mixture contained 10 C atoms; therefore, the occurrence of the oxidative cleavage of C=C double bonds<sup>79</sup> was ruled out. When IRA was fed over Cu/Fe/O, its conversion (23%) was lower than the one obtained over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> under the same conditions, but the two materials displayed a similar activity for the ODH, because the OPA yields with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and Cu/Fe/O were 11% and 12%, respectively. The superior selectivity of Cu/Fe/O to the desired products (*S* OPA = 51%) arose from its negligible activity for the unwanted dehydration of IRA to DD. Similarly, with Cu/Fe/O also the selectivity to CO<sub>x</sub> was higher than that obtained with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>.

To better understand the structure–activity relationship governing the reaction scheme, the two catalysts were further characterized by means of  $\text{NH}_3$ - and  $\text{CO}_2$ -TPD to compare their acid–base surface features, and by means of TPR with  $\text{H}_2$  to compare their reducibility. The  $\text{NH}_3$ - and  $\text{CO}_2$ -TPD profiles for Cu/Fe/O are shown in Fig. S12a and b† respectively, while those for  $\text{V}_2\text{O}_5/\text{TiO}_2$  are reported in Fig. S13a and b† respectively. Also, the density of weak, medium-strength and strong acidic and basic sites measured by deconvolution of the experimental desorption profiles is reported in Table 2 for both materials. Cu/Fe/O was amphoteric and possessed a higher overall density of acidic sites ( $0.98 \mu\text{mol m}^{-2}$  of  $\text{NH}_3$ ) than basic sites ( $0.66 \mu\text{mol m}^{-2}$  of  $\text{CO}_2$ ). However, the acidic sites of Cu/Fe/O were of medium-strength (two desorption events centred at 223 and 303 °C), while the distribution of basic sites was more complex and several types of sites were shown (four desorption events centred at 117, 242, 310 and 440 °C).

$\text{V}_2\text{O}_5/\text{TiO}_2$  was amphoteric as well, but it possessed an overall density of both acidic and basic sites higher compared to  $\text{Cu}/\text{Fe}/\text{O}$  ( $3.6 \mu\text{mol m}^{-2}$  of  $\text{NH}_3$  and  $3.0 \mu\text{mol m}^{-2}$  of  $\text{CO}_2$ ). In conclusion, the stronger acidity, in terms of both density and desorption temperature, of  $\text{V}_2\text{O}_5/\text{TiO}_2$  is likely to be responsible for the unwanted dehydration of IRA to DD. The redox properties of  $\text{Cu}/\text{Fe}/\text{O}$  and  $\text{V}_2\text{O}_5/\text{TiO}_2$  were characterized by means of TPR with  $\text{H}_2$  and their reduction profiles as well as a detailed discussion can be found in Chapter S2 and Fig. S14 in the ESI.† The ODH of IRA was further investigated using the  $\text{Cu}/\text{Fe}/\text{O}$  catalyst with the aim to increase the yield of OPA. Two catalytic tests were carried out by increasing either the reaction



**Scheme 2** Proposed reaction pathways for a) the desired ODH of IRA towards OPA and b) the parallel parasitic dehydration of IRA towards a mixture of decadiene (DD) isomers.

**Table 2** Distribution of weak, medium-strength and strong acidic and basic sites on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and Cu/Fe/O measured by means of ammonia and carbon dioxide temperature programmed desorption

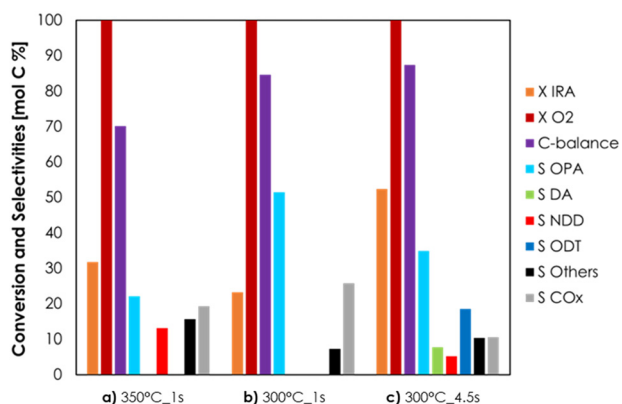
|                                                 | Acidity [ $\mu\text{mol m}^{-2}$ of desorbed NH <sub>3</sub> ] |                     |                     |       | Basicity [ $\mu\text{mol m}^{-2}$ of desorbed CO <sub>2</sub> ] |                     |                     |       |
|-------------------------------------------------|----------------------------------------------------------------|---------------------|---------------------|-------|-----------------------------------------------------------------|---------------------|---------------------|-------|
|                                                 | Weak <sup>a</sup>                                              | Medium <sup>b</sup> | Strong <sup>c</sup> | Total | Weak <sup>a</sup>                                               | Medium <sup>b</sup> | Strong <sup>c</sup> | Total |
| V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> | 0                                                              | 3.6                 | 0                   | 3.6   | 0.13                                                            | 3.0                 | 0                   | 3.13  |
| Cu/Fe/O                                         | 0                                                              | 0.98                | 0                   | 0.98  | 0.29                                                            | 0.17                | 0.2                 | 0.66  |

<sup>a</sup> Desorption below 200 °C. <sup>b</sup> Desorption between 200 and 350 °C. <sup>c</sup> Desorption above 350 °C.

temperature, from 300 to 350 °C (Fig. 2a), or the contact time from 1 to 4.5 s (Fig. 2c) and the results were compared to those of the catalytic tests carried out at 300 °C and  $\tau = 1$  s (Fig. 2b). The increase of temperature from 300 °C to 350 °C, while maintaining a contact time of 1 s (Fig. 2a), led to only a moderate increase of IRA conversion (from 23% to 32%). At the same time, OPA selectivity shrank from 51% to 22% because it was consumed by consecutive reactions, such as the formation of 10-nonadecadienones (NDD, red bars,  $S = 13\%$ ) and other unknown by-products (black bars,  $S = 16\%$ ). Also, the carbon balance decreased from 85% at 300 °C down to 70% at 350 °C, suggesting the occurrence of other unwanted reactions (*e.g.*, homogeneous reactions, coking and fouling). The increase of the contact time from 1 s to 4.5 s at 300 °C (Fig. 2c) led to a more significant increment of IRA conversion (from 23% to 52%) but also in this case OPA underwent consecutive reactions that decreased its selectivity from 51% down to 35% and led to the formation of decenoic acids (DA, green bars  $S = 8\%$ ) and 10-dodecatrienals (ODT, blue bars,  $S = 19\%$ ). Remarkably, increasing the contact time did not negatively affect the carbon balance, suggesting that some unwanted reactions (*e.g.*, gas-phase homogeneous reactions, coking and fouling) were

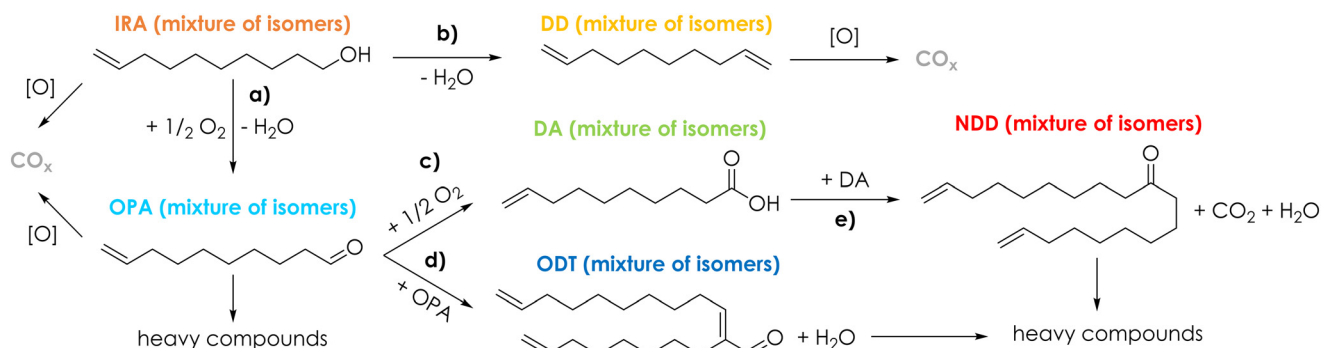
fostered mainly by high temperatures, in agreement with the results of the blank runs at 350 °C (Fig. S10 and S11†). Summarising this new information, a more detailed reaction scheme is shown in Scheme 3. The presence of DA among the reaction products was explained by the consecutive oxidation of OPA (Scheme 3, reaction c), which was fostered by harsher reaction conditions. Then, the resulting DA underwent a ketonization reaction<sup>80</sup> forming the symmetric C<sub>19</sub> ketone NDD (Scheme 3, reaction e); in agreement with previous results<sup>43,80</sup> the ketonization was particularly favoured at 350 °C and DA were quantitatively transformed into NDD. Finally, the C<sub>20</sub> aldehyde ODT was formed by the aldol condensation of OPA with itself (Scheme 3, reaction d), which was fostered by an increase of the contact time (*e.g.*, 4.5 seconds). Considering the stoichiometry of the selective ODH of IRA to OPA (Scheme 3, reaction a), the O<sub>2</sub> fed into the system was always two-fold the one required for the complete conversion of IRA. However, O<sub>2</sub> was always quantitatively consumed under all conditions reported in Fig. 2, because it was unselectively converted to overoxidation products (*i.e.*, CO<sub>2</sub>). Results reported in Fig. 2 showed that an increase of the contact time was the most effective way to improve IRA conversion without fostering its overoxidation to CO<sub>x</sub>. Therefore, we decided to investigate in more depth the behaviour of the Cu/Fe/O catalyst under these conditions (*e.g.*, 300 °C of temperature,  $\tau = 1$  s, feed mixture IRA/O<sub>2</sub>/N<sub>2</sub> = 5/5/90 mol%) as a function of time on stream; the results are shown in Fig. 3. During the first hour of reaction, the Cu-ferrite was extremely active, and the conversion of IRA was complete, but the C-balance was lower than 20% and CO<sub>x</sub> were almost the sole products of the reaction. Then, starting from the second hour on stream, the selectivity to condensable products and the C-balance increased, and stabilized after 3 h on stream. At the same time, the conversion of IRA decreased steadily down to half of its initial value during 5 h on stream.

Therefore, we decided to stop the feeding of IRA and regenerate the catalyst *in situ* by feeding 50 mL min<sup>-1</sup> of air diluted with 10 mL min<sup>-1</sup> N<sub>2</sub> at 400 °C for 3 h. Then, the feeding of IRA was resumed and, surprisingly, a completely different product distribution was obtained: in fact, OPA became the main product of the reaction over the regenerated Cu/Fe/O ( $S_{\text{OPA}} = 70\%$ ,  $X_{\text{IRA}} = 45\%$ , values calculated as the average value between the 7th and the 16th hour on stream). At the same time, the obtained C-balance was excellent, and the selectivity to the consecutive products NDD and ODT, which were produced in significant amounts over the fresh Cu/Fe/O, dropped from 18 down to 3% and



**Fig. 2** ODH of IRA over Cu/Fe/O as a function of reaction temperature and contact time. Reaction conditions: volume of catalyst = 1 cm<sup>3</sup> ( $\tau = 1$  second) or 3 cm<sup>3</sup> ( $\tau = 4.5$  second), IRA/O<sub>2</sub>/N<sub>2</sub> = 5/5/90 mol%. Symbols: Isosorval Alcohol conversion (X IRA, orange), oxygen conversion (X O<sub>2</sub>, dark red) carbon balance (C-balance, purple), opalene selectivity (S OPA, light blue), decenoic acid selectivity (S DA, green), 10-nonadecadienone selectivity (S NDD, red), 2-octyldecatrienal selectivity (S ODT, blue), other by-products' selectivity (S Others, black) and CO<sub>x</sub> selectivity (S CO<sub>x</sub>, grey). Mean values calculated at the steady-state during the last 3 h of time on stream.





**Scheme 3** Proposed complete reaction scheme: a) ODH of IRA towards OPA; b) parallel parasitic dehydration of IRA towards DD; c) overoxidation of OPA towards DA; d) aldol condensation of OPA to ODT; e) ketonization of DA to NDD; other reactions include the formation of heavy compounds on the catalyst surface and the total oxidation to  $\text{CO}_x$ .

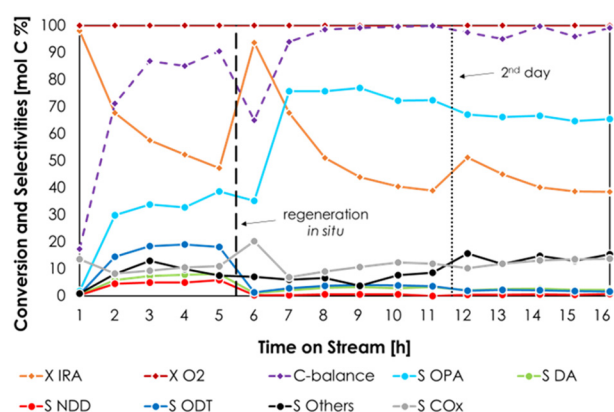
from 5 to 0%, respectively. Finally, the regenerated Cu/Fe/O catalyst maintained a stable catalytic performance for 10 h. Interestingly, during the very first hour of reaction  $\text{CO}_2$  was the major product over both the fresh and the freshly regenerated Cu/Fe/O catalyst. The outcome of the catalytic test reported in Fig. 3 indicated that the regeneration *in situ* after the first run played a key role in improving the catalyst selectivity to OPA.

### Characterization of Cu/Fe/O after reaction and after regeneration

The redox mechanism of ODH postulates that, as a consequence of the reduction of a metal cation (e.g.,  $\text{Cu}^{2+}$  or  $\text{Fe}^{3+}$  in the case of Cu/Fe/O) by the organic reactant, the formation of the co-produced water occurs at the expense of the lattice oxygen of the metal oxide. Then, the catalytic cycle

is closed by the reoxidation of the reduced metal by the molecular  $\text{O}_2$  in the gaseous feed. Considering that under all the reaction conditions investigated so far, the conversion of  $\text{O}_2$  was quantitative, it is likely that the reoxidation of the catalyst was limited by the complete consumption of  $\text{O}_2$  in the feed, resulting in a catalyst that under reaction conditions was presumably strongly reduced. Upon the ODH of IRA followed by *in situ* regeneration, the fresh Cu/Fe/O underwent a transformation that significantly enhanced its selectivity to the desired product OPA. Therefore, a small portion of the catalyst employed in the experiment shown in Fig. 3 was withdrawn from the reactor before and after the *in situ* regeneration; then, these materials were thoroughly characterized. Samples were labelled as follows: Cu/Fe/O-F (fresh), Cu/Fe/O-AR (after reaction) and Cu/Fe/O-R (regenerated).

The XRD powder patterns of Cu/Fe/O-F, Cu/Fe/O-AR and Cu/Fe/O-R are shown in Fig. 4a and b. The diffractogram of Cu/Fe/O-AR (Fig. 4a, red) was characterized by the pattern of a spinel phase as it was for Cu/Fe/O-F, plus three peaks attributable to metallic Cu centred at 43, 50 and 74  $2\theta$  degrees. Therefore, Cu/Fe/O was reduced during the ODH of IRA leading to the segregation of metallic Cu over a Fe-enriched spinel. The formation of the latter was confirmed by the small shift towards lower  $2\theta$  angles of the reflections of the spinel phase (Fig. 4b). Moreover, the reflections attributable to the Fe-enriched spinel-phase were sharper than the ones of Cu/Fe/O-F, indicating that the crystallinity of the catalysts increased during the ODH of IRA; hence, the CSD size of the spinel calculated by the Scherrer equation (eqn (1)) increased from 5 nm to 10 nm and the SSA dropped from  $165 \text{ m}^2 \text{ g}^{-1}$  to  $63 \text{ m}^2 \text{ g}^{-1}$ . In the diffractogram of Cu/Fe/O-R (Fig. 4a, light blue) the reflections of metallic Cu disappeared leaving only a spinel phase, plus a few small reflections attributable to hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ); no reflections attributable to CuO or  $\text{Cu}_2\text{O}$  were found. The XRD characterization suggested that upon regeneration all metallic Cu was oxidised to Cu(II) and re-incorporated into the spinel structure of the catalyst, as demonstrated by the shift of the reflections of the spinel phase of Cu/Fe/O-R with



**Fig. 3** ODH of IRA over Cu/Fe/O as a function of the time on stream. Reaction conditions: volume of catalyst =  $1 \text{ cm}^3$ , temperature =  $300^\circ\text{C}$ ,  $\text{IRA}/\text{O}_2/\text{N}_2 = 5/5/90 \text{ mol}\%$ , contact time ( $\tau$ ) = 4.5 seconds. Symbols: Isosorvala Alcohol conversion (X IRA, orange), oxygen conversion (X  $\text{O}_2$ , dark red) carbon balance (C-balance, purple), opalene selectivity (S OPA, light blue), decenoic acid selectivity (S DA, yellow), 10-nonadecadienone selectivity (S NDD, red), 2-octyldodecatrional selectivity (S ODT, blue), other by-products' selectivity (S Others, black) and  $\text{CO}_x$  selectivity (S  $\text{CO}_x$ , grey).



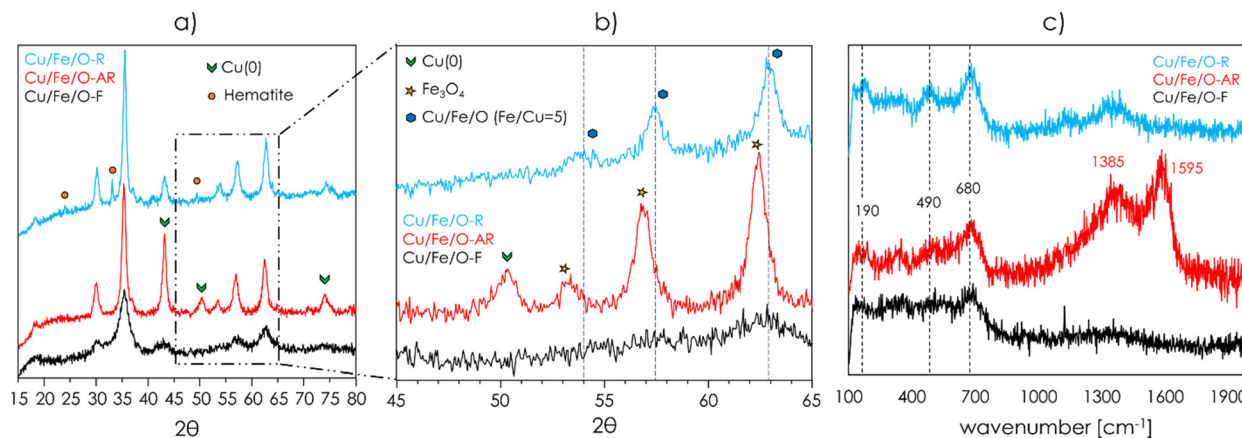


Fig. 4 a) and b) XRD powder patterns of Cu/Fe/O-F (fresh, black), Cu/Fe/O-AR (after reaction, red) and Cu/Fe/O-R (regenerated, light blue); c) Raman spectra (excitation source Ar<sup>+</sup> laser, 514.5 nm) of Cu/Fe/O-F (fresh, black), Cu/Fe/O-AR (after reaction, red) and Cu/Fe/O-R (regenerated, light blue).

respect to Cu/Fe/O-AR (Fig. 4b). However, a partial segregation of very small, well-dispersed, nanoparticles of CuO could not be excluded yet. Also, upon *in situ* regeneration a small fraction of the Fe-enriched spinel was oxidised to hematite and its crystallinity increased further (spinel CSD size = 15 nm, SSA = 55 m<sup>2</sup> g<sup>-1</sup>).

As mentioned previously, the reduction of Cu/Fe/O-F was investigated by means of TPR with H<sub>2</sub>. The reduction profile (Fig. S14<sup>†</sup>) showed that the material was reduced in the same temperature range at which the ODH of isorosalva alcohol took place (*e.g.*, maximum of desorption centred at 295 °C). Moreover, the H<sub>2</sub> uptake (19.9 mL; 96 mL g<sup>-1</sup>) calculated from the integrated area of the TPR profiles up to 450 °C corresponded to the amount required to obtain metallic Cu(0) and Fe<sub>3</sub>O<sub>4</sub>, in agreement with the outcome of the XRD characterization carried out over Cu/Fe/O-AR shown in Fig. 4a.

The Raman spectra of Cu/Fe/O-F, Cu/Fe/O-AR and Cu/Fe/O-R are reported in Fig. 4c. The spectrum of Cu/Fe/O-F was characterized by broad and poorly defined bands, with the most intense being centred at 680 cm<sup>-1</sup> and corresponding to the A<sub>1g</sub> vibrational mode of ferrite spinels.<sup>81</sup> The spectra of Cu/Fe/O-AR and Cu/Fe/O-R were more defined, owing to their higher crystallinity, and displayed also two bands centred at 490 cm<sup>-1</sup> and 190 cm<sup>-1</sup>, corresponding to the vibrational modes F<sub>2g</sub>(2) and F<sub>2g</sub>(1) respectively, in agreement with the results of Shebanova *et al.*<sup>81</sup> The presence of two strong

bands centred at 1385 and 1595 cm<sup>-1</sup> in the Raman spectrum of Cu/Fe/O-AR confirmed that during the ODH of IRA a certain amount of coke was formed over the catalyst surface, as suggested by the low C-balance obtained during the first 6 h of the catalytic tests shown in Fig. 3. The segregation of metallic Cu nanoparticles was clearly observed when high resolution TEM imaging was carried out over Cu/Fe/O-AR (Fig. 5), because the denser Cu appeared black or dark grey with respect to the light grey Fe-enriched spinel. Cu(0) segregated forming nanoparticles with a broad size distribution, ranging from a few nanometres to around 50 nm; the bigger nanoparticles were responsible for the diffraction peaks attributable to Cu(0) in the diffractogram of Cu/Fe/O-AR shown in Fig. 4a. An EDS microanalysis (shown in Fig. S15<sup>†</sup>) demonstrated that the black/dark grey nanoparticles contained mainly Cu (up to 78 atomic%), while the light grey nanoparticles were enriched in Fe (Fe/Cu atomic ratio = 12.9). The Fe-enriched spinel particles in Cu/Fe/O-AR maintained the quasi-spherical morphology of the parent Cu/Fe/O-F (see Fig. S8<sup>†</sup>) but their diameter increased from 5 to around 10 nm, in agreement with CSD sizes calculated from XRD. The high-resolution TEM characterization of Cu/Fe/O-R showed that after the *in situ* regeneration some nanoparticles were still present, suggesting that a fraction of the segregated Cu(0) in the parent Cu/Fe/O-AR was oxidised to CuO without being re-incorporated in the spinel structure of Cu/Fe/O. These

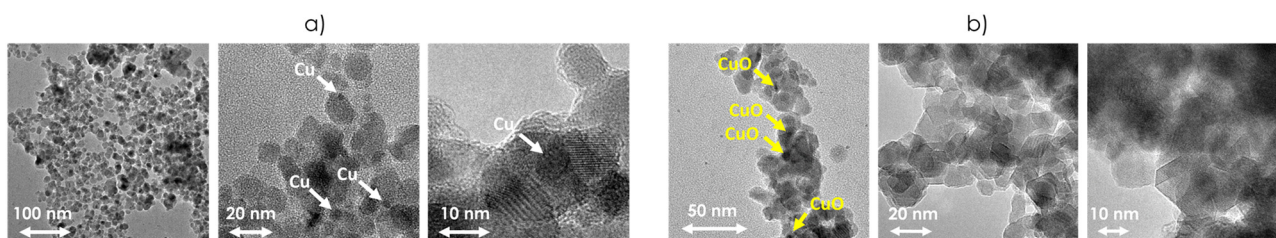


Fig. 5 High resolution TEM electron images of a) Cu/Fe/O-AR and b) Cu/Fe/O-R.



nanoparticles of CuO were too small to be detected by means of XRD. Moreover, the light grey spinel particles became more crystalline, their average diameter increased further, and their quasi-spherical shape was lost in favour of a cubic morphology.

### ODH of Isosorval Alcohol over Cu-supported catalysts

The results reported in the previous section suggest that the Cu-ferrite can be considered a precursor of the real catalyst, which was made of small CuO nanoparticles supported over a Fe/Cu spinel, with the latter being formed upon a cycle of reactions followed by *in situ* regeneration. Starting from this hypothesis, a catalyst consisting of CuO supported over maghemite (CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, 6 wt% of CuO) was prepared and its catalytic activity was compared to those of fresh Cu/Fe/O and two other materials containing only Fe (pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and only Cu (CuO/SiO<sub>2</sub>, 6 wt% of CuO). The results of a catalyst screening carried out at 300 °C,  $\tau$  = 1 s and with a feed consisting of IRA/O<sub>2</sub>/N<sub>2</sub> = 5/5/90 mol% are reported in Fig. 6.

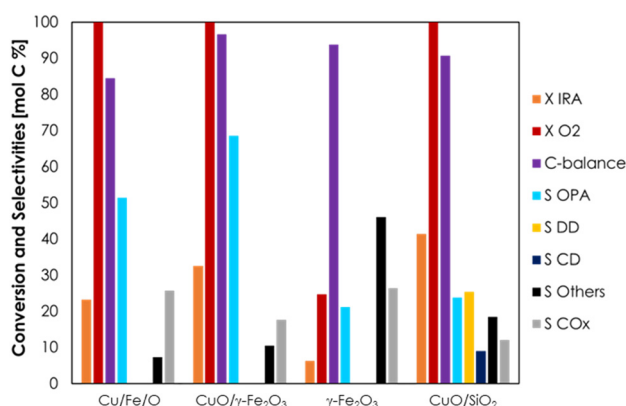
The activity of iron oxide alone ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) in the ODH of IRA to OPA was very low because the catalyst underwent a fast deactivation, leading to a negligible IRA conversion after only 4 h on stream, as shown in Fig. S16.† Its lack of activity has been attributed to the absence of Cu, meaning that its presence is crucial for the ODH reaction. The material containing only copper (CuO/SiO<sub>2</sub>) performed poorly as well, displaying unsatisfactory activity and poor selectivity to OPA (*S* OPA = 24%, lower than that obtained with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>). Moreover, this catalyst fostered the dehydration of IRA to DD (*S* = 25%) and its consecutive cyclization to alkylated cyclic alkenes with 10 carbon atoms (CD, *S* = 9%) such as butyl-cyclohexene and pentyl-cyclopentene, as shown in Scheme S1

(ESI†). On the other hand, a remarkable cooperative effect between Cu and Fe occurred in the case of CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which displayed enhanced activity and improved selectivity with respect to both  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and CuO/SiO<sub>2</sub>. This material also outperformed Cu/Fe/O: in fact, when Cu was supported over maghemite (CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), the conversion of IRA was 33% (compared to 23 for the Cu/Fe/O catalyst), while OPA selectivity was 69% (compared to 51 for Cu/Fe/O); at the same time, the selectivity to CO<sub>x</sub> decreased from 26 to 18% and the selectivity to other unknown compounds remained almost the same compared to Cu/Fe/O. Remarkably, this material was selective to OPA from the very beginning of the reaction, without the need for any “activation” procedure (Fig. S17†).

The synergistic effect between Cu and Fe observed for CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can be ascribed to the extremely high dispersion of Cu over the surface of maghemite as suggested by the TEM and EDS characterization (Fig. S9†). In fact, maghemite seemed to be capable of strongly bonding and stabilizing highly dispersed CuO-species (*e.g.*, small clusters or overlayers) or even incorporating Cu(II) into its lattice, possibly thanks to its surface defects and cationic vacancies.<sup>82</sup> As a consequence, both the conversion and the selectivity to OPA were improved, thanks to the formation of isolated active sites. A similar behaviour was observed for the regenerated, fully oxidized Cu/Fe/O-R catalyst, which was characterized by the presence of small nanoparticles of CuO dispersed over its surface, as shown by TEM characterization (Fig. 5b). However, this material displayed a transient activity with very high selectivity to total oxidation products during the first hour of reaction after regeneration (Fig. 3), which then dropped favouring the formation of OPA already during the second hour of reaction. In the literature it has been pointed out that in order to achieve high selectivity in partial oxidations with copper-based catalysts, CuO must be reduced to a certain extent in order to form isolated surface domains with a limited number of active lattice oxygen atoms, in agreement with the “site isolation” principle.<sup>83</sup> In line with this concept, some industrially relevant partial oxidations are carried out with catalysts containing Cu(0)<sup>55</sup> or Cu(I).<sup>84</sup> On the other hand, supported Cu(II)O is well known as a very active and selective catalyst for the total oxidation of methane<sup>85</sup> and VOCs (*e.g.*, toluene<sup>86</sup>), and high activities have been correlated with increasingly high dispersion of CuO on the support by several authors.<sup>85,86</sup> Hence, it is likely that the aforementioned change of selectivity of Cu/Fe/O-R from CO<sub>2</sub> (total oxidation) to OPA (selective partial oxidation, ODH) was due to the partial reduction of CuO nanoparticles to Cu(0). Although a similar behaviour might also be expected for CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, it was not observed in the test reported in Fig. S17,† probably due to the higher dispersion of CuO-species and the lower Cu-loading (5 wt% expressed as metal) with respect to Cu/Fe/O (14.3 wt%).

### Characterization of Cu-supported catalysts after reaction

A comparison between the XRD patterns before and after the ODH of IRA for CuO/SiO<sub>2</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is reported in Fig. S18–S20,† respectively. The diffractogram of



**Fig. 6** ODH of IRA over Cu/Fe/O, CuO/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and CuO/SiO<sub>2</sub>. Reaction conditions: volume of catalyst = 1 cm<sup>3</sup>, temperature = 300 °C, IRA/O<sub>2</sub>/N<sub>2</sub> = 5/5/90 mol%, contact time ( $\tau$ ) = 1 second. Symbols: Isosorval Alcohol conversion (X IRA, orange), oxygen conversion (X O<sub>2</sub>, dark red) carbon balance (C-balance, purple), opalene selectivity (S OPA, light blue), decadiene selectivity (S DD, yellow), cyclic decene selectivity (S CD, dark blue), other by-products' selectivity (S Others, black) and CO<sub>x</sub> selectivity (S CO<sub>x</sub>, grey). Mean values calculated at the steady-state during the last 3 h of time on stream.





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