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Lead-containing solid "oxygen reservoirs" for selective hydrogen combustion

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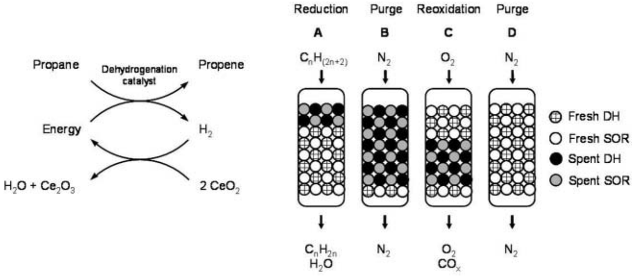
Lead-containing catalysts can be applied as solid "oxygen reservoirs" in a novel process for propane oxidative dehydrogenation. The catalyst lattice oxygen selectively burns hydrogen from the dehydrogenation mixture at 550 °C. This shifts the dehydrogenation equilibrium to the desired products side and can generate heat, aiding the endothermic dehydrogenation reaction. We compared the activity, selectivity and stability of three types of lead-containing solid oxygen reservoirs: alumina-supported lead oxide, lead-doped ceria, and lead chromate ($PbCrO_4$). The first is active and selective, but not stable: part of the lead evaporates during the redox cycling. Stability studies of a biphasic material, consisting of doped ceria with a separate PbO phase, show that the PbO phase is not stabilised by the ceria. Evaporation of lead and segregation of lead from the doped ceria occurs during prolonged redox cycling (125 redox cycles at 550 °C, 73 h on stream). The activity of this catalyst does increase over time, which may be related to the segregation of lead. Segregation of lead into a separate phase also occurs when starting from lead-doped ceria ($Ce_{0.92}Pb_{0.08}O_2$). The activity of this catalyst, however, does not increase with time on stream. Lead chromate ($PbCrO_4$) shows the highest selectivity (~100%) and activity (2.8 mol O kg^{-1}) of all solid oxygen reservoirs tested (doped cerias, perovskites, and supported metal oxides). The activity is comparable to the theoretical maximum activity of CeO_2 (2.9 mol O kg^{-1}). This activity does drop, however, during the first 60 redox cycles, to about 25% of the starting value, but this is still higher than the best results reported for doped cerias.

Introduction

The industrial demand for small alkenes is high. Worldwide propene demand, for example, is expected to top 80 million tonnes in 2010.[1–3] The main routes to propene are steam cracking, fluid catalytic cracking, and catalytic dehydrogenation.[4] All these processes are endothermic. Advantageous on-demand production of alkenes is achieved by catalytic dehydrogenation, but the process is equilibrium limited and suffers from catalyst deactivation due to coking.[5–7] Oxidative dehydrogenation (ODH), where oxygen or an oxygen-containing molecule such as N_2O or CO_2 is added to the gas feed, can overcome these limitations, allowing exothermic, non equilibrium limited, and on-demand production of the alkenes.[7–11] However, the mixing of hydrocarbons and gaseous oxygen at elevated temperatures is potentially hazardous and limits selectivity.[7,12] These drawbacks can be met by using a redox process, where the dehydrogenation is combined with selective hydrogen combustion.[5,13–18] The dehydrogenation is performed over conventional Pt-Sn or Cr catalysts (typically at 550–600 °C), with a solid "oxygen reservoir" (SOR) added. The latter metal-oxide catalyst selectively combusts the hydrogen *in-situ* from the dehydrogenation mixture, using its lattice oxygen (Scheme 1, left).[13,14,19] This process generates heat, aiding the endothermic dehydrogenation. It also increases the yield, by shifting the equilibrium to the products side. Moreover, it is safer, since no gaseous oxygen is used. Following the reduction of the SOR lattice, the oxygen vacancies are replaced using air, creating a cyclic redox process. Using two catalysts allows for separate tuning of the dehydrogenation and selective hydrogen combustion. Scheme 1, right, illustrates a possible industrial redox dehydrogenation process. The selective hydrogen combustion can be performed by supported metal oxides, but they sinter under redox cycling.[5,14–16,20] We found that doped cerias, in which part of the cerium atoms are replaced with dopant atoms, are active, selective and stable catalysts in



Scheme 1 Left: combined propane dehydrogenation and selective hydrogen combustion: the selective hydrogen combustion consumes part of the hydrogen formed during the dehydrogenation step, shifting the equilibrium to the products side and generating heat. Right: cartoon of the complete redox cycle. After the dehydrogenation step A, the bed is flushed with nitrogen (B), and the catalysts are regenerated through reoxidation (C). This burns coke from the dehydrogenation catalyst and restores the lattice oxygen of the SOR. After another nitrogen flush (D) the reactor is ready for the next redox cycle.

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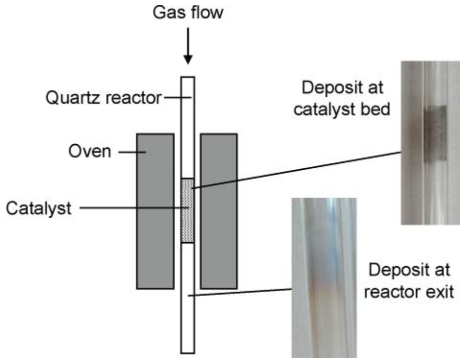
this selective hydrogen combustion.[19,21] The catalytic properties depend strongly on the type of dopant used.[22] Our screening study, using 26 different dopant atoms, showed that doping with lead results in high selectivity and activity. Indeed, out of 97 catalysts tested, a 10 mol% Pb-doped catalyst showed the highest activity and high selectivity.[22] The lead, however, easily segregates from the ceria, forming a separate PbO phase, which is not stable in the redox cycling. The high activity and selectivity of the lead-doped cerias prompted us to investigate the selectivity and stability of various lead-containing SOR materials.

Results and discussion

We studied the activity, selectivity and stability in the selective hydrogen combustion of three types of lead-containing SOR catalysts: alumina-supported lead oxide, lead-doped ceria, and lead chromate ($PbCrO_4$). In a typical reaction, 250 mg of catalyst was placed on a quartz wool plug in a quartz reactor and heated to 550 °C in 1% v/v O_2 in Ar. The selectivity and activity were assessed over 125 redox cycles, each consisting of an 18 min oxidation step (1% v/v O_2 in Ar), a 4 min purge in pure Ar, a 10 min reduction step (4 : 1 : 1% v/v C_3H_8 : C_3H_6 : H_2 in Ar, at 50 mL min^{-1} total flow), and a second 3 min purge in pure Ar. The selectivity and activity are assessed during this step using the data of six GC measurements, spread over the 10 min interval. The selectivity is determined as the ratio $\frac{\text{conversion}_{H_2}}{\text{conversion}_{\text{total}}} \times 100$, and the activity as the percentage of the hydrogen feed combusted by each catalyst (labelled "hydrogen activity"). Note that the oxygen source for this combustion is the catalyst lattice oxygen, which has to be refilled once depleted, hence the redox cycling.

1. Alumina-supported lead oxide

Both Grasselli and co-workers,[14,15] and ourselves[20] showed that supported oxides such as PbO, Bi_2O_3 or In_2O_3 can catalyze the selective oxidation of hydrogen in the presence of C_2 and C_3 hydrocarbons. We showed that these catalysts give excellent selectivity (>99.8%), and the active oxide loading can be as high as 30–50%.[20] However, most of these metals melt below or around 500–700 °C, and thus sinter during the reduction step.[14] Part of the metal evaporates and a metal deposit is observed on the reactor wall after the catalytic tests. This deposit is typically found at the end of the quartz reactor, where it exits the oven (cold spot), and sometimes near the reactor bed itself (see Scheme 2). To see whether this loss of active metal affects the activity and selectivity of the catalyst, we have subjected catalyst **1**, an alumina-supported PbO catalyst (1 mmol PbO per g catalyst) to 125 redox cycles at 550 °C (73 h on stream, see Fig. 1). Indeed, a very clear metal deposit was observed after the reaction at the reactor exit, and near the reactor bed (not shown). The data in Fig. 1 show, however, that this does not affect the selectivity and activity of the catalyst, within this time frame (73 h).



Scheme 2 Schematic of the oven fitted with a quartz reactor and catalyst, and photos showing a metal deposit at the reactor exit (Bi_2O_3/Al_2O_3), and at the reactor bed (note that the catalyst is removed).

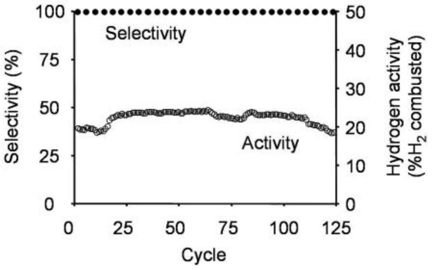


Fig. 1 Selectivity and activity for catalyst **1**, PbO/Al_2O_3 (1 mmol PbO g^{-1}) for a total of 125 redox cycles (73 hours on stream). The selectivity of the catalyst is 100%. A slight negative conversion of propene is observed, possibly originating from to the formation of propene *via* propane dehydrogenation. For clarity, part of the 125 selectivity-data points have been removed.

2. Lead-doped ceria

2.1 Catalyst preparation and characterisation. Doped ceria catalysts can be easily prepared batch–wise, by co–melting the appropriate metal nitrate hydrate precursors (or chlorides or ammonium metallates, when nitrates are not available) at 120 °C.[19,23] After the precursors liquefy, the pressure is lowered to about 10 mbar and a solid mixed metal nitrate forms. This is then converted into the doped ceria by calcining in static air at 700 °C for 5 h. X-ray diffraction is performed to ensure the catalysts consist of a uniform phase. This procedure works well when the dopant precursors melt below 120 °C, or dissolve in to the molten cerium nitrate (which has a melting point of ~65 °C), and at a maximum dopant concentration of 10 mol%. The melting point of most nitrates used in our study lie below 120 °C, but the melting point of lead nitrate is very high (470 °C, decomposes). Furthermore, it does not dissolve easily in the molten cerium nitrate. This results in formation of a separate PbO phase, when the standard experimental procedure is used. The lead nitrate does, however, dissolve well in water. We therefore adjusted the experimental procedure as follows: water is added dropwise to the lead nitrate, under continuous stirring, until it dissolves. The amount of water added should be as little as possible, since the addition of too much water results in phase segregation in the finished catalyst. When the lead nitrate has completely dissolved, the cerium nitrate is added and mixed to a slurry. This mixture is gently heated on a heating plate, under continuous stirring, until the cerium nitrate melts. **CAUTION!** this step should be performed in a fume hood since $NO_{x(g)}$ may be formed. The crucible is quickly placed in a 120 °C vacuum oven, placed in the same fume hood, and the pressure is lowered to about

10 mbar within about 10 min. After 4 h, the sample is calcined in static air at 700 °C for 5 h. This adjusted experimental procedure increases the success rate of the synthesis.

2.2 Stability in the selective hydrogen combustion reaction. We have tested the selectivity, activity and stability of two types of lead-doped ceria catalysts: a biphasic catalyst (**2**), where part of the lead is present as separate PbO, and monophasic lead-doped ceria (**3**, $Ce_{0.92}Pb_{0.08}O_2$). We analysed the biphasic **2** to assess if the ceria can stabilise the lead oxide phase. Ceria reduces at fairly low temperatures, starting from about 470 °C, which is below our reaction temperature of 550 °C. Because of this, strong metal-support interaction (SMSI) can occur. Metal oxides supported on ceria can spread out over the ceria surface, forming a Ce–metal–O surface phase, and the ceria can "crawl over" (or "decorate") the metal (oxide) particles during the redox cycling.[24,25] Indeed, we observed the disappearance of a separate CuO phase during the redox cycling for one of our copper-ceria catalyst. Possibly, the stability of PbO supported on ceria may be higher than that of alumina-supported PbO (*i.e.*, less sintering and metal evaporation). We therefore subjected catalyst **2**, Pb-doped ceria (8 mol% Pb), with part of the lead present as PbO, to 125 redox cycles at 550 °C. The selectivity and activity data of this catalyst is shown in Fig. 2. Interestingly, the activity increases up until the hundredth cycle, and then stabilises. This change in activity does not affect the selectivity. After the 73 h on stream, there is a clear metal deposit on the quartz reactor near the reactor bed, indicating that part of the lead has evaporated. The increase in activity could be related to the segregation of lead during the long term redox cycling.

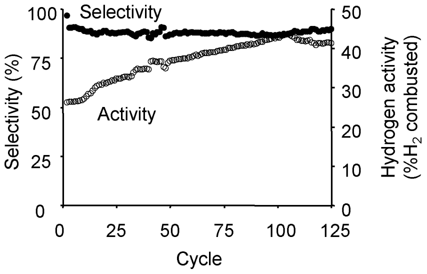


Fig. 2 Selectivity and activity of catalyst **2**, $Ce_{0.92}Pb_{0.08}O_2/PbO$, for a total of 125 redox cycles (73 hours on stream).

The separate PbO phase of catalyst **2** had formed during the synthesis of the catalyst. To see if phase separation can also occur during in the selective hydrogen combustion reaction, 125 redox cycles at 550 °C were performed using the monophasic catalyst **3** ($Ce_{0.92}Pb_{0.08}O_2$). Fig. 3 shows the activity and selectivity of this catalyst in the selective hydrogen combustion. Contrary to **2**, the activity remains constant during the 125 redox cycles. Interestingly, the activity of **3** is comparable to final activity of **2**. XRD analysis of fresh and spent catalyst **3** show, however, that part of the lead has segregated from the ceria into a separate phase. The crystallite size has also increased from 14 nm (fresh) to 20 nm (spent, note this was not analysed for **2**). As was the case for the biphasic catalyst **2**, a clear band is seen at the reactor bed. A light band has also formed at the reactor exit. It follows that the lead-doped ceria is not stable under the redox cycling at 550 °C.

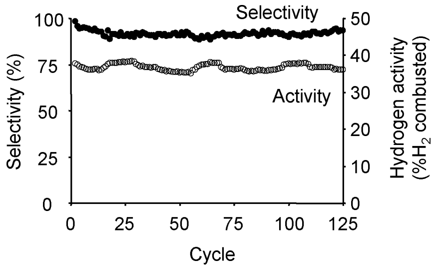


Fig. 3 Selectivity and activity of catalyst **3**, $Ce_{0.92}Pb_{0.08}O_2$, for a total of 125 redox cycles (73 hours on stream).

3. Lead chromate

The high activity and selectivity of lead-doped ceria prompted us to search for other lead-containing oxides which might be suitable SORs. By chance, we had already synthesised $SrPbO_3$, which was formed when attempting to make lead and strontium-doped ceria ($Ce_{0.87}Pb_{0.05}Sr_{0.08}O_2$). This catalyst shows activity and selectivity values comparable to lead-doped ceria, but is less stable: the activity drops already after 10 redox cycles (not shown). We then studied lead chromate ($PbCrO_4$), since it is a lead-containing oxide with a high melting point (844 °C), and chromium is one of the "good" dopant atoms (it is, however, toxic). First, we made a $PbCrO_4$–ceria catalyst (**4**), by mixing about 5 mol% $PbCrO_4$ with cerium nitrate, heating this in a 120 °C vacuum oven, lowering the pressure to about 10 mbar in 10 min, and calcining for 5 h at 700 °C. This did not result in a Pb/Cr-doped ceria, but in a mixture of $PbCrO_4$ and CeO_2 (as determined by XRD). The catalyst is very active, combusting 100% of the hydrogen feed at the start of the reduction cycle, and performing propane dehydrogenation at the end of the reduction cycle (see Fig. 4). The catalyst does combust part of the propene, however, resulting in a lower selectivity than lead-doped ceria. We then tested the $PbCrO_4$ itself (catalyst **5**). This consists of very fine powder of low surface area (<1 m^2 g^{-1}). The powder tends to coagulate into small lumps, even when dried at 110 °C, possibly due to static charging. It follows that the material in

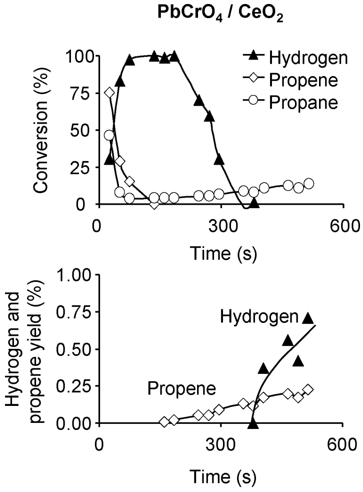


Fig. 4 Top: time resolved conversion profile of $PbCrO_4/CeO_2$ (**4**) at 550 °C, showing the C_3H_8 (○), C_3H_6 (◇) and H_2 (▲) conversion during a reduction cycle. Bottom: Hydrogen (▲) and propene (◇) yields (at the end of the reduction cycle propene and hydrogen are produced instead of converted).

this form is not an ideal catalyst; indeed, we had to lower the amount of sample from 250 mg to about 40 mg, to prevent high reactor back pressures. Still, the $PbCrO_4$ (**5**) is very active and selective (see Fig. 5). Both the selectivity and activity of this catalyst are the highest of all catalysts tested. The typical initial unselective conversion, which is observed for doped cerias, perovskites and most supported metal oxides, is not present. Also, no CO or CO_2 is formed during reoxidation, which means that no coking has occurred. Some CO and CO_2 is formed during the reduction cycle, indicating that hydrocarbon combustion does occur, but this is not enough to result in a detectable propane or propene conversion (see Fig. 5). Note that the activity of the $PbCrO_4$ almost equals the theoretical maximum of CeO_2 (an oxygen release of 2.8 and 2.9 mol O kg^{-1} catalyst, respectively). Importantly, this activity is determined under the selective hydrogen combustion reaction conditions, that is at elevated temperatures and using the hydrocarbon/hydrogen gas mixture (the activity, usually expressed as the percentage of H_2 combusted, is converted into "mol O released per kg catalyst" for comparison). Also, the maximum activity of ceria based catalysts is determined from full (surface and bulk) reduction of Ce^{4+} to Ce^{3+}. This is hard to achieve at the reaction temperature of 550 °C.

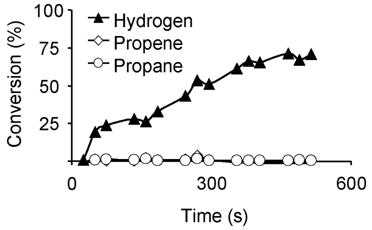


Fig. 5 Time resolved conversion profile of $PbCrO_4$ (**5**) at 550 °C, showing the C_3H_8 (○), C_3H_6 (◇) and H_2 (▲) conversion during a reduction cycle. Note that a 40 mg sample instead of 250 mg was used.

When the $PbCrO_4$ catalyst is subjected to prolonged redox cycling, however, the activity drops. Fig. 6 shows the performance of the $PbCrO_4$ catalyst (**5**) over 125 redox cycles (73 h on stream). During the first 60 cycles, the activity drops to about one quarter of the starting value. Interestingly, this coincides with a drop in hydrocarbon combustion (the amount of CO_2 and CO detected in the reduction step). Importantly, at the end of the steep drop in activity (from cycle 40 onwards) no CO_2 is observed anymore. The catalyst is now truly 100% selective (this phenomena has been observed for two separate batches of catalyst). Note that the "low" activity of the $PbCrO_4$ is still twice that of the best doped ceria. Also, we used the "as received" $PbCrO_4$. The activity loss could be due to sintering of the $PbCrO_4$ crystallites (the catalyst bed had shrunk), but formation of a hard outer shell of the coagulated powder will also result in loss of activity by preventing gas flow through part of the bed. To achieve and maintain a better flow through the bed we mixed 50 mg of $PbCrO_4$ with 200 mg of inert SiC using a spatula. The two do not mix well, however, the $PbCrO_4$ still has a tendency to coagulate into separate particles. Fig. 7 shows that, indeed, the drop in activity still occurs, even a bit sooner as compared to the pure $PbCrO_4$. Again, the amount of CO_2 (hydrocarbon combustion) drops to zero together with the drop in activity. No band was seen at the reactor bed after the 125 cycles. Possibly, some metal deposit was present at the reactor exit, but this was hard to tell.

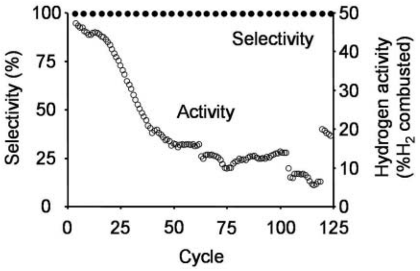


Fig. 6 Selectivity and activity of catalyst **5**, $PbCrO_4$, for a total of 125 redox cycles (73 hours on stream). Note that a 40 mg sample was used, instead of 250 mg. For clarity, part of the 125 selectivity-data points have been removed.

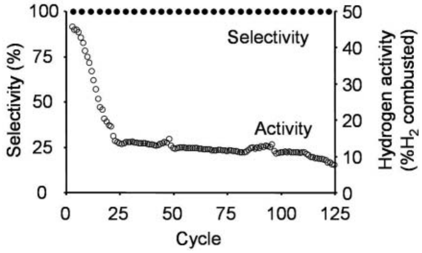


Fig. 7 Selectivity and activity of catalyst **5**, $PbCrO_4$ mixed with SiC (50 mg and 200 mg, respectively) for a total of 125 redox cycles (73 hours on stream). For clarity, part of the 125 selectivity-data points have been removed.

Future work should focus on increasing the stability of the $PbCrO_4$ catalyst without compromising its activity. This could be achieved by adding a small amount of alumina, similar to the copper–zinc–alumina methanol synthesis catalyst.[26,27]

Besides $PbCrO_4$, we have also tested nickel chromite ($NiCr_2O_4$, high activity but low selectivity), copper chromite ($Cu_2Cr_2O_4$, selectivity 85%, activity 60% H_2 combustion), chromium molybdate ($Cr_2(MoO_4)_3$, inactive) and manganese molybdate ($MnMoO_4$, inactive).

Conclusions

We have compared the activity, selectivity and stability of three types of lead-containing solid oxygen reservoirs: alumina-supported lead oxide, lead-doped ceria, and lead chromate ($PbCrO_4$). These solid oxygen reservoirs can be used for the selective combustion of hydrogen from a mixture with propane and propene. The alumina-supported lead oxide is active and selective, but not stable: part of the lead evaporates during the redox cycling. Stability studies of a biphasic $Ce_{0.92}Pb_{0.08}O_2/PbO$ catalyst show that the separate PbO phase is not stabilised by the ceria. Moreover, phase segregation and lead evaporation also occur when using monophasic lead-doped ceria.

Overall, lead chromate ($PbCrO_4$) shows the highest selectivity (~100%) and activity (2.8 mol O kg^{-1}). The activity is comparable to the theoretical maximum activity of CeO_2 (2.9 mol O kg^{-1}). Although it drops during the first 60 redox cycles, to about 25% of the starting value, it is still higher than the best doped cerias.

Experimental

Materials and instrumentation

Chemicals were purchased from Sigma–Aldrich or Merck and used as received. Gasses were purchased from Praxair and had a purity of 99.5% or higher. The O_2, He, Ar and N_2 streams were purified further over molecular sieves and/or BTS columns. All gas flows were controlled by Bronkhorst mass flow controllers. The specific surface areas were measured by N_2 adsorption at 77 K on a Sorptomatic 99 (CE Instruments) and evaluated using the BET equation. Powder X-ray diffraction measurements were performed using a Philips PW-series X-ray diffractometer with a Cu tube radiation source ($\lambda = 1.54$ Å), a vertical axis goniometer and a proportional detector. The 2θ detection measurement range was 10°–93° with a 0.02° step size and a 5 second dwell time.

Procedure for catalyst synthesis

Synthesis of alumina-supported lead oxide: this catalyst was synthesised in a specially designed reactor, allowing for the simultaneous impregnation of 6 supports, described in detail earlier.[20] The appropriate amount of $Pb(NO_3)_2$ was dissolved in 20 mL demineralised water. Alumina (1.00 g) was placed in the impregnation reactor. The reactor was evacuated and 0.61 mL solution was injected using a syringe. The reactor was vehemently shaken for 4 min using a vortex instrument. The material was dried overnight at 120 °C and exposed to air for 24 h at 25 °C. Consecutive impregnations were carried out to achieve the desired loading, after which the material was dried overnight and then calcined in ceramic vessels at 650 °C for 5 h (heating rate 300 °C h^{-1}) under a flow of dry air (125 mL min^{-1}).

Synthesis of the doped cerias: the metal nitrate precursors were weighed into a crucible and just enough water was added to dissolve the metal nitrates (usually 4–6 drops). The desired amount of cerium nitrate was added, mixed to a slurry, and the crucible was placed on a heater under continuous stirring. After about 5 minutes, the crucible was placed in a 140 °C vacuum oven. Pressure was reduced to <10 mbar in about 10 minutes. The latter step was performed carefully to prevent vigorous boiling. After 4 h, the crucible was placed in a muffle oven and calcined for 5 h at 700 °C in static air (ramp rate: 300 °C h^{-1}). The resulting solid was pulverized, ground and sieved in fractions of 125–212 μm (selectivity assessment) and <125 μm (XRD and BET measurements). The final metal concentration was calculated from the amount of precursor weighed in, corrected for the water content as determined by ICP on a reference set of catalysts.[19]

Procedure for testing catalytic activity

Activity and selectivity were determined on a fully automated system built in house, which was described in detail previously.[19] In a typical experiment, about 250 mg of sample was placed on a quartz wool plug in a 4 mm id quartz reactor. The reactor was placed in a water cooled oven and heated to 550 °C in 1% v/v O_2 in Ar. At this temperature, sixteen consecutive redox cycles were performed, consisting of an 18 minute oxidation step in 1% v/v O_2 in Ar at 50 mL min^{-1} total flow, 4 minute purge in pure Ar, a 10 minute reduction step in 4 : 1 : 1% v/v $C_3H_8 : C_3H_6 : H_2$ in Ar at 50 mL min^{-1} total flow, with 5 mL min^{-1} N_2 added as internal standard, and a 3 min purge in pure Ar. The gas hourly space velocity (GHSV) is 13 200 h^{-1} (at the typical bed volume of 0.25 cm^3 and the reduction cycle's total flow of 55 mL min^{-1}). The weight hourly space velocity (WHSV) is 1.2 h^{-1}, and is calculated from the weight of $C_3H_8 + C_3H_6 + H_2$ per h per the weight of the catalyst. The selectivity is determined in the reduction step as the relative conversions of H_2, C_3H_6, and C_3H_8, as determined by GC. The first data point of each reduction cycle (after 25 s), is not included in the final selectivity calculation, since all catalysts, good or bad, show conversion of the hydrocarbons at this point. Activity is determined as the percentage hydrogen combusted during the reduction step.

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