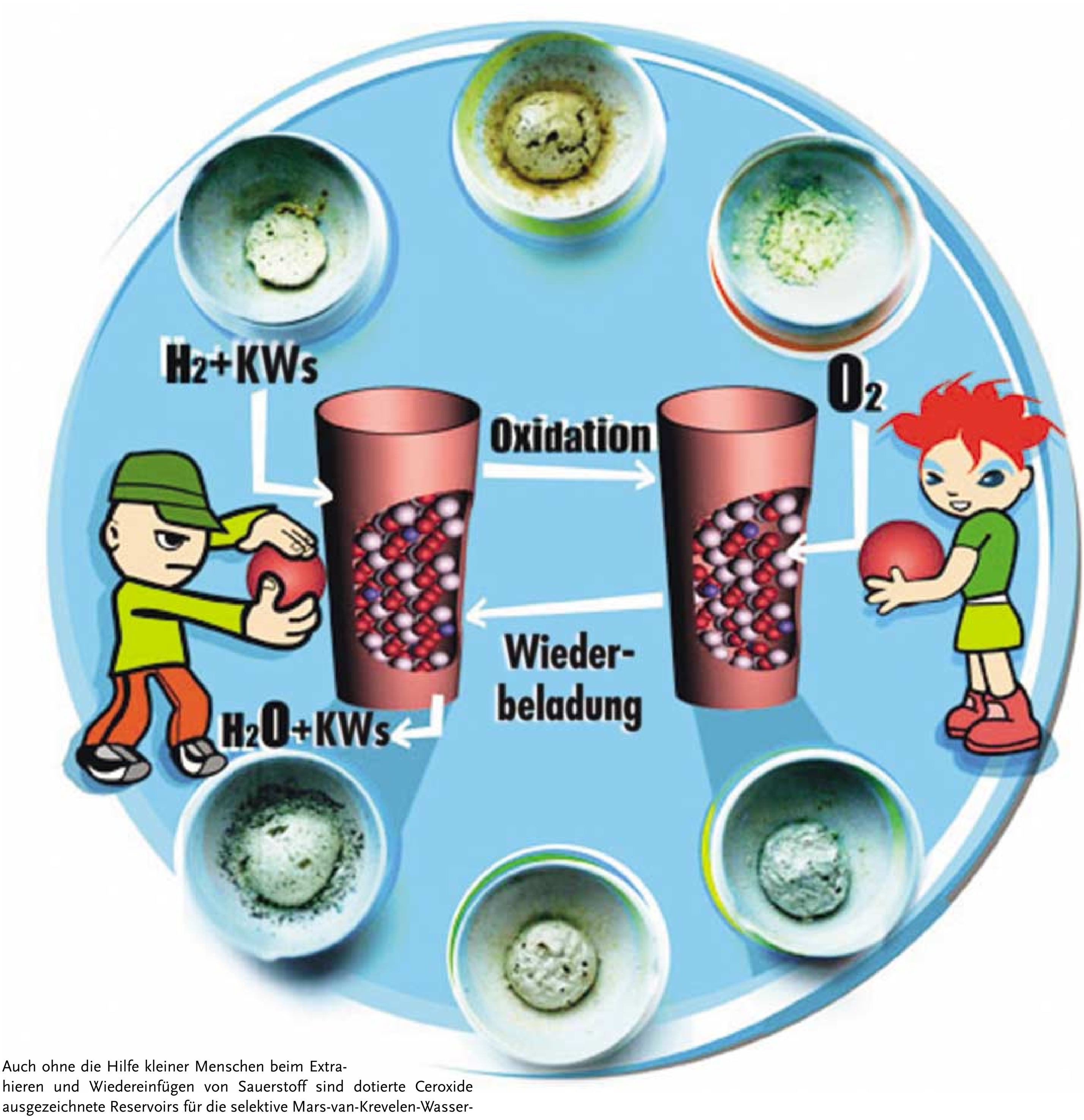
Zuschriften



Auch ohne die Hilfe kleiner Menschen beim Extrahieren und Wiedereinfügen von Sauerstoff sind dotierte Ceroxide ausgezeichnete Reservoirs für die selektive Mars-van-Krevelen-Wasserstoffoxidation. So wurde mit $Ce_{0.9}W_{0.1}O_y$ aus einer Wasserstoff/Ethan/Ethylenmischung nur Wasserstoff verbrannt (97% Selektivität, 0% Verkoken). Einzelheiten hierzu finden Sie in der Zuschrift von G. Rothenberg et al. auf den folgenden Seiten.

DOI: 10.1002/ange.200351545

Clean Hydrogen Oxidation

Solvent-Free Synthesis of Rechargeable Solid Oxygen Reservoirs for Clean Hydrogen Oxidation**

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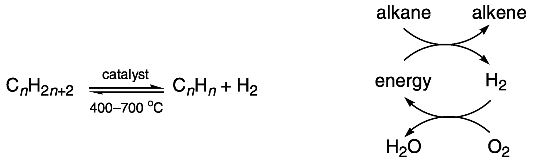
Industrial dehydrogenation of alkanes to alkenes is a huge commercial process,[1,2] that nonetheless suffers from unfavorable thermodynamics. It is an equilibrium that unfortunately favors the reactants and consumes expensive energy (Scheme 1, left). In principle, a closed cycle can be envisaged where this energy is supplied by combustion of the hydrogen by-product, also shifting the equilibrium to the desired side (Scheme 1, right). Recent studies by Grasselli and co-workers,[3–5] Lin et al.,[6] and our own studies[7] showed that this selective oxidation of H_2 in the presence of alkanes at 500–700 °C is possible by using supported oxides of p-block metals as catalysts. The problem is, however, that most of these supported metals melt below the reaction temperature, so when the metal oxide is reduced to metal(0) it liquefies, causing sintering and deactivation.



Scheme 1. Dehydrogenation equilibrium (left) and catalytic cycle for oxidative dehydrogenation (right).

Cerium oxide and ceria-based mixed metal oxides ($Ce_xM_{1-x}O_y$) are known as versatile solid oxygen exchangers. The redox cycle $Ce^{3+} \rightleftharpoons Ce^{4+} + e^-$ facilitates oxygen storage and release from the fluorite lattice. This makes them ideal for direct oxidation applications, such as automotive three-way catalysis[8] and hydrocarbon fuel cells.[9,10] The selectivity of pure CeO_2 in hydrogen oxidation is poor, but the redox chemistry of doped cerium oxides is sensitive to crystal structure defects[11] and may be tuned, in principle, by substituting some Ce ions with ions of different size and/or charge. With this in mind, we searched for doping elements that will give stable rechargeable "oxygen reservoirs" for selective hydrogen oxidation. As Zr enhances ceria stability and Pb increases its selectivity, groups IIIB–VIB and IIIA–VA were a logical starting point. Herein we report the parallel synthesis of a set of ten bimetallic cerium oxides of Bi, La, In, Mo, Pb, Sn, V, W, Y, and Zr (catalysts **1**–**10**, respectively), and study their application in clean hydrogen oxidation. Cerium tungsten oxide ($Ce_{0.9}W_{0.1}O_y$) is discovered to be an excellent hydrogen oxidation catalyst, with practically zero coking levels, good thermal stability, and selectivity $>97\%$.

Single-phase mixed metal oxides can be prepared by precipitation,[12,13] sol–gel methods,[14] or combustion of glycine[15] or citric acid[16] in concentrated HNO_3. We needed a fast and simple protocol to produce catalyst samples in parallel on a 5–10 gram scale. For this, we modified the method reported by Inomata and co-workers.[17] We used no solvents, and instead synthesized the mixed metal oxides directly by boiling ground mixtures[18] of the solid nitrate precursors under vacuum, followed by calcination (for full experimental details see Supporting Information).

The catalysts were tested in a cyclic redox reaction setup with a feed stream simulating the effluent at the end of the ethane dehydrogenation process (20% v/v C_2H_6, 20% C_2H_4, 5% H_2, and balance He). In a simplified description of the system, the hydrogen in the feed reacts in each cycle with some of the lattice oxygen atoms, leaving vacancies in the lattice (Figure 1 C). These vacancies are then refilled by an O_2 stream (Figure 1 B).

Each reaction was repeated 19 times at 600 °C to examine the rechargeability and stability of the materials. Table 1 gives the key surface parameters, the average activity (as% of available oxygen), and the selectivity towards hydrogen oxidation for catalysts **1**–**10**. The absolute amount of O atoms available after each recharging is shown in

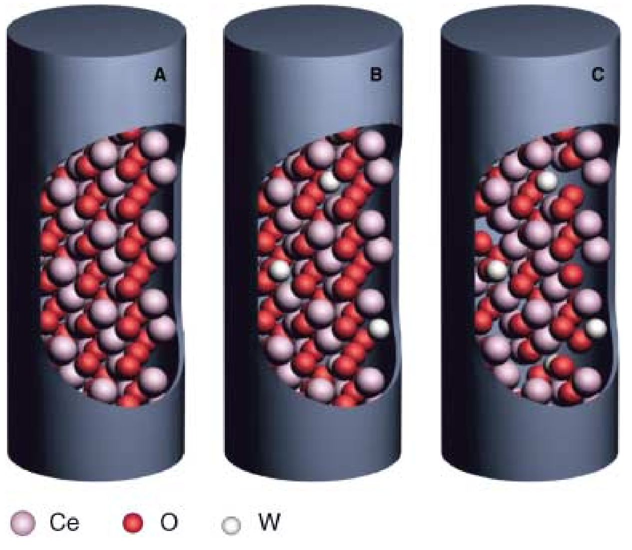


Figure 1. Schematic drawn to scale showing the fluorite structure of pure CeO_2 (A), and the vacancies present in the doped $Ce_{0.9}W_{0.1}O_y$ reservoirs when fully charged (B) and after releasing 30% of its oxygen atoms (C).

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[**] We thank Dr. E. Eiser for XRD measurements, M. Mittelmeijer-Hazeleger for surface characterization, and A. Rothenburg and M. Schenk for artwork.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351545

Table 1: Characteristics and performance of the oxygen reservoirs.

Entry	Catalyst/composition	Surface area [$m^2 g^{-1}$]	Pore volume [$mL g^{-1}$]	Pore diameter [nm]	Average activity[a] [%]	Selectivity[b] [%]
1	**1**/$Ce_{0.9}Bi_{0.1}$	44.7	0.15	6.0	33	15
2	**2**/$Ce_{0.9}In_{0.1}$	69.9	0.25	11.5	35	24
3	**3**/$Ce_{0.9}La_{0.1}$	55.0	0.20	13.3	44	34
4	**4**/$Ce_{0.9}Mo_{0.1}$	12.5	0.06	19.0	11	18
5	**5**/$Ce_{0.9}Pb_{0.1}$	33.0	0.14	7.2	29	11
6	**6**/$Ce_{0.9}Sn_{0.1}$	64.5	0.22	9.2	16	75
7	**7**/$Ce_{0.9}V_{0.1}$	26.4	0.10	9.5	28	10
8	**8**/$Ce_{0.9}W_{0.1}$	35.7	0.14	14.0	23	97[c]
9	**9**/$Ce_{0.9}Y_{0.1}$	42.2	0.10	17.6	22	<2
10	**10**/$Ce_{0.9}Zr_{0.1}$	71.2	0.23	9.4	39	35

[a] Mol% fraction of lattice oxygen atoms available for oxidation, compared to the theoretical limit when all the cerium ions are reduced to Ce^{3+}. The values given are the average of 19 repeated experiments, the distribution is ±3%. [b] Mol% O_2 used to burn H_2 at 600°C, determined by the amount of H_2O detected by GC and selective MS. The values given are the average of triplicate experiments. [c] Six repeated experiments gave 97, 98, 97, 95, 98, and 97%.

Figure 2. The most active combinations are **3**, **10**, and **2**, but it is the high selectivity of CeW **8** that triumphs: over 97% of its oxygen uptake is used to oxidize hydrogen (compare entries 2, 3, 10, with 8 in Table 1).

Coking is a thorny problem in industrial catalysis. In conventional catalytic dehydrogenation (e.g. with Pt-Sn/Al_2O_3) the coke is usually burned off the catalyst to regenerate it and the excess heat is "paid" towards the endothermic equilibrium.[19] However, in oxidative dehydrogenation this energy is not needed. In this case, the coking of the catalyst after the oxygen has been consumed from the lattice can cause severe heat excess problems. Figure 3 shows that catalyst **8** is exceptionally inert towards coke formation, with total coke levels below the GC detection limit (<0.5%). Note that **4** also gives low coking levels (although the selectivity to hydrogen oxidation is poor), in agreement with earlier results reported for molybdenum oxides.[5]

The advantage of these materials over the silica-supported metal oxides[7] is that the catalyst remains a solid, with no liquid phase forming in the reactor even at 600°C. The stable hydrogen uptake in repeated experiments (Figure 2) is a further indication that these materials do not sinter during the reduction step. This compensates for the moderate surface area of these materials compared to silica and alumina (Table 1). Powder X-ray diffraction spectra confirm that homogeneous solid solutions are formed. Only one crystalline phase is observed, and the original cubic fluorite structure is retained when 10% of the Ce ions are replaced (at these low doping values, no appreciable peak shifts are expected[20,21]). However, although the structure is retained the doping ions will create stress in the lattice and possibly ease the transport of oxygen atoms through interstitial sites. In some cases, charge vacancies will also be created (though not for Zr), thus enabling the transfer of O-atoms through ion-vacancy mechanisms.

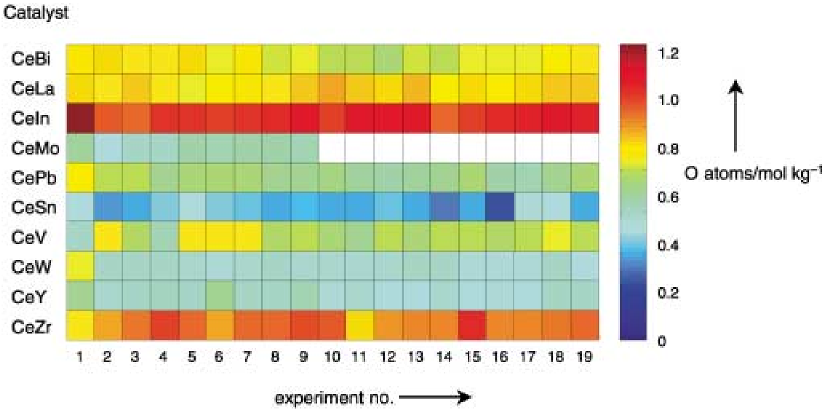

Figure 2. Absolute amount of oxygen atoms (in mol kg^{-1}) available after each recharging of the bimetallic oxide catalysts (white = n/a).

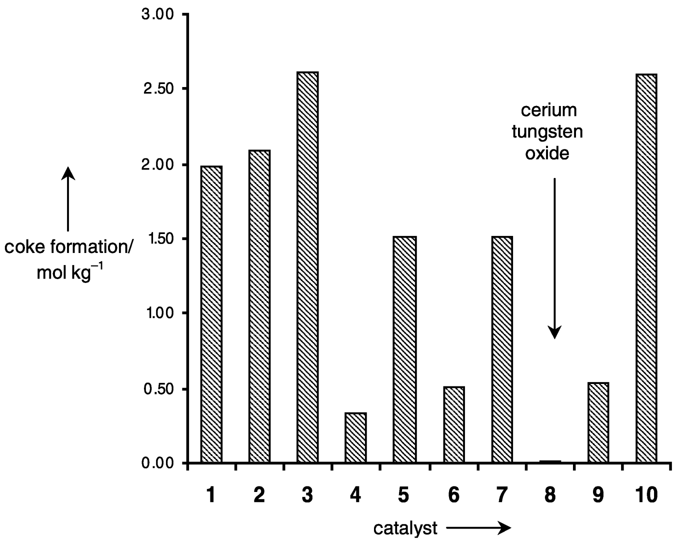

Figure 3. Average amount coke formed (in mol kg^{-1}) on catalysts **1**–**10** after the available oxygen has been consumed. Values are the average of 19 experiments, with a dispersion of ±2%.

We show here that metal-doped cerium oxide can be easily synthesized in parallel and make stable and selective solid oxygen reservoirs. These reservoirs can be recharged many times without losing their activity. Further work will focus on elucidating the reaction mechanism, and especially on understanding the influence of the different dopants and their oxidation states on the redox chemistry of the ceria lattice.[22] At this stage, we venture only to say that the fact that lattice oxygen atoms are used in the oxidation phase and not O_2 may explain the high selectivity towards hydrogen oxidation. It may be that H_2 molecules diffuse into the lattice,[23] where the bulky alkanes and alkenes cannot enter. Another possibility is that H_2 reacts much faster with O atoms that migrate to the surface. Future work will include transient kinetic measurements to gain further understanding into this interesting system.

Detailed experimental procedures for the synthesis of catalysts **1**–**10**, for performing the hydrogen oxidation experiments, and details of the powder XRD measurements are found in the Supporting Information.

Received: April 1, 2003 [Z51545]

Keywords: cerium · dehydrogenation · green chemistry · heterogeneous catalysis · oxidation

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