Journal of Catalysis **184,** 77–86 (1999)
Article ID jcat.1998.2363, available online at http://www.idealibrary.com on IDEAL®

Metal Oxides As Selective Hydrogen Combustion (SHC) Catalysts and Their Potential in Light Paraffin Dehydrogenation

John G. Tsikoyiannis, David L. Stern, and Robert K. Grasselli*[,1]

*Strategic Research Center, Mobil Technology Company, 600 Billingsport Road, Paulsboro, New Jersey 08066-0480; and *Department of Chemical Engineering, University of Delaware, Newark, Delaware, 19716-3116 and Institute of Physical Chemistry, University of Munich, Sophienstrasse 11, D-80333 Munich, Germany*

Received July 17, 1998; revised November 23, 1998; accepted November 25, 1998

An alternative approach to light paraffin dehydrogenation (thermodynamically limited) and oxydehydrogenation (thermodynamically not limited) is a combination process of dehydrogenation (DH) with selective hydrogen combustion (SHC). By selectively combusting the hydrogen produced in the DH reaction, the overall combination process becomes thermodynamically not limited. While dehydrogenation is commercially practiced, the olefin yields are equilibrium limited, and the process is endothermic, requiring large inputs of external heat, and cyclic, requiring frequent catalyst regenerations. Oxydehydrogenation, while not equilibrium limited, suffers from low selectivity at high conversions with currently known catalysts and is therefore not practiced commercially.

For these reasons we have launched a study of DH-SHC. The first task is the discovery and identification of good SHC catalysts, which are reported here. We have discovered that certain metal oxides oxidize hydrogen with great preference to propane and propylene, making them good candidates for an eventual DH-SHC process. Among the best are Bi_2O_3 (>99% sel.), $Bi_2Mo_3O_{12}$ (99% sel.), and $In_2Mo_3O_{12}$ (98.4% sel.). In stark contrast to these compositions stands V_2O_5, which attacks hydrocarbons with great preference to hydrogen, resulting in a hydrogen oxidation selectivity of only 6.1%. It is noteworthy that all of the good SHC catalysts contain elements which have a lone pair of electrons in their prevailing oxidation state at the start of the reaction (redox mode) or under steady-state operating conditions (cofed mode).

The experiments were carried out at atmospheric pressure and in the range of 500°C with gravimetric methods using a Cahn balance, and redox and cofed methods using an automated microreactor.

The best SHC compositions identified in this study constitute promising candidates for a proposed DH-SHC process and their viability in this context is reported in a separate study (1).

Key Words: **dehydrogenation (DH); selective hydrogen combustion (SHC); Bi_2O_3; molybdates.**

INTRODUCTION

Dehydrogenation of paraffins to produce the corresponding olefins is an equilibrium process between paraffin, olefin, and hydrogen [paraffin ↔ olefin + hydrogen], and the maximum yields of olefins attainable in such a process are thermodynamically limited. For example, at 500°C the maximum theoretically attainable yield of propylene from propane permitted by thermodynamics is 20%; that of isobutylene from isobutane is 33% (2). Another drawback of conventional dehydrogenation processes is that they are endothermic, requiring the addition of an external heat supply, which is expensive.

Dehydrogenation processes of lower paraffins practiced on a commercial scale comprise the following: Oleflex (UOP) (3), STAR (Phillips Petroleum Co.) (4), Catofin (Houdry—United Catalysts Inc.—ABB Lummus Crest) (5), Linde-BASF (6), and Snamprogetti-Yarsintez (7). The catalysts used are either promoted Pt supported on various carriers (preferred are alumina and Group II spinels) (8–10) or variously doped chromia–aluminas (11–13). Although the efficiencies of these processes and their respective catalysts are highly optimized, they nonetheless all suffer from the common disadvantages that their olefin yields are thermodynamically limited and that they are all heat deficient.

For these reasons, attempts have been made lately to investigate oxidative dehydrogenation (oxydehydrogenation) as an alternative to dehydrogenation (14–19). In oxydehydrogenation, oxygen is added to the paraffin feed as dioxygen or air, in order to make the process exothermic and to remove the thermodynamic yield limitation of the dehydrogenation process. The energy needed to overcome the thermodynamic limitation is obtained by the heat of formation of the coproduced water molecule [paraffin + oxygen → olefin + water]. Theoretically, 100% yields of olefins are permitted by thermodynamics in oxydehydrogenation, with the potential of becoming the ultimate light paraffin dehydrogenation process. Unfortunately, no catalysts have yet been discovered that could realize this

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[1] To whom correspondence should be addressed. Fax: 302-831-2085 (USA); 011-49-89-2180-7600 (Germany).

0021-9517/99 $30.00

potential. Various research groups have attempted to rise to this challenge; however, thus far the highest olefin yields that anybody has obtained are only about 20% at 70% selectivity (20).

In an effort to go beyond the scope of currently recorded literature, aiming at further increasing olefin yields and staying outside thermodynamic yield limitations, we explored an alternate process and catalyst approach which is described here. The approach consists of combining conventional dehydrogenation (DH) with selective hydrogen combustion (SHC) and thereby eliminating the thermodynamic limitation of the overall process. The main idea is to selectively combust *in situ* (redox mode) or *ex situ* (cofed mode) the hydrogen formed during the dehydrogenation process, herewith removing the thermodynamic limitation and attaining olefin yields in excess of equilibrium [paraffin –DH cat. → olefin + hydrogen; hydrogen + oxygen –SHC cat. → olefin + water]. For the overall process to succeed, it is necessary to use two different catalysts, having two different catalytic functions. It is imperative that the SHC catalyst attack and oxidize the hydrogen with great preference to the paraffin and olefin. If such catalysts can be found and made compatible with a given DH catalyst, then the process not only would be free of thermodynamic limitations giving higher than equilibrium olefin yields, but also could be made thermoneutral or slightly exothermic, needing no external supply of heat. Both scenarios are highly attractive from a commercial point of view and hence worthy of study.

For the overall process to succeed it is necessary that the SHC catalysts be highly selective for hydrogen combustion over paraffin and olefin combustion, since any loss of hydrocarbon to combustion products (CO_x) lowers the overall yield and selectivity of the olefin and must be avoided or at least minimized. Similarly, it is important that for an ultimate DH-SHC process, DH catalysts be chosen that are steam resistant and CO_x compatible. Such systems exist and are reported in the literature (e.g., (3)). This paper does not address these more applied aspects of the proposed combination process; these are addressed in subsequent publications (1).

The first task which needs to be addressed towards achieving the overall goal of an efficient DH-SHC process, and which is reported here, is the identification of SHC catalysts, a subject which is to the best of our knowledge not available from the literature. Towards this goal we elected to study an array of metal oxides and mixed metal oxides which we thought might exhibit the desired SHC properties. In a certain analogy to the behavior with which a small select group of elements of given mixed metal oxides abstract α-hydrogen from olefins (21), and methylene hydrogen from allyl surface intermediates (22), we postulated that in a similar manner oxides containing said elements, capable of existing in several oxidation states and, importantly, having a lone pair of electrons in their oxidation state prevailing under initial and/or steady-state reaction conditions, e.g., Bi^{3+}, In^{3+}, Sb^{3+}, Te^{4+}, etc., might also exhibit good SHC properties. This working hypothesis constituted the basis for our selection of catalysts to be examined for SHC behavior. The experimental approach of the study centered on the determination of the ease of lattice oxygen $[O]_L$ removal from selected metal oxides by hydrogen and comparing it to that of propane and propylene. This was accomplished by gravimetric techniques using a Cahn balance and by microreactor redox and cofed experiments. The details of these approaches are listed below (under Experimental).

EXPERIMENTAL

Catalyst Preparation

The catalysts used in this study were prepared by refluxing aqueous solutions of the appropriate metal nitrates (i.e., bismuth, indium, iron, chromium, cerium, lanthanum, aluminum, or lead) in the absence (for simple metal oxides) or presence (for metal molybdates) of ammonium heptamolybdate and in the presence of silica sol (Ludox AS-40). In the case of MoO_3/SiO_2, the source of the metal was ammonium heptamolybdate; in Sb_2O_4/SiO_2 it was finely divided Sb_2O_3, and in the case of V_2O_5/SiO_2 it was ammonium metavanadate. The resulting slurries were, refluxed for 16 h, dried at 120°C for 16 h, pulverized, air dried at 290°C for 4 h, and ultimately calcined in air at 600°C for 4 h. The calcined solids were then pelletized and sized to 20–40 mesh, before use in catalytic and characterization studies. All of the catalysts were silica supported (80% active phase, 20% silica), unless specified differently.

Gravimetric Experiments

A Cahn balance (Cahn 1000 Vacuum Electrobalance) with 1/100 mg sensitivity was employed for the gravimetric experiments. The solids (catalysts) to be examined (30–60 mg) were finely powdered and thinly spread on the bottom of the quartz sample pan and a downward flow of nitrogen, air, or a reducing gas (hydrogen, propane or propylene) of about 500 cm^3/min was swept over the samples in the reduction or reoxidation experiments. The temperature of the three zone furnace was computer controlled to lock onto the respective desired temperature levels.

In typical redox experiments, the oxidized catalysts were reduced in hydrogen at 1 atm and 500°C, and were then reoxidized in air at the same temperature. Similar cycles were also carried out with other reducing gases, typically propane, propylene, and H_2/C_3 mixtures.

The weight versus time curves of the reduction phase were differentiated with respect to time, in order to calculate the reduction rate. The reduction rate was then plotted

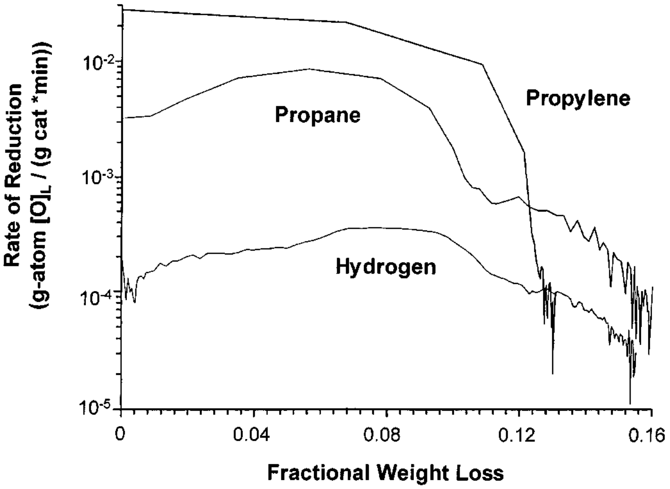

FIG. 1. Reduction of V_2O_5 at 500°C by hydrogen, propane, and propylene.

as a function of catalyst weight, which is a measure of the oxidation state of the oxide. Typical rate curves are shown in Figs. 1–3. Zero fractional weight loss corresponds to a fully oxidized catalyst, which is the initial state of the catalyst. Maximum fractional weight loss corresponds to the maximum extent of reduction, which can be estimated from stoichiometry. Reduction rates are expressed in g-atom lattice oxygen, $[O]_L$, extracted per minute per gram (Fig. 1) on per gram-formula weight, g-FWT (Figs. 2–4), of the fully oxidized solid.

Removal of lattice oxygen by hydrogen results in the formation of H_2O, by hydrocarbon in the formation of partial or complete oxidation products. Based on stoichiometry, 1 lattice oxygen atom is required for the SHC, as well as for the oxydehydrogenation of propane to propylene (both are 2 electron oxidations). For complete combustion of propane to CO_2 and H_2O, 10 lattice oxygens are required (a 20 electron oxidation).

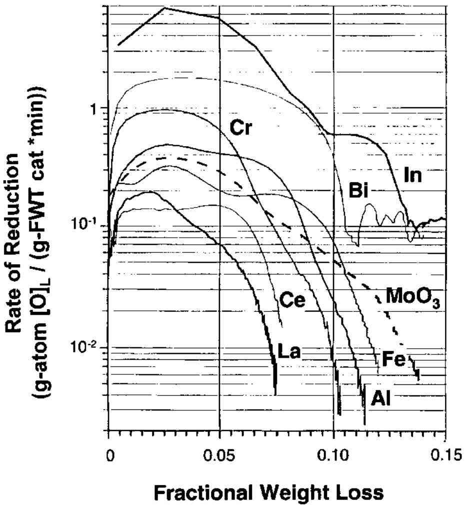

FIG. 2. Reduction of $Me_2Mo_3O_{12}$/20% SiO_2 (where Me = Bi, In, Fe, Cr, Al, Ce, and La) by hydrogen at 500°C.

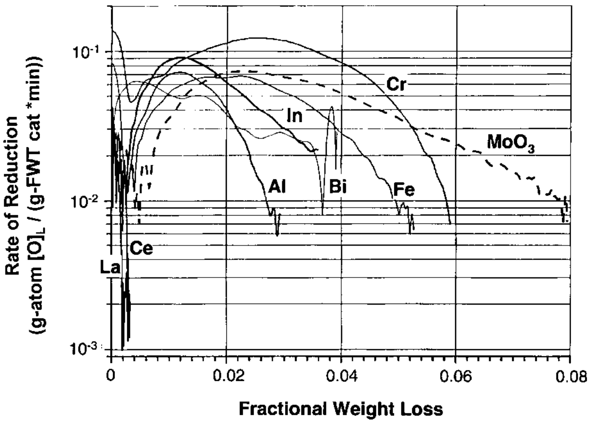

FIG. 3. Reduction of $Me_2Mo_3O_{12}$/20% SiO_2 (where Me = Bi, In, Fe, Cr, Al, Ce, and La) by propane at 500°C.

Under these premises, the oxidation rates for propane and propylene are considered to be equal to those shown for lattice oxygen removal in Figs. 1–3, but are actually somewhat lower because oxygenated products, particularly CO_x, are also produced. This fact does not alter the overall conclusions drawn from the observed gravimetric results.

Redox and Cofed Mode Experiments

An automated microreactor unit was used for redox and cofed mode experiments. The fixed bed reactor can be operated in a pulse, redox mode, in which case a measured amount of reactant is passed over the catalyst in a prescribed amount of time (pulse) and the reactor effluent collected in an evacuated 5 liter glass bulb for subsequent GC analysis, or in a continuous, cofed mode, in which case the reactor effluent is analyzed periodically before it is vented.

A redox cycle consists of a reduction phase (flow of a reducing gas at a flowrate, F [cm^3/min], for a specified amount of time, t [min]) followed by an oxidation phase (flow of air for a measured amount of time, typically 5 min). The reduction and (re)oxidation phases are separated by a helium purge phase. Only the gases from the reduction phase and the helium phase following it were collected in the bulb. After completion of four redox cycles, the accumulated products were sampled for GC analyses.

In the redox mode, the feed was composed of an equimolar mixture of 15% hydrogen and 15% propane, or 15% hydrogen and 15% propylene, with the rest being helium. There is no oxygen included in the above reducing feeds in the redox mode experiments, while 7.5% oxygen was added to the reducing feeds in the cofed mode experiments.

A useful quantity in redox experiments is ($H_2/[O]_L$), the hydrogen to lattice oxygen ratio, which we define as the molar ratio of the total amount of dihydrogen fed during the reduction phase to the theoretical amount of lattice oxygen (gram atoms) available in a catalyst; e.g., in the case of Bi_2O_3 it is the amount of lattice oxygen which would be removed from the lattice by hydrogen, if all of the catalysts Bi^{3+} were to reduce to Bi^0—in V_2O_5 if all of the V^{5+} were to reduce to V^{3+}. Such deliberations prior to an experiment were useful, so as not to exceed unnecessarily the total lattice oxygen capacity of a catalyst in a given redox experiment. Unless otherwise stated, all redox mode experiments reported here were conducted at $H_2/[O]_L = 1$.

The experiments were carried out in the temperature range of 450 to 550°C, which are typical temperatures for dehydrogenation. It is a practical temperature at which the SHC catalysts will ultimately have to operate in order to be compatibly matched for a potential DH-SHC process.

RESULTS AND DISCUSSION

Gravimetric Studies

Gravimetric studies using a Cahn balance were undertaken to determine the reduction behavior of various metal oxides. The reductants used were hydrogen, propane, and propylene. The aim of the study was to determine whether any of the solids studied might possess the ability to preferentially oxidize hydrogen over propane and/or propylene. If such materials were to be identified, they might have potential as SHC catalysts and could be used in combination with conventional DH catalysts in a combined DH-SHC process to enhance the equilibrium limited yields of olefins attainable from paraffins when only dehydrogenation catalysts are used in the process. By controlling the extent of the SHC process, the overall DH-SHC process could be made thermoneutral or slightly exothermic, which would give an additional economic advantage to commercial operation.

The rates of reduction of V_2O_5 by hydrogen, propane, and propylene examined in the Cahn balance at 500°C are shown in Fig. 1. As indicated by the final percentage weight loss, V_2O_5 is reduced by all three reductants to a composition having the empirical formula of V_8O_{13}, which corresponds to approximately $V_2O_4 + 3\,V_2O_3$. The reduction rate is highest for propylene and smallest, by at least an order of magnitude, for hydrogen. V_2O_5 is therefore much more easily reduced by propane or propylene than it is by hydrogen. It is therefore not selective for hydrogen combustion and is not a candidate for SHC catalysis.

The rates of reduction of a series of mixed metal molybdates of the general formula $Me_2Mo_3O_{12}$, where $Me =$ Bi, In, Fe, Cr, Al, Ce, and La, at 500°C are shown for hydrogen in Fig. 2 and for propane in Fig. 3. The catalysts were supported on 20% SiO_2. As seen, the rates of catalyst reduction by hydrogen are at least an order of magnitude higher for these molybdates than they are for propane. It is obvious from these results that the behavior of the studied metal molybdates ($Me_2Mo_3O_{12}$) stands in stark contrast to that of V_2O_5, with the molybdates attacking hydrogen in great preference to the hydrocarbons, making this class of catalysts highly selective for the preferential combustion of hydrogen over that of hydrocarbons. Hence, they are splendid candidates for SHC catalysis.

In another set of gravimetric experiments using the Cahn balance, the SHC behavior of some $Me_2Mo_3O_{12}$ compositions, Bi_2O_3, MoO_3, and V_2O_5 was examined and is summarized for comparison in Table 1. In this table, $W_{H,max}$ (wt%) denotes the actual maximum catalyst wt% loss of a given oxide obtained upon reduction with hydrogen, and

TABLE 1

Activity and Selectivity of Some Metal Oxides for Selective Hydrogen Combustion (SHC) at 500°C

Catalyst fresh	$W_{H,max}$ (wt%)	$[O]_{H,max}$ (g atom)	Catalyst after H_2 red.	$W_{P,max}$ (wt%)	$[O]_{P,max}$ (g atom)	Catalyst after propane red.	$R_{H,max}$	$R_{P,max}$	T_{H7}	S_H
Bi_2O_3	9.8	2.85	$Bi_2O_{0.15}$ $(Bi + 0.03\,Bi_2O_3)$	1.0	0.29	$Bi_2O_{2.7}$ $(Bi_2O_3 + 0.2\,Bi)$	7.0	0.11	1.01	>99.9
$Bi_2Mo_3O_{12}$	14.0	7.86	$Bi_2Mo_3O_{4.14}$ $(Bi + MoO_2 + 0.5\,Mo)$	4.0	2.24	$Bi_2Mo_3O_{9.76}$ $(BiMoO_6 + 2\,MoO_2)$	2.0	0.07	3.0	99.3
$In_2Mo_3O_{12}$	23.9	10.60	$In_2Mo_3O_{1.4}$ $(In + 0.7\,MoO_2 + Mo)$	4.3	1.9	$In_2Mo_3O_{10.1}$	9.5	0.14	0.8	99.9
$La_2Mo_3O_{12}$	7.5	3.55	$La_2Mo_3O_{8.45}$	0.3	0.14	$La_2Mo_3O_{11.86}$	0.27	0.05	47.5	99.4
$Ce_2Mo_3O_{12}$	7.8	3.70	$Ce_2Mo_3O_{8.30}$	0.3	0.14	$Ce_2Mo_3O_{11.86}$	0.27	0.10	28.0	98.8
$Al_2Mo_3O_{12}$	11.4	3.80	$Al_2Mo_3O_{8.20}$	3.7	1.23	$Al_2Mo_3O_{10.77}$	0.90	0.13	6.7	97.5
$Cr_2Mo_3O_{12}$	10.3	3.76	$Cr_2Mo_3O_{8.24}$	6.1	2.23	$Cr_2Mo_3O_{9.77}$	1.60	0.21	5.0	94.8
$Fe_2Mo_3O_{12}$	12.0	4.44	$Fe_2Mo_3O_{7.56}$ $(FeMoO_3 + 0.4\,MoO_2 + 0.1\,Mo)$	5.3	1.96	$Fe_2Mo_3O_{10.04}$ $(FeMoO_4 + 0.5\,MoO_2)$	0.53	0.11	12.0	94.2
MoO_3	13.4	1.2	$MoO_{1.8}$ $(MoO_2 + 0.1\,Mo)$	4.4	0.40	$MoO_{2.6}$ $(MoO_3 + 0.9\,MoO_2)$	0.88	0.17	7.2	93.2
V_2O_5	15.4	1.75	$V_2O_{3.25}$ $(V_2O_4 + 3\,V_2O_3)$	15.3	1.75	$V_2O_{3.26}$ $(V_2O_4 + 3\,V_2O_3)$	0.35	8.5	22.0	11.0

$[O]_{H,max}$ (g atom) is the corresponding maximum amount of lattice oxygen removed by hydrogen. $W_{P,max}$ (wt%) and $[O]_{P,max}$ are the respective maximum quantities obtained with propane as the reductant. Also listed in the table are the empirical compositions of the metal oxides after reduction (calculated from the respective, experimentally measured weight losses). $R_{H,max}$ (mg-atom$[O]_L$/g cat min) is the maximum observed reduction rate of the oxide by hydrogen and $R_{P,max}$ (mg-atom$[O]_L$/g cat min) that by propane. $T_{H,7}$ (min) is the elapsed time for the removal of lattice oxygen by hydrogen corresponding to a 7 wt% catalyst reduction (weight loss). The SHC selectivity, S_H, is defined as the fraction (expressed in Table 1 as percent) of the lattice oxygen removed from the catalyst by hydrogen, when an equimolar mixture of H_2 and propane is fed as the reducing gas over the catalyst. (See also Appendix.)

The results summarized in Table 1 reveal that with all catalysts except V_2O_5, the maximum weight loss observed with hydrogen as the reductant ($W_{H,max}$) is much larger than that observed with propane as the reductant ($W_{P,max}$). The most effective lattice oxygen removal, i.e., reduction, by hydrogen is observed with Bi_2O_3, Bi-molybdate, and In-molybdate. Their respective hydrogen selectivities, S_H, are in excess of 99%, while the hydrogen selectivity of V_2O_5 is only 11%.

The Ce- and La-molybdates are also very selective for SHC; however, they are at least 10 times less active than the Bi- and In-analogues. Since both SHC activity and selectivity are required to ultimately maximize the olefin yields attained in a two catalyst system (DH-SHC) operation, the best SHC catalyst candidates from this list, for such a process, are Bi_2O_3, and Bi- and In-molybdates.

For each molybdate studied, we also replotted the reduction rate curves of Fig. 1 by normalizing the data with respect to the hypothetical MoO_3 content of the respective molybdates (i.e., based on $Me_2Mo_3O_{12} = \text{“}Me_2O_3 \cdot 3\,MoO_3\text{”}$) and compared them to the reduction rate curves of neat MoO_3. As is seen in Fig. 4, the extent of the reductions of the Fe, Cr, Al, Ce, and La molybdates is comparable to that of the MoO_3 phase, indicating that the Mo^{6+} has been reduced to at least Mo^{4+} by hydrogen at maximum reduction (see also Table 1). Fe-molybdate is more strongly reduced, suggesting that also Fe^{3+} is reduced to Fe^{2+}, which is consistent with the empirical formula calculated from the observed maximum net weight loss (Table 1). The Al and La cations remain in the 3+ oxidation state throughout the reduction since they are presumed to be valence invariant under the conditions tested. It is more difficult to make a judgment about the final oxidation states of Ce and Cr. Probably the majority oxidation states at maximum reduction are still 3+, but some 2+ states cannot be excluded. The In- and Bi-molybdate phases are much more strongly reduced by hydrogen than the remaining molybdates of this series. Not only is Mo^{6+} strongly reduced, but so are Bi^{3+} and In^{3+}. At the maximum reduction level measured, the latter are essentially reduced to the bare metallic states (Table 1).

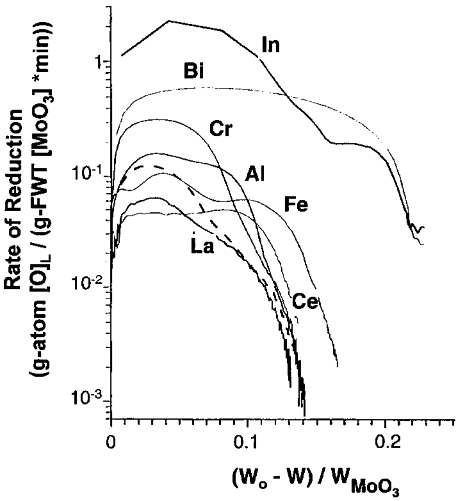

FIG. 4. Reduction rates of hydrogen over $Me_2Mo_3O_{12}$/20% SiO_2 (where Me = Bi, In, Fe, Cr, Al, Ce, and La) normalized to the hypothetical MoO_3 content of the respective molybdates, i.e., $Me_2Mo_3O_{12} = \text{“}Me_2O_3 \cdot 3\,MoO_3\text{.”}$

The maximum reduction rates with hydrogen $R_{H,max}$ (Table 1), for Bi_2O_3(7.0), $Bi_2Mo_3O_{12}$(2.0), and $In_2Mo_3O_{12}$ (9.5), are very high with respect to the remaining catalysts studied (possible exception being $Cr_2Mo_3O_{12}$), indicating their high efficiency for hydrogen combustion. This same preferred efficiency for SHC by the same trio of catalysts is also apparent (Table 1) from the quantity T_{H7}, which is the time (min) required to remove 7% of the lattice oxygen from said catalysts by hydrogen at 500°C. The respective T_{H7} values are Bi_2O_3(1.01), $Bi_2Mo_3O_{12}$(3.0), and $In_2Mo_3O_{12}$(0.8); all of these reaction times are much shorter than those needed to achieve the same level of reduction by the remaining catalysts studied.

The overall observations of SHC activity and selectivity summarized in Table 1 suggest that the lattice oxygens associated with Bi^{3+} and In^{3+} ions are extremely effective in activating hydrogen and are hence highly selective for SHC.

In still another set of demonstrative gravimetric experiments, the above oxides were reduced in separate experiments for 5 min at 500°C with hydrogen and propane, respectively, and the extent of reduction was recorded (Table 2). The experiments were designed to measure comparative rates of reduction. Among the catalysts tested, Bi_2O_3 is reduced by hydrogen most readily with 85.9% of the lattice oxygen removed in 5 min. Following in the ease of reduction are Bi- and In-molybdates, with 47.7% of their respective lattice oxygen removed in the same time span. Least easily reduced by hydrogen are MoO_3 (3.0%) and V_2O_5 (2.0%). Most readily reduced by propane is V_2O_5 (30.9%), and least readily are Bi- and In-molybdates (0.7%

TABLE 2

Selective Hydrogen Combustion (SHC) Behavior of Some Metal Oxides over a Five Minute Reduction Span at 500°C

Catalyst	$[O]_{H,5}$ (wt%)	$[O]_{H,5}$ (%)	$[O]_{H,5}/[O]_{H,max}$ (%)	$[O]_{P,5}$ (wt%)	$[O]_{P,5}$ (%)	$[O]_{P,5}/[O]_{H,max}$ (%)	S_H
$Bi_2Mo_3O_{12}$	10.3	47.7	72.9	0.10	0.47	0.7	99.0
$In_2Mo_3O_{12}$	12.9	47.7	54.0	0.21	0.78	0.9	98.4
$Al_2Mo_3O_{12}$	5.36	14.9	47.0	0.25	0.70	2.2	95.5
Bi_2O_3	8.85	85.9	90.3	0.44	4.27	4.5	95.3
$Fe_2Mo_3O_{12}$	3.32	10.2	27.7	0.21	0.65	1.8	94.0
$Cr_2Mo_3O_{12}$	6.97	21.2	67.7	0.91	2.77	8.8	88.4
$La_2Mo_3O_{12}$	1.02	4.0	13.4	0.17	0.67	2.3	85.7
$Ce_2Mo_3O_{12}$	1.04	4.1	13.3	0.27	1.07	3.5	79.3
MoO_3	1.0	3.0	7.5	0.28	0.84	2.1	78.3
V_2O_5	0.9	2.0	5.8	13.6	30.9	88.3	6.1

and 0.9%, respectively). Based on these results, the selectivity (S_H) for selective hydrogen combustion is highest for Bi-molybdate (99.0%), followed by In-molybdate (98.4%), with the least selective being V_2O_5 (6.1%). These results are in overall agreement with those of Table 1, and confirm that Bi- and In-molybdates, as well as Bi_2O_3, are excellent SHC catalysts, while V_2O_5 is not.

As an aside, the hydrogen selectivity preference over propane (S_H) of Bi_2O_3 is "only" 95.3% under the conditions of the experiments recorded in Table 2, while it is >99.9% under the conditions recorded in Table 1. The apparent discrepancy of these results lies in the fact that in Table 1 only the initial, differential selectivities of hydrogen and propane oxidation (fresh catalyst) are considered, while in Table 2 they are the integral selectivities over a relatively long (5 min) time interval, which result also in some paraffin oxidation. The 95.3% hydrogen selectivity of Bi_2O_3 is still very high, particularly in view of the severity of operation. Specifically, in an actual SHC process, the operating conditions would be adjusted in such a way that the candidate SHC catalyst would be reduced much less in any given cycle (redox mode) or under steady-state conditions (cofed mode) than the 90.3% in the experiment at hand.

From a scientific point of view, it is noteworthy that the above-discussed gravimetric results confirm our working hypothesis mentioned in the Introduction. Namely, the three best selective hydrogen combustion catalysts contain cations (i.e., Bi^{3+} or In^{3+}) which have a lone pair of electrons, and might be key (or at least one of the key requirements) for the effective and preferential activation of the hydrogen molecule over hydrocarbons. Conceivably, because of these intrinsic electronic properties these elements become key players in SHC catalysis.

Redox Mode Studies

In order to further substantiate the validity of the gravimetric studies, revealing that certain metal oxides are much superior selective hydrogen combustion catalysts than others, microreactor experiments were conducted to that end, in both redox and cofed modes.

As already explained under Experimental, in redox mode experiments a given metal oxide catalyst is exposed to reducing gases (hydrogen and/or propane/propylene) in the absence of an oxidant (dioxygen or air) for a given amount of time. In the course of the experiment, the lattice oxygen of the solid catalyst is progressively removed by the reducing gases, producing oxidized products which desorb from the catalyst surface and a reduced catalyst. Water is produced with hydrogen as feed; propylene, waste products, and water are produced from propane; and oxygenated intermediates, waste products, and water are produced from propylene. The amount of catalyst reduction is a function of the intrinsic properties of the solid, the choice of the reductant, reaction temperature, and the duration of the experiment. By utilizing the information obtained in the above-discussed gravimetric experiments, the duration of the redox experiments was set such that the total amount of hydrogen (or propane) introduced in said time interval would not exceed the theoretical amount of lattice oxygen available and contained in said catalyst to oxidize the reductants by a two electron oxidation (i.e., to H_2O in the case of H_2, or to propylene and H_2O in the case of propane). Between reduction cycles, whenever more than one reduction cycle was performed, reoxidation of the catalyst was carried out with air, at the same temperature as was the reduction, to restore the catalyst to the fully oxidized state. The extent of catalyst reoxidation depends on the intrinsic redox properties of a given system and the severity of the preceding reduction process (temperature, feed concentration, depth of catalyst reduction). With systems where no permanent catalyst restructuring (damage) occurs, the reoxidation is complete and the catalyst returns to its fully oxidized state. Such behavior would be ideal for SHC catalysis.

It might be useful at this juncture to briefly discuss the concept of SHC catalysis employed in redox mode in

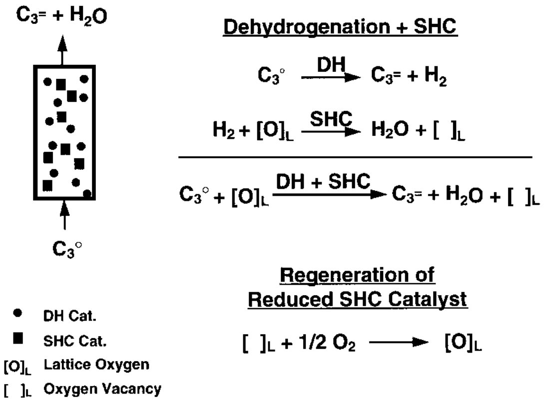

FIG. 5. Schematic of DH-SHC redox operation with the DH and SHC catalysts intermixed in a one reactor.

conjunction with dehydrogenation catalysis. There are two major possibilities for the overall (DH-SHC) process, employing the redox version of SHC. In the first version (Fig. 5) the two catalysts (i.e., the DH and SHC catalysts) are intermixed in a single reactor. The paraffin (e.g., propane) is fed over this catalyst mixture, and the hydrogen produced by the DH catalyst is oxidized *in situ* by the lattice oxygen of the SHC catalyst, allowing the production of olefin (e.g., propylene) yields in excess of equilibrium. The SHC catalyst reduces in the course of this operation, giving up its lattice oxygen in the oxidation of the hydrogen. Hereafter, the catalyst mixture must be subjected to a reoxidation cycle, in order to reoxidize the reduced SHC catalyst back to its original state. After this reoxidation, the catalyst system is ready to undergo another catalytic (DH-SHC) cycle. Therefore, this process method is cyclic rather than continuous.

The second version (Fig. 6) of a combined DH plus redox mode SHC process employs two separate reactors in series. In the first reactor, the DH catalyst produces the olefin and hydrogen in equilibrium yields (at best). In the second reactor the lattice oxygen of the SHC catalyst oxidizes the hydrogen contained in the DH effluent, thereby reducing the concentration of the hydrogen in the vapor phase, so that the effluent exiting the SHC reactor can now be led to a subsequent DH reactor, where the olefin yield produced in this third reactor can and should exceed the equilibrium level. The overall process is still cyclic, since the SHC catalyst must be reoxidized periodically to its catalytically effective original and fully oxidized state.

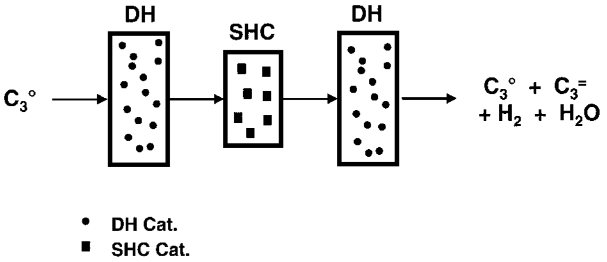

FIG. 6. Schematic of DH-SHC redox operation with the DH and SHC catalysts in separate reactors in series.

In this paper, we are not addressing the details of the various combined HD-SHC process possibilities. It is first imperative to firmly establish which oxide compositions have the potential to serve as good SHC catalysts. Therefore, we devote here our attention exclusively to the identification of SHC compositions and treat the combined DH-SHC process possibilities in a subsequent publication (1).

As already seen above from our gravimetric studies, the Bi_2O_3/20% SiO_2 system is one of the best candidates for SHC catalysis. For these reasons it was examined in redox mode at 550°C by exposing it to a feed composed of an eqimolar mixture of hydrogen and propylene over a number of cycles. The results of these competitive experiments (i.e., hydrogen and propylene are competing for the lattice oxygen of the catalyst) are shown in Fig. 7. The conversion of propylene was negligibly small (<0.5%), yielding mostly CO_2. No hydrogenated products (propane) or cracked products (ethane) were observed. Hence, virtually all of the lattice oxygen removed from the Bi_2O_3 was removed by the reacting hydrogen to produce H_2O. At least 70% of the lattice oxygen was utilized during the reduction phase of each cycle, which was readily replenished upon reoxidation with air, in reoxidation cycles interposed between each sequential reduction cycle. After 120 reduction cycles, a 15% reduction of the SHC activity of Bi_2O_3 was observed. This loss in SHC activity is due to an increase in the Bi_2O_3 crystallite size and a concomitant loss of dispersion of the active phase on the SiO_2 support. The active phase reconstruction is caused by the multiple harmful too

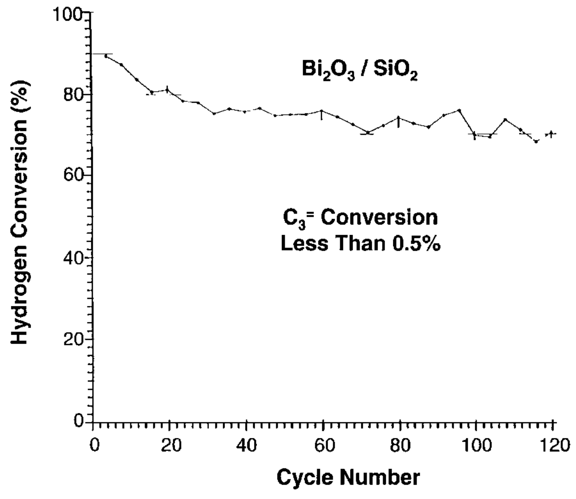

FIG. 7. Competitive conversion of hydrogen and propylene in redox mode over Bi_2O_3/20% SiO_2 vs number of redox cycles at 550°C. Feed composition = 15% hydrogen, 15% propylene, 70% He. Regeneration of the catalyst by air between reduction cycles at 550°C.

TABLE 3

Selective Hydrogen Combustion (SHC) of Some Metal Oxides at Various Flow Rates and 550°C

Catalyst	WHSV (cm^3/g min)	H_2 Conv. (%)	C_3^0 Conv. (%)	$C_3^=$ Conv. (%)
Bi_2O_3	170	74	<0.5	—
	100	66	<0.5	—
	60	88	0.8	—
Bi_2O_3	170	77	—	<0.5
	100	67	—	0.7
	40	80	—	1.2
Sb_2O_4	170	40	—	<0.5
	40	16	—	1.5
Pb_2O_3	170	16	—	<0.5
	40	~10	—	2.5
In_2O_3	170	18	—	1.4
	40	25	—	2.5
V_2O_5	170	81	23	—
	40	11	24	—

deep reductions. Shorter redox cycles, i.e., less deep reductions, will lessen catalyst damage and lead to longer sustained high catalyst efficiency (closer to that of the fresh catalyst). Alternatively, various Bi-compounds (including select molybdates) are much more stable to repeated redox cycles than is Bi_2O_3 alone. This will be the subject of a forthcoming publication.

The SHC activities of Bi_2O_3 and V_2O_5 at different flow rates, but at the same H_2/[O] ratio of 1.0, are shown in Table 3. As explained above, a H_2/[O] ratio of 1.0 simply means that irrespective of flowrate the total duration of a redox experiment or cycle is only so long as to pass over the Bi_2O_3 catalyst the stoichiometric amount of hydrogen theoretically required to reduce Bi^{3+} to Bi^0, and in the case of V_2O_5 to reduce V^{5+} to V^{3+}. As is apparent from the results, the hydrogen conversion is not very different at different flowrates for the Bi_2O_3 catalyst, while the propane conversion is not very different for the V_2O_5 catalyst. This suggests that the intrinsic reaction rate of hydrogen oxidation by the lattice oxygen of the Bi-oxide is much higher than the flowrates used in the experiments, as is the intrinsic rate of propane oxidation by lattice oxygen of the V-oxide. Within these experimental constrains the respective catalysts remain active and selective. Conversely, as is well known in oxidation catalysis, the rates of hydrogen oxidation and hydrocarbon oxidation will drop sharply and eventually vanish, as the lattice oxygen of the metal oxide becomes significantly depleted (at about 70–90% reduction with Bi_2O_3). For obvious reasons and as a limiting case in redox mode experiments (i.e., no dioxygen present), all oxidations of reductants have to cease in the absence of available lattice oxygen.

From Table 3 it is again apparent that the efficiency with which Bi_2O_3 oxidizes hydrogen is enormous in comparison to its oxidation of propane or propylene. About 99% of the lattice oxygen of Bi_2O_3 reacted with H_2 while less than 1% reacted with propane to produce propylene and CO_x. Similarly superior is the efficiency of Bi_2O_3 for hydrogen oxidation over that of propylene oxidation. These data are consistent with, and confirm, our gravimetric findings discussed above.

Also in Table 3 are summarized comparative data on Sb_2O_4, Pb_2O_3, In_2O_3, and V_2O_5. It is seen that Sb-, Pb-, and In-oxides all preferentially attack hydrogen to propylene, and are thus similar in behavior to that of Bi_2O_3. They hold some potential as SHC catalysts, but need further study and definition.

In sharp contrast stands V_2O_5, which oxidizes propane (and propylene) with great preference to hydrogen. This comes particularly to the fore at somewhat longer contact times, e.g., at a WHSV of 40 cm^3/g min, where 24% of the propane feed was converted to propylene (27% selectivity) and CO_x (73% selectivity), but only 11% of the H_2 to H_2O. As a result about 94% of the V_2O_5 lattice oxygen atoms reacted with propane to produce propylene and CO_x while only 6% of the lattice oxygen atoms reacted with H_2 to produce H_2O. It is obvious that V_2O_5 is a rather ineffective SHC catalyst and cannot be used for such a purpose. Again, here, the data, observations, and conclusions gathered from the redox mode microreactor experiments are consistent with the observations and conclusions drawn from the above-discussed gravimetric experiments.

Cofed Mode Studies

The process arrangement of the cofed mode (Fig. 8) is identical to the second version of the redox mode (Fig. 6), except that in the cofed mode dioxygen is supplied in sufficient quantity to the SHC reactor to convert the hydrogen, coming from the first DH reactor, to water. The idea is to keep the SHC catalyst continuously regenerated by dioxygen, and hence in a high and catalytically effective state. The effluent from the SHC reactor, free of hydrogen and oxygen, is brought to a second DH reactor, where subsequent dehydrogenation of the hydrogen lean stream leads to olefin yields in excess of the thermodynamic limitation. A simple calculation based on thermal data predicts that the propylene yield at 550°C using the scheme shown in Fig. 8

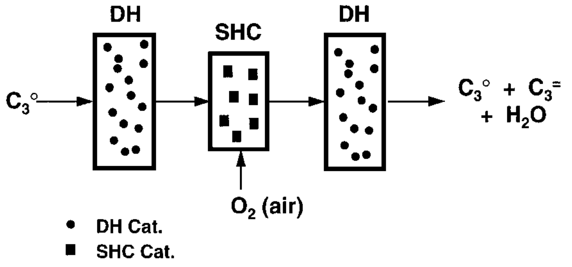

FIG. 8. Schematic of DH-SHC cofed operation. Regeneration of the SHC catalyst occurs continuously with cofed O_2.

(DH-SHC-DH) would theoretically increase to 46.3% from the 31.6% attainable by conventional DH alone. This is approximately a 47% olefin yield enhancement. The potentially continuous process operation of the cofed mode presents an advantage over either of the redox modes discussed above, both of which are inherently cyclic in nature. However, distinct advantages of the redox operation are that air instead of dioxygen could be used to regenerate the SHC catalyst and that the reduction and reoxidation are completely separated from each other, eliminating potential safety hazards.

In order to explore whether SHC catalysts identified as effective in redox operation are also effective in cofed mode, we examined the SHC properties of some of these in the presence of cofed oxygen under steady-state conditions. Specifically, the activity and selectivity of Bi_2O_3 in the cofed mode were examined in the automated microreactor setup, using H_2/propane/O_2 and H_2/propylene/O_2 feed mixtures. The respective H_2/hydrocarbon mixtures were equimolar, and the amount of dioxygen was stoichiometric, i.e., sufficient to convert all of the H_2 to water. Such competition experiments, using these three reactant gas mixtures, should provide an insight into which metal oxides are suitable also for cofed SHC operation.

The conversions of hydrogen and propane at 500°C as a function of residence time (1/WHSV) are shown in Fig. 9. The propane conversion, mostly to CO_2, was always less than 2%, while the conversion of hydrogen exceeded 90% at high residence time. This indicates that the deliberately limited (stoichiometric) supply of cofed oxygen had been utilized very effectively and selectively to preferentially combust the hydrogen gas.

The corresponding results with a H_2/propylene mixture at 450°C are shown in Fig. 10. The solid lines correspond to a 15% $C_3^=$/15% H_2/7.5% O_2/62.5 He feed. The dashed line is the propylene conversion obtained in the absence of cofed hydrogen, with a feed composition of 15% $C_3^=$/0% H_2/7.5% O_2/77.5 He. The selectivity of Bi_2O_3 for hydrogen combustion in the presence of propylene is still high, although not as high as in the hydrogen/propane/oxygen case. It is, however, noteworthy that the propylene conversion is lower when hydrogen is present than when it is absent, indicating preferential reaction of hydrogen under reaction conditions on the oxide surface, thereby helping to inhibit the activation and combustion of propylene to CO_x. This is a favorable intrinsic property of Bi_2O_3 and its compounds (e.g., Bi-molybdates), which can be beneficially exploited in an overall DH-SHC process concept.

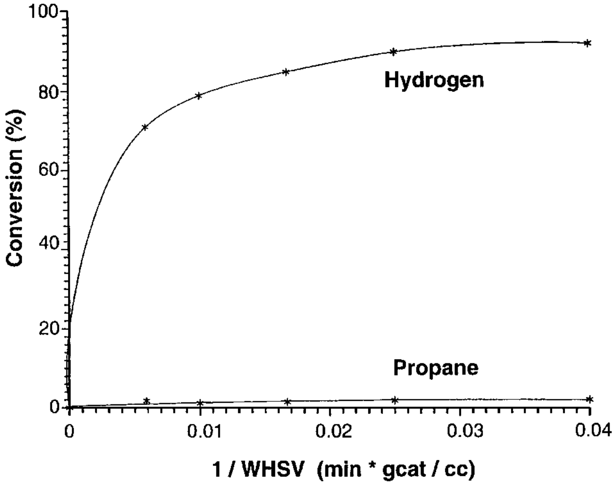

FIG. 9. Competitive conversion of hydrogen and propane in cofed mode over Bi_2O_3/20% SiO_2 vs residence time (1/WHSV) at 500°C. Feed composition = 15% hydrogen, 15% propane, 7.5% O_2, 62.5% He.

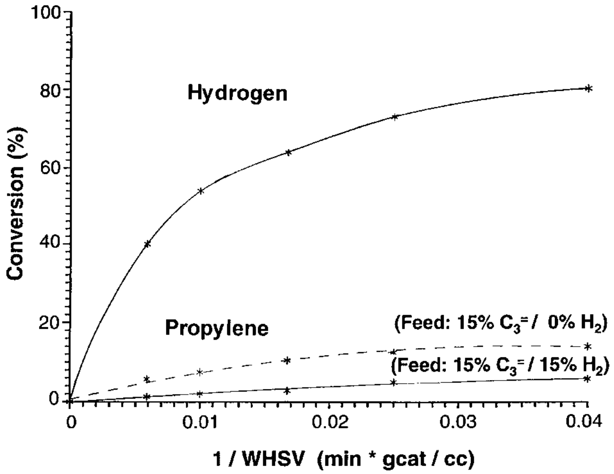

FIG. 10. Competitive conversion of hydrogen and propylene in cofed mode over Bi_2O_3/20% SiO_2 vs residence time (1/WHSV) at 450°C. Feed composition = 15% hydrogen, 15% propylene, 7.5% O_2, 62.5% He, or 15% propylene, 7.5% O_2, 77.5% He.

Although the lattice oxygen content of the catalysts was not experimentally determined after the cofed experiments, it is presumed to be essentially the same as at the beginning of the experiment. This presumption is based on the relative ease of reoxidation compared to reduction of Bi-molybdates, particularly at elevated temperatures, i.e., >350°C (23). Since oxygen breakthrough needs to be avoided, it is possible that in fixed bed operation the SHC catalyst might be slightly reduced on the exit line. To prevent this from occuring, periodic reversal of the feed flow, through appropriate valving is suggested. Again, these more practical aspects of the process are addressed in additional publications (1).

SUMMARY

A number of metal oxides were identified as superb SHC catalysts. The named oxides attack hydrogen with great preference to light hydrocarbons, such as propane or propylene, when mixtures of these are passed over them at temperatures in the range of 500°C. Most effective among these oxides is Bi_2O_3 with a selectivity in excess of 99%, followed by $Bi_2Mo_3O_{12}$ with a 99% selectivity and $In_2Mo_3O_{12}$ with a 98.4% selectivity. Other trivalent molybdates, as well as MoO_3 by itself also oxidize hydrogen preferentially to hydrocarbons, but with lower hydrogen selectivities: Al(95.5), Fe(94.0), Cr(88.4), La(85.7), Ce(79.3), and Mo(78.3). In marked contrast to these compositions is V_2O_5, which is unselective for hydrogen combustion with only a 6.1% selectivity; it preferentially attacks (and combusts) hydrocarbons, e.g., propane and propylene.

The most selective hydrogen oxidants, Bi_2O_3, $Bi_2Mo_3O_{12}$, and $In_2Mo_3O_{12}$, are also the most active ones. Under comparable experimental conditions (Cahn balance, H_2, 500°C, 5 min), the lattice oxygen removed amounted to 85.9, 47.7, and 47.7%, respectively, of the theoretical limit. The remaining molybdates studied lie in the range of 21.2% ($Cr_2Mo_3O_{12}$) to 4.0% ($Ce_2Mo_3O_{12}$) and are hence less desirable as SHC catalysts. Least effective are MoO_3(3.0) and V_2O_5(2.0).

The compositions Bi_2O_3, $Bi_2Mo_3O_{12}$, and $In_2Mo_3O_{12}$ exhibit the highest activities and the highest selectivities for hydrogen oxidation. Hence, they are currently our top choices as SHC catalysts for proposed future DH-SHC combination processes to attain olefin yields in excess of equilibrium. The actual process studies are reported in separate publications (1).

As an aside and possibly of some scientific merit is our observation that the best SHC compositions contain at least one element which has a lone pair of electrons at its oxidation state prevailing during initial (redox) and/or steady-state (cofed) process operations. It is hypothesized that these electronic states facilitate the attack of the hydrogen molecule by the lattice oxygen, by means of the intrinsic properties imposed on the activated lattice oxygen by the specified elements (cations) of the named compositions. To this group of cations belong Bi^{3+}, In^{3+}, and Sb^{3+}, identified in this study as potentially key ingredients of effective SHC catalysts. Future studies are aimed at expanding this list of candidates and at further enhancing the fundamental understanding of the workings of SHC catalysts.

APPENDIX

The selectivity S_H for hydrogen conversion over that of the hydrocarbon (i.e., propane) can be estimated from the data of Figs. 2 and 3, assuming that the rate curves for the individual reducing agents are also valid for equimolar H_2/C_3 mixtures. Assuming that $[O]_H$ and $[O]_P$ are the amounts of lattice oxygen incorporated into the combustion products of H_2 and C_3, respectively, then

$$d[O]_H/dt = R_H([O])$$

$$d[O]_P/dt = R_P([O])$$

with

$$[O]_H = [O]_P = 0 \quad \text{at } t = O,$$

where $[O] = [O]_H + [O]_P$ is the extent of reduction, and R_H and R_P are the reduction rates with hydrogen and propane, respectively, and are graphically represented in Figs. 2 and 3. The fraction of lattice oxygen consumed by hydrogen after completion of the reduction, $S_H = [O]_H/([O]_H + [O]_P)$, is given by

$$S_H = 1/[O]_{max} \int_0^{[O]_{max}} R_H/(R_H + R_P)\, d[O],$$

where $[O]_{max}$ is the lattice oxygen availability. S_H was calculated numerically and is listed in Table 1.

ACKNOWLEDGMENT

R.K.G. acknowledges gratefully the receipt of an Alexander v. Humboldt prize during which time this paper was written.

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