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Selective oxidation of propylene to propylene oxide using combinatorial methodologies

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Abstract

Direct oxidation of propylene by oxygen to propylene oxide (PO) has been studied through the application of the techniques of combinatorial catalysis. Catalytic materials containing single and binary metal components were prepared by impregnating standard γ-Al_2O_3 pellets. In the first stage, 34 single component catalytic materials at three different metal loading levels were prepared and screened for PO activity and selectivity using array channel microreactors and mass spectrometry. Experiments were conducted at a GSHV of 20,000 h^{-1}, 101 kPa pressure and over a temperature range of 200–350 °C. Following a matrix inversion technique to deconvolute the mass spectrometric intensity measurements, signals that were directly attributable to PO were calculated. From these determinations, the elements Rh, Mn, and Mo were the most PO active single metal catalysts on γ-Al_2O_3. For acetone (AT) Rh, Pb, and Ir were somewhat effective, while Cu, Mn, and W favored some acrolein (AL) formation. In the second step, catalytic materials containing binary combinations of metals were prepared using a variety of strategies. However, the binary catalytic materials that exhibited the highest PO production levels always contained Rh. The binary combinations that exhibited superior PO production levels were Rh–V, Rh–Cr, Rh–Sn, Rh–In, Rh–Mo, and Rh–Sm, albeit substantial CO_2 formation. On the other hand, Rh–Ag, Rh–Zn, and Rh–Cr combinations were significant leads with regard to high PO and low CO_2 production. These findings call for the undertaking of detailed secondary screening studies to confirm the primary screening results reported here and to obtain information on the durabilities of these catalytic materials.

Keywords: Parallel catalyst evaluation; High-throughput screening; Mass spectrometry

1. Introduction

Propylene oxide (PO) is one of the most important building blocks used in the production of a large variety of valuable consumer products. Over 10 billion pounds of PO reproduced annually, and are converted into products such as urethane forms, polymers, cosmetics, and food emulsifiers and additives [1].

At present there are two major industrial processes used for the synthesis of PO: the chlorohydrin and peroxide processes [2]. In the chlorohydrin process, propylene is reacted first with HOCl forming propylene chlorohydrin (PC), followed by the reaction of PC with $Ca(OH)_2$ to form PO and $CaCl_2$ as a co-product. Nearly 50% of PO capacity is currently based on this method. The major drawback of the chlorohydrin process is that it requires the use of chlorine, which is an expensive, toxic and corrosive reagent and can also produce highly toxic chlorinated organic by-products. In addition, the handling of large volumes of chlorined

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water and the disposal of co-product $CaCl_2$ also creates significant ecological problems [2].

In the peroxide process, organic peroxides are first produced by liquid phase air oxidation of the parent feedstock, followed by epoxidation in the presence of a transition metal catalyst and the formation of PO and a co-product [2]. The economic viability of this method of production of PO depends largely on the market value of the co-product. The two most widely used feedstocks are isobutane, which yields isobutanol as a co-product (TBHP-process), and ethylbenzene, which yields styrene as the co-product (SMPO-process) [2]. To meet economical as well as ecological issues, numerous efforts have been made in search for an alternative process for these conventional methods.

The direct gas-phase oxidation of propylene by molecular oxygen has long been the most desirable as well as challenging goal of production of PO. However, despite considerable effort, no economically viable catalyst has yet been found. Most publications show either low selectivity or low conversion. Although the direct oxidation of ethylene by molecular oxygen to ethylene oxide has been commercialized with a silver catalyst, it is known that the analogous direct oxidation of propylene exhibits a low selectivity of less than 15% [3]. Some patents suggest the use of metal-promoted silver catalysts for PO synthesis. These promoted catalysts also exhibit low selectivity to PO [4,5]. Multi-component systems such as copper–phosphate–potassium, uranium dioxide, or thallium–cobalt mixed oxides have been reported for the gas-phase oxidation of propylene, all of which suffer from low PO selectivity [6]. In fact, the production of PO by the direct, i.e. non-catalytic, gas-phase interaction of propylene and oxygen was higher than in the presence of catalysts considered [6].

Gold exhibited high selectivity when finely dispersed on titania catalysts in the presence of hydrogen. Haruta and co-workers have reported of more than 90% PO selectivity with 1–2% conversion at temperatures between 303 and 393 K and at a space velocity of about 1000 h^{-1} [7]. In subsequent papers [8–11] the researchers also reported PO and/or propanal (PaL) formation from propylene, and the promotional effect by cesium which had significant influence on H_2 and O_2 consumption over Au/Ti-MCM-41 catalysts. While Nijhuis et al. [12] confirmed the reproducibility of the results over Au/TS-1 and Au/TiO_2, they have also suggested that high yields of PO may be limited by the oligomerization of PO. Some recent patents also claim high selectivity to PO by passing propylene, H_2 and O_2 over novel supported precious metal catalysts (mainly Au-based); however, the yields were generally under 1% [13].

Silica-supported, sodium promoted iron oxide catalysts were found to catalyze the gas-phase oxidation of propylene with nitrous oxide. PO selectivity of 40–60% at 6–12% propylene conversion was achieved [14]. However, the use of nitrous oxide as a reactant renders this process uneconomical.

In conclusion, a significant need continues to exist for the development of an efficient direct route to propylene oxide through the use of heterogeneous catalysis. In order to address this need, our laboratory initiated an effort for the discovery and optimization of highly active and selective catalysts to convert propylene and oxygen into PO through the use of combinatorial catalysis tools and methodologies.

1.1. Combinatorial approach

Combinatorial catalysis or high-throughput experimentation is increasingly becoming an indispensable tool for discovery and optimization of new materials, including heterogeneous catalysts [15]. Having a large impact in the pharmaceutical and biotechnology industries, the combinatorial approach is rapidly spreading to every field of science and engineering where the synthesis and evaluation of large diversities of new materials are needed. Combining automatic synthesis procedures with fast and accurate analytical instruments the time periods associated with the discovery and optimization of new materials can dramatically be shortened compared to traditional methods [16–25].

Heterogeneous catalysis, where compositional and structural change of the material greatly influences its activity and selectivity, is also poised to benefit from this new technology [15,22]. In the combinatorial approach, large diversities of distinct catalytic materials are prepared, processed and tested in parallel using specialized reactors and requisite instruments. Although the concept of parallel testing of catalytic materials is not new [26], it is only recently that such approaches became viable due to advances made in laboratory instrumentation, automation, robotics, computers and software.

In this report the first systematic application of combinatorial methodologies to the selective catalytic oxidation of propylene to propylene oxide is presented. The catalytic activities and selectivities of single metals as well as their binary combinations on γ-Al_2O_3 were studied at various metal loadings as a function of temperature at atmospheric pressure. Other support materials, such as titania, ceria, zirconia and silica are presently under investigation and the results of these studies will be reported in the future.

2. Experimental

Catalyst preparation and testing were performed using the experimental systems shown in Fig. 1, the details of which have been presented previously [18]. The reactor part consists of four microreactor arrays (A), a quartz gas feed line and a stainless-steel heating block (B) to control the temperature of the reactor. The position of the reactor relative to the detection system is controlled by the computerized precision motion system (C). An electron impact quadrupole mass spectrometer (MS) is stationed at the front of the reactor, which measures mass-to-charge ratio of ionized molecules.

All of the catalytic materials were prepared using the following standardized procedure. First, libraries of metal salt solutions were prepared by dispensing pre-determined volumes of stock solutions into arrays of glass tubes (see Fig. 1). Table 1 lists the commercially available metal salts used in this investigation. A standard pellet of γ-Al_2O_3 (23 mg, 4 mm diameter by 1 mm high cylinders) was then introduced into each glass tubes of the library to affect impregnation. However, pellets were immersed in 50:1 of deionized H_2O prior to their contact with the metal salt solutions. The libraries were then heated at a rate of 10 °C/min to 110 °C, and dried at that temperature overnight. After drying, the library was heated to

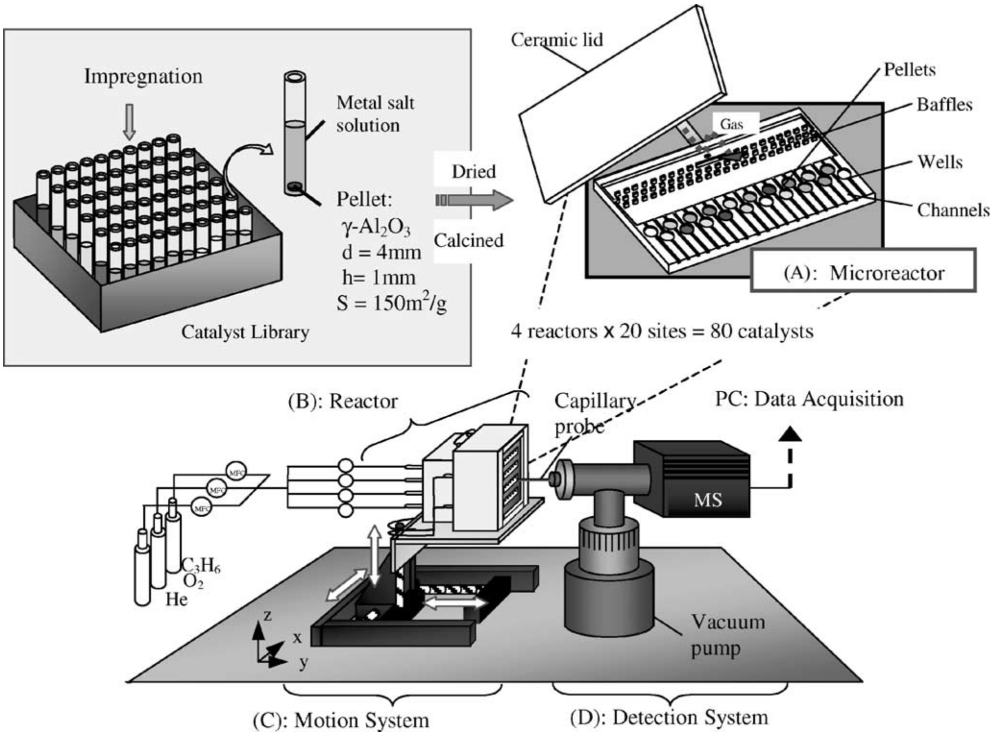

Fig. 1. Combinatorial catalysis system. Catalyst library is prepared by impregnating standard pellets of γ-Al_2O_3. Catalyst evaluation system consists of four array channel microreactors (A) placed inside a stainless-steel heating block (B). Computer controlled *x*–*y*–*z* motion system (C) moves the reactor block, and products are withdrawn by a capillary tube and analyzed by MS (D).

Table 1
Metal salt precursors used

Group	Me	Precursor
[1A]	Li	$LiNO_3$
	Na	$NaNO_3$
	K	$K\ NO_3$
[2A]	Mg	$Mg(NO_3)_2$
	Ca	$Ca(NO_3)_2$
	Sr	$Sr(NO_3)_2$
	Ba	$Ba(NO_3)_2$
[3A]	Y	$Y(NO_3)_3$
	Ce	$Ce(NO_3)_3$
	Sm	$Sm(NO_3)_3$
[4A]	Ti	$(NH_4)_2TiO(C_2O_4)_2$
[5A]	V	NH_4VO_3
	Nb	$NbCl_5$
[6A]	Cr	$Cr(NO_3)_3$
	Mo	$(NH_4)_2MoO_4$
	W	$(NH_4)_{10}W_{12}O_4$
[7A]	Mn	$MnCl_2$
[8A]	Fe	$Fe(NO_3)_3$
	Co	$Co(NO_3)_2$
	Ni	$Ni(NO_3)_2$
	Ru	$RuCl_6$
	Rh	$RhCl_3$
	Pd	$PdCl_2$
	Os	$(NH_4)_2OsCl_6$
	Ir	$IrCl_6$
	Pt	$PtCl_6$
[1B]	Cu	$Cu(NO_3)_2$
	Ag	$AgNO_3$
	Au	$HAuCl_6$
[2B]	Zn	$Zn(NO_3)_2$
[3B]	In	$In(NO_3)_3$
[4B]	Sn	$SnCl_2$
	Pb	$PbCl_4$
[5B]	Bi	$Bi(NO_3)_3$

500 °C at a rate of 20 °C/min, and calcined at that temperature for 2 h. Both the drying and calcination processes were performed at ambient pressure. In the case of multimetallic catalysts, elements were co-impregnated using mixtures of precursor solutions. However, when incompatible solutions were involved, e.g. $AgNO_3$ and chlorides, sequential impregnation was practiced. The levels of metal loading were also explored by ICP-AES (Thermo-Jarrel, Ash-Iris 1000, Atomic Emission Spectrometer). For this, both the supernatants and the acid-dissolved (HF) solutions of pellets were monitored.

Calcined pellets were placed into the wells of the ceramic array microreactors, and the microreactors were then placed inside the stainless-steel heating block, which holds four such arrays. With 20 pellets per microreactor bank, up to 80 different catalytic materials can be tested in a single experiment. Thermocouples and electrical heating cartridges are inserted within the heating block, with proportional–integral–derivative (PID) controllers maintaining the temperature of the reactors. The feed gases delivered by the quartz feed line were also preheated to the reaction temperature. The system was designed in such a way that all the 20 sites in each array had identical reaction conditions, while each bank could be run under different operating conditions. Nevertheless, in the present set of studies, all the microreactors were operated under identical conditions [17,18]. This way, the results would primarily be sensitive to the catalytic materials prepared and not to operating conditions. Consequently, it was possible to rapidly rank order of catalytic materials for their performance towards product formation.

Experiments were performed under atmospheric pressure and in the temperature range of 200–350 °C with 50 °C increments and at GSHV of 20,000 h^{-1}. It should be noted that this space velocity is significantly higher than those reported in the literature by a factor of about 10 [7–13]. Consequently, lower conversions of propylene would be expected in the experiments reported here. A variety of feed gas mixtures were evaluated first to obtain a suitable feed composition that produced high PO signals as measured by the MS. These investigations resulted in the selection of the following feed gas composition: C_3H_6 40%, O_2 10%, He 50%. High purity gases (+99.99%) were acquired from standard sources (Matheson, Cucamonga, CA), and were used directly without any treatment. Gas flows were controlled by digital electronic mass flow controllers (MKS, Andover, MA). All the experiments, including data acquisition by MS, were conducted under total computer control. Product gases exiting the microreactor channels were sequentially withdrawn by a capillary sampling line and analyzed immediately by the mass spectrometer. The mass spectrum covering the 2–60 amu range was scanned four times for each reactor and averaged to improve signal to noise ratio. Nearly 1 min was allotted to position the capillary sampling probe into the microreactor channels, to flush and saturate the lines with fresh product samples and to complete the multiscan mass spectrometric analysis. Thus, it was possible to screen 80 catalytic materials in about 2 h. As discussed in earlier publications, it is possible to significantly increase the speed of data acquisition by using faster scan speeds. However, this is achieved at a loss of signal to noise ratio, which can be detrimental for the detection of low concentration species.

2.1. Data analysis

The partial oxidation of propylene can form a large variety of products besides propylene oxide [6,27]. These co-products include acetone, acrolein and propanal, all of which have close molecular weights and with overlapping mass spectrometric fragmentation patterns [28]. Consequently, electron impact mass spectrometry cannot directly be used to assess PO levels present in microreactor effluents. Consequently, we developed and utilized a matrix inversion technique to deconvolute the MS signals and to arrive at measurements that were directly attributable to PO [27].

This was accomplished by considering the following properties of mass spectrometry. First, the total intensity measured at any mass number (n) is a linear combination of all the contributions from different compounds in the gas mixture plus the background:

$$I_n^{\text{total}} = I_n^{\text{compounds}} + I_n^{\text{background}}$$

where the background intensity that can be obtained from a blank site in the reactor array. In addition, the ratios of the abundances of the fragments of a compound A (α^{A}) are constant in a given experiment, that is:

$$\alpha_{nm}^{\mathrm{A}} = \frac{I_n^{\mathrm{A}}}{I_m^{\mathrm{A}}}$$

where I_n and I_m are abundances at mass numbers n and m, respectively. The α_{nm}^{A} values for all the compounds expected to be present in a mixture can be determined in separate experiments. For the partial oxidation of propylene, the likely products are shown in Table 2, together with the corresponding α values of the mass peaks relative to the largest peak observed (denoted by 1) for each compound.

In the present experiments all the major mass ion numbers indicated in Table 2 were monitored. For example, the following four equations would be considered to obtain the levels of PO in the presence of AT, AL, PaL as interferences:

$$I_{55} = \alpha_{55}^{\mathrm{AL}}\, I_{56}^{\mathrm{AL}} + \alpha_{55}^{\mathrm{PaL}}\, I_{58}^{\mathrm{PaL}}$$

$$I_{56} = I_{56}^{\mathrm{AL}} + \alpha_{56}^{\mathrm{PaL}}\, I_{58}^{\mathrm{PaL}}$$

$$I_{57} = \alpha_{57}^{\mathrm{AL}}\, I_{56}^{\mathrm{AL}} + \alpha_{57}^{\mathrm{AT}}\, I_{58}^{\mathrm{AT}} + \alpha_{57}^{\mathrm{PO}}\, I_{58}^{\mathrm{PO}} + \alpha_{57}^{\mathrm{PaL}}\, I_{58}^{\mathrm{PaL}}$$

$$I_{58} = I_{58}^{\mathrm{AT}} + I_{58}^{\mathrm{PO}} + I_{58}^{\mathrm{PaL}}$$

These four equations can then be solved for the four unknown product intensities, I_{58}^{AT}, I_{58}^{PO}, I_{58}^{AL} and I_{58}^{PaL} to obtain the level of PO (e.g. I_{58}^{PO}) in the mixture. This procedure was undertaken for all the possible contributing species in all the experiments. For select promising catalysts, the validity of these calculations was also confirmed by gas chromatography/mass

Table 2
Intensity factor α

	Mass number									
	41	42	43	45	55	56	57	58	59	60
PR	1.000	0.662	0.026							
AL		0.026			0.703	1.000	0.055			
AT	0.064	0.207	3.049				0.030	1.000	0.034	
PO							0.163	1.000	0.036	
PaL	0.019	0.038	0.017		0.027	0.019	0.268	1.000	0.062	
AlL	0.077	0.021	0.064		0.064		1.000		0.011	
iPL	0.064	0.030	0.143	1.000					0.045	
PoL	1.288	2.045	0.621	0.227			0.152		1.652	1.000

PR: propylene, AL: acrolein, AT: acetone, PaL: propanal, AlL: allyl alcohol, iPL: isopropyl alcohol, PoL: propanol.

spectrometry (GC/MS, Hewlett-Packard 5890/5972). In this case, the peak elution times together with mass spectral fingerprints shown in Table 2 were considered. Clearly, under some experiments when PO is not a dominant product, considerable uncertainty would exist on the accuracy of the I_{58}^{PO} signals calculated by the above procedure, especially when PaL is also produced. This uncertainty arises from the fact that $\alpha_{57}^{\mathrm{PaL}}/\alpha_{57}^{\mathrm{PO}}$ is only 1.64 (0.268/0.163, see Table 2), which renders the numerical separation of the combined $I_{58}^{\mathrm{PO}} + I_{58}^{\mathrm{PaL}}$ signals into its components difficult. However, under these circumstances, the combined $I_{58}^{\mathrm{PO}} + I_{58}^{\mathrm{PaL}}$ signals or the total I_{58} intensity measured by the mass spectrometer would still be useful as a primary screening protocol. As a consequence of these issues, the PO concentrations reported here should be used with caution. As in any catalyst discovery program, the initial leads must be followed up by the more detailed secondary screening experiments to validate the results of primary screening and to better establish the selectivities of the promising catalytic materials. Time on stream or durability testing of catalyst leads can also be undertaken in the secondary screening program.

Intensities for each compound were calculated separately by linear regression, and were converted into absolute concentrations using pre-determined intensity–concentration calibration curves [27]. In the present experiments, propylene conversions were deliberately kept at levels 1–2% to maintain isothermal operating conditions in the microreactors. Otherwise hot spots may arise at certain sites, and this will render the rank ordering of the catalytic materials difficult. Propylene conversions were determined from the following relation:

$$\text{Conversion (\%)} = \frac{(\mathrm{C_3H_6})_{\mathrm{in}} - (\mathrm{C_3H_6})_{\mathrm{out}}}{(\mathrm{C_3H_6})_{\mathrm{in}}} \times 100$$

3. Results and discussion

3.1. Single component catalytic materials

With 34 elements and three loading levels (0.1, 1.0, and 10 wt.% of 23 mg pellet), 102 single component catalytic materials were prepared, processed and tested for PO productivity using the experimental procedures described earlier. This range of loading is expected to create a good diversity of catalytic materials from well dispersed small metal/metal-oxide ensembles at 0.1% loading to large clusters at 10% loading. The specifics of the preparation method, e.g. the calcination temperature and atmosphere, also influences metal dispersion and cluster size. However, these issues were largely avoided in the current program by adopting a standard preparation method. Clearly when high-throughput characterization techniques become available, they can be used to characterize the catalytic materials prepared.

First, the general effects of temperature and feed gas composition were explored to identify suitable operating conditions conducive to PO formation. In Fig. 2, the effects of reaction temperature (A) and feed propylene concentration (B) on PO concentration (i.e. the I_{58}^{PO} signals converted into parts per million (ppm) using calibration standards) in reactor effluents are presented. As can be seen from these results, the temperature of 250 °C and a feed gas composition of 40% propylene, 10% oxygen, and 50% helium, appeared optimal with regard to maximizing the PO signals as measured by MS. The effect of temperature on PO formation is obvious as high temperatures are expected to result in the formation of total oxidation products. Higher propylene and oxygen concentrations also resulted in lower PO levels, probably due to excessive combustion.

In Fig. 3, the reactor exit concentrations of PO, in parts per million units, again derived from the I_{58}^{PO} signals, are presented together with those of AT and AL at 250 °C for each of the 34 elements and loadings. An inspection of Fig. 3 reveals that the most PO active catalysts were 1.0% Rh, followed by 0.1% Rh, 10% Mn, and 10% Mo. The maximum PO level observed was about 1000 ppm at 1.0% Rh at 1% conversion of $\mathrm{C_3H_6}$. Similarly, the most acrolein active elements were Cu, Mn, and W and those producing the most acetone were Rh, Pb, and Ir.

A close examination of the results presented in Fig. 3 also reveal several features. First, although the PO productivity of Rh catalysts increased with increasing loading from 0.1 to 1%, the PO levels were significantly lower for the 10% Rh catalysts. On the other hand, increases in both Mo and Mn loadings steadily increased PO production within the entire range explored. These results demonstrate the fact that

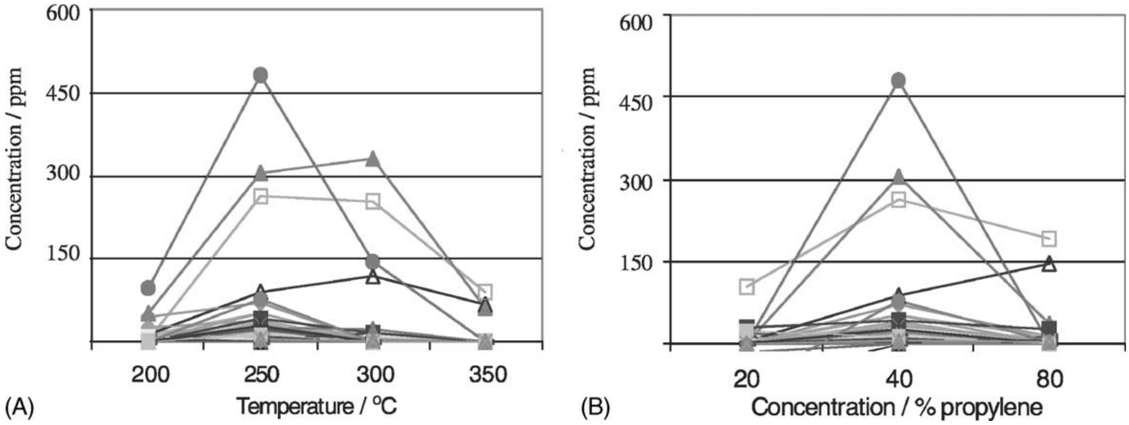

Fig. 2. The effects of operating conditions on mass 58 intensity using a variety of Rh-containing catalysts. (A) $T = 200–350\,^{\circ}C$, 40% propylene feed, $20{,}000\,h^{-1}$ GHSV (left); (B) $T = 250\,^{\circ}C$, 20–80% propylene feed, $20{,}000\,h^{-1}$ GHSV (right). Most of the catalysts performed best at $T = 250\,^{\circ}C$, 40% propylene.

different metals disperse differently on the γ-Al_2O_3 substrate forming different catalytic clusters and sites, and call for the need to undertake characterization studies.

The catalytic materials investigated also produced significant levels of CO_2 as shown in Fig. 4, reaching levels as high as 8000 ppm. Not surprisingly Rh, Pt, Pd, and Ir were also the most effective combustion catalysts. However, in all of these cases, CO_2 production steadily increased with metal loading. Clearly, the catalytic materials determined to be highly active for the corresponding products should be characterized fully to develop a better understanding of their morphology, as well as their surface chemical and physical structures responsible for the observed catalytic function.

3.2. Binary catalytic materials

Binary catalytic materials were prepared by combining the metals at loadings identical to the single

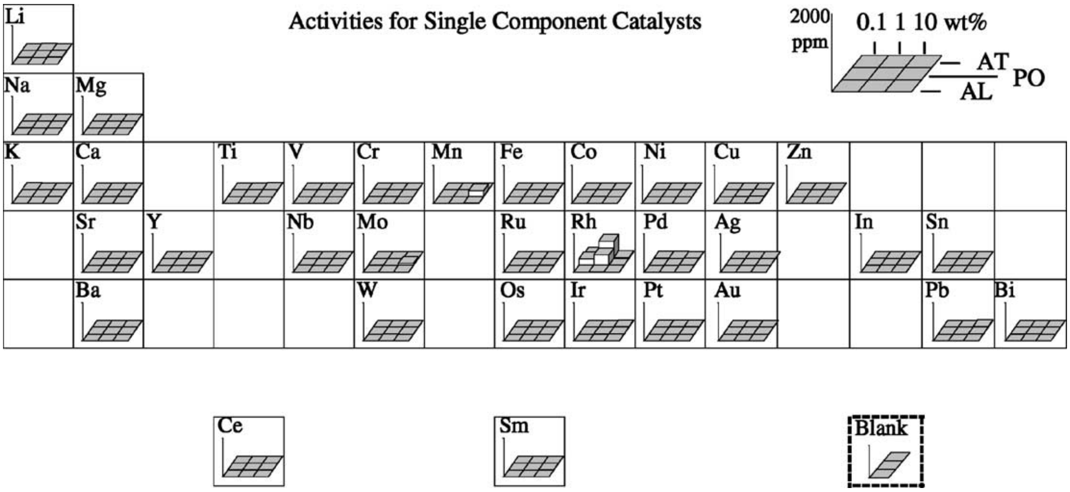

Fig. 3. Reactor exit concentrations of PO, AT and AC as a function of metal loading in the periodic table format. Feed gas $20{,}000\,h^{-1}$ GHSV, $C_3H_6/O_2 = 4/1$, $T = 250\,^{\circ}C$, 40% propylene.

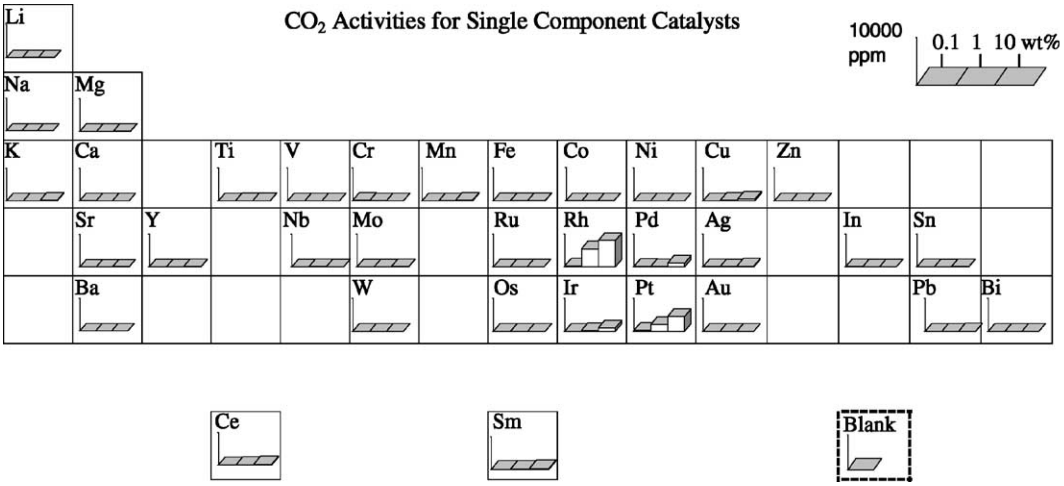

Fig. 4. Reactor exit concentrations of CO_2 as a function of metal loading in the periodic table format. Feed gas 20,000 h^{-1} GHSV, $C_3H_6/O_2 = 4/1$, $T = 250\,^\circ C$, 40% propylene.

component experiments described above. The reactivity performances of the binary catalytic materials were then evaluated under the same operating conditions of 40% propylene and 10% oxygen feed, temperature of 250 °C, and 20,000 h^{-1} of GHSV. Three different procedures were used to prepare the binary combinations:

Set A. Selection from periodic groups: In this case two elements, one PO active and one PO inactive, were selected from each periodic group resulting in a total of 153 different catalytic materials.

Set B. Selection from Top 20: Top 20 PO active elements were selected and combined to generate 190 different catalytic materials.

Set C. Rh-based catalysts: Rhodium, the highest PO producing single metal, was combined with other elements at three loading levels, to generate 102 different catalytic materials. The level of Rh was kept at 1% in each case.

In Fig. 5 the levels of PO formed in parts per million by the binary catalytic materials, prepared in accordance with the protocols of Sets A and B, are presented. Specific catalyst compositions are indicated by the intersection of the metal weight fractions indicated on the y- and x-axes. An examination of the results presented in Fig. 5A and B reveal that binary combinations of catalysts containing 1% rhodium consistently exhibited superior performance. In fact, as a consequence of these findings that Set C studies, as presented below, were planned and undertaken.

In Fig. 6, the reactor exit concentrations of PO, in ppm units, together with those of acetone and acrolein are presented for the Set C of catalytic materials. In Fig. 7, the corresponding levels of CO_2 are shown. As evident from Fig. 6, a large number of Rh-based binary catalytic materials produced significantly higher levels of PO, reaching levels as high as 2000 ppm at 1% conversion of C_3H_6. A closer examination of Fig. 6 also reveals a number of significant features. First, the combination of Rh with elements both on the right and left of the periodic table generated superior catalytic materials. For example, the combinations Rh–Sn and Rh–In were superior to Rh–Ag, Rh–Cu, Rh–Pt. Similarly, the combinations Rh–V, Rh–Cr, Rh–Mo and Rh–W were superior to Rh–Fe, Rh–Os, and Rh–Ru. Second, many of these elements were excellent PO promoters at lower loadings as seen in Fig. 6. In fact, the effectiveness of V, Nb, Mo, W, Ag, Cu, Pt, S, and Ir in promoting PO formation decreased steadily with increased loading. These results also call for detailed characterization studies to better understand the underlying surface physics and chemistry responsible for the observed catalytic results.

As seen in Fig. 6, with the exception of Rh–Sn, Rh-based binary catalytic materials were not effective with regard to acetone and acrolein production. On the other hand, many Rh-based binary materials exhibited significant CO_2 production as shown in Fig. 7. Clearly, an ideal catalyst will have high PO productivity while

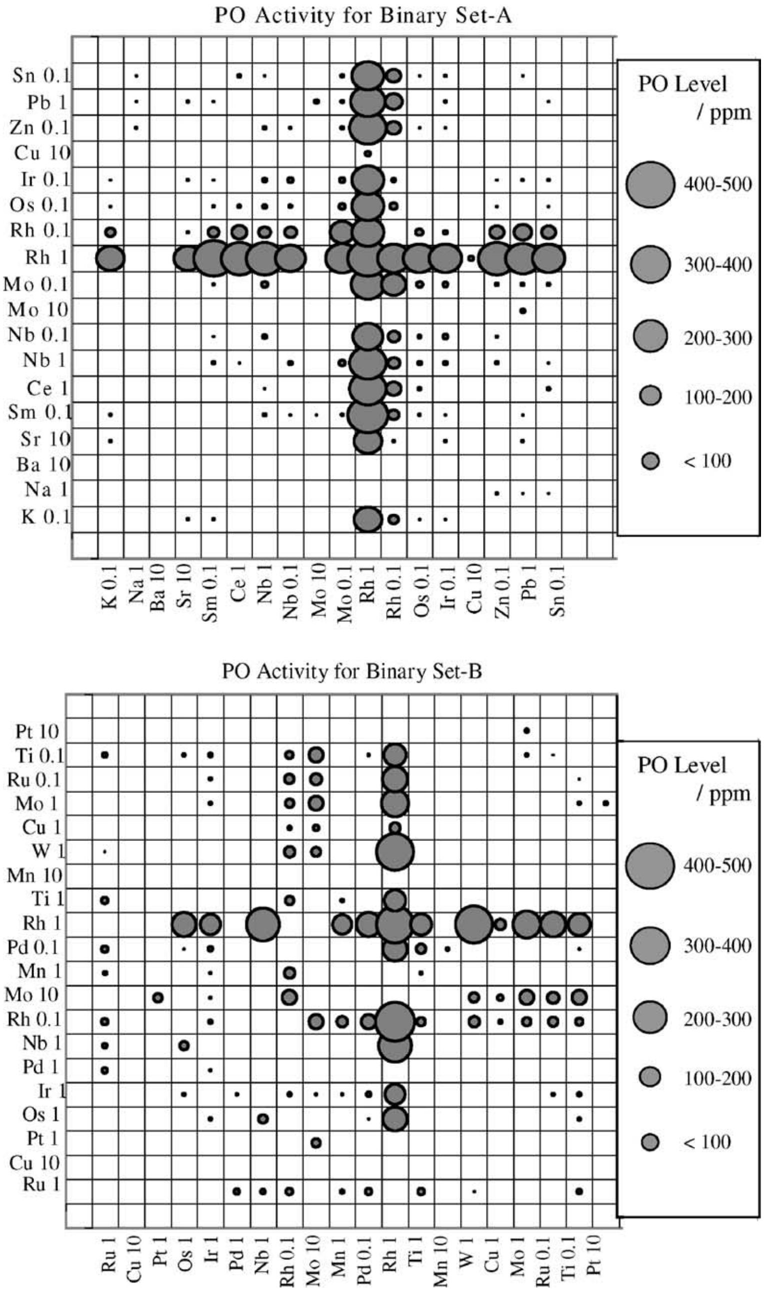

Fig. 5. Reactor exit concentrations of PO for the binary Set A (top), and binary Set B (bottom). Feed gas 20,000 h^{-1} GHSV, $C_3H_6/O_2 = 4/1$, $T = 250\,^{\circ}C$, 40% propylene.

maintaining low levels of CO_2. A comparative analysis of Figs. 6 and 7 indeed reveals the presence of several leads with these catalytic characteristics. For example, Rh–Ag, Rh–Zn, and Rh–Cr combinations have both high PO and low CO_2 productivities, suggesting their further evaluation, characterization and optimization.

In Fig. 8 the top 20 PO producing single and binary catalytic materials, prepared in Sets A, B, and C, are

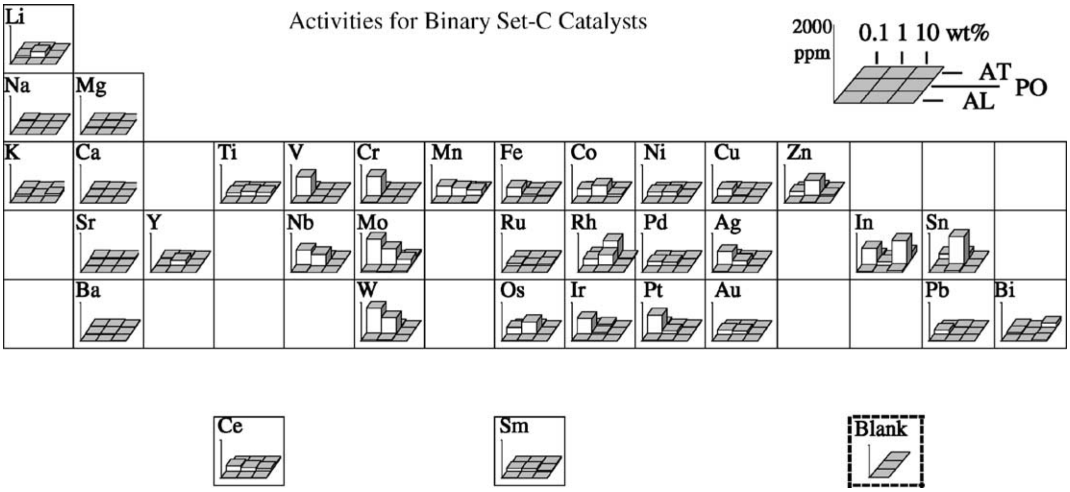

Fig. 6. Reactor exit concentrations of PO, AT and AC as a function of metal loading in the periodic table format for Set C. Feed gas 20,000 h^{-1} GHSV, $C_3H_6/O_2 = 4/1$, $T = 250\,^{\circ}C$, 40% propylene.

compared to one another using1% Rh catalyst as the benchmark, i.e. 1% Rh is indexed as 1.0. As can be seen from this figure, the binary combinations of 1% Rh with other metals (i.e. Set C) produced a larger number of PO active catalytic materials than those prepared by Sets A and B. For example, 18 out of 102 Rh-containing binary catalytic materials in Set C outperformed 1%Rh. This compares to 6 in 153 in Set B and 4 in 190 in Set B. It is particularly interesting to note that the combination of the best single component catalysts did not produce as many successful materials, indicative of the presence of a strong antagonistic effect between catalyst components under the conditions investigated.

In conclusion, in a short period of time, measured in months, nearly 1000 catalytic materials, comprising 34 single metals and their binary combinations impregnated on γ-Al_2O_3 at different loadings were

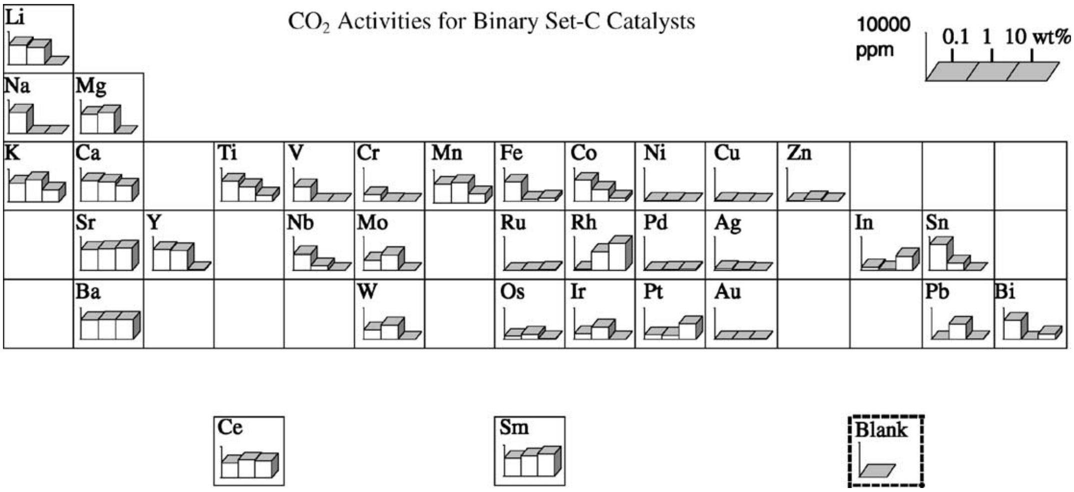

Fig. 7. Reactor exit concentrations of CO_2 as a function of metal loading in the periodic table format for Set C. Feed gas 20,000 h^{-1} GHSV, $C_3H_6/O_2 = 4/1$, $T = 250\,^{\circ}C$, 40% propylene.

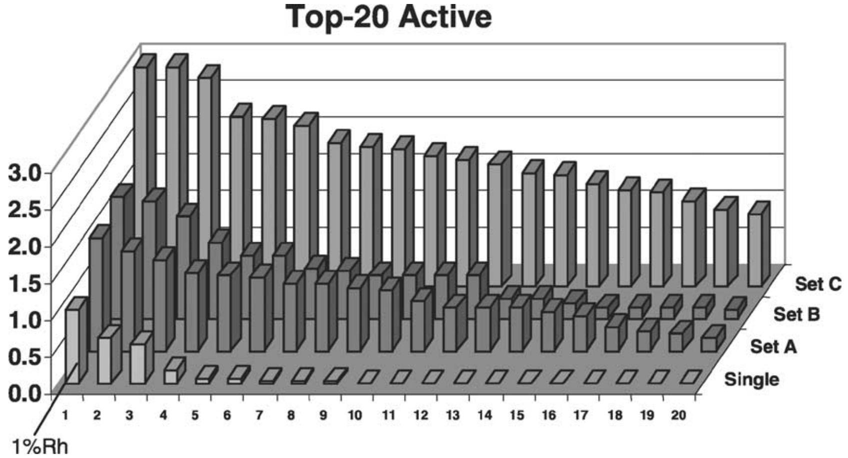

Fig. 8. Comparison of the relative rankings of catalytic materials developed by each set with regard to reactor exit PO concentrations normalized to 1.0% Rh/Al_2O_3. Set C resulted in the production of a larger number of superior catalytic materials than Sets A and B.

prepared, processed and tested for their activities towards the direct production of PO from propylene and oxygen. These primary screening studies revealed that Rh is a particularly PO active metal, both as a single component and in binary combinations. The binary combinations that exhibited superior PO production levels were Rh–V, Rh–Cr, Rh–Sn, Rh–In, Rh–Mo, and Rh–Sm, albeit substantial CO_2 formation. On the other hand, Rh–Ag, Rh–Zn, and Rh–Cr combinations were significant leads with regard to high PO and low CO_2 production. Clearly, these primary leads must be followed by detailed secondary screening studies to confirm the primary screening results reported here, to better establish product selectivities, e.g. by using GC/MS, and to obtain information on the durabilities of these catalytic materials.

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