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Selective combinatorial catalysis; challenges and opportunities: the preferential oxidation of carbon monoxide

Wen Li, Francisco J. Gracia, Eduardo E. Wolf*

Department of Chemical Engineering, Center for Catalysis & Reaction Engineering,
University of Notre Dame, Notre Dame, IN 46556, USA

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Abstract

This work presents a knowledge-based approach for the selection of catalysts along with an experimental methodology to be used with high throughput and combinatorial catalytic experimentation. As a demonstration of this methodology, new results on the activity and selectivity of different catalysts for the preferential oxidation of CO are presented. Two families of catalysts were selected on the basis of existing literature results, one family consisted of Pt and Pd supported on alumina and titania promoted with ceria, and the other family of the same metals interdispersed in various oxides. The activity of an array of up to 50 samples is studied using in situ infrared thermography (IRT). The materials that showed the highest activity in the IRT studies were selected for further evaluation in a parallel reactor with 10 microreactors and then in a single recycle reactor. The results show that titania supported Pt catalysts promoted with ceria show the highest activity and selectivity for the PROX reaction. Thus the selective combinatorial approach, which is a restricted approach of combinatorial catalysis, can lead quickly to new catalytic results.

Keywords: IRT; Combinatorial catalysis; Preferential oxidation of CO; Pt; Pd; Ceria; TiO_2

1. Introduction

Combinatorial methods and high throughput experimentation (HTE) have resulted in successful drug discoveries and materials [1–3], and several laboratories in industry and academia have started to apply combinatorial methods to catalytic research [3–13]. The application of combinatorial methods to heterogeneous catalysis, however, requires careful consideration not only of material composition, but also of the surface structure. The surface structure of metals supported on porous substrates is difficult to determine a priory and it depends critically on the method of preparation and often on the reaction environment. Hence, to measure the catalytic activity using a combinatorial methodology or high throughput experimentation, it is necessary to devise methodologies that account for such effects. Otherwise, HTE and combinatorial approaches can lead to large amounts of useless results if the sensitivity of catalysts to the various factors affecting their surfaces and hence their catalytic activity is not accounted for.

The approach to combinatorial catalysis taken in our group is from an academic perspective where the main objective is to accelerate the discovery of catalytic phenomena, i.e. new catalytic materials and reaction mechanisms, constrained by limited equipment and human resources. Ours, as well as

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* Corresponding author. Tel.: +1-574-631-5897;
fax: +1-574-631-8366.
E-mail address: ewolf@nd.edu (E.E. Wolf).

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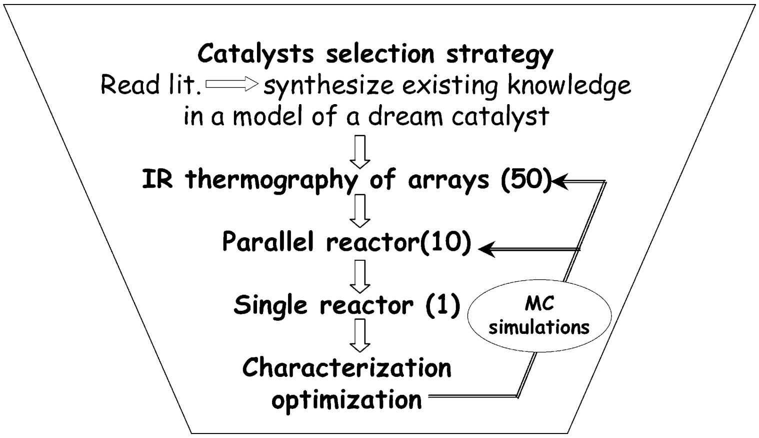

Fig. 1. The inverted pyramid experimental approach for HTE and combinatorial catalysis.

those of other groups [4,7,10–13], are examples of a knowledge-based approach focused on materials that have shown fundamental characteristics that can lead to catalytic activity for the reaction under consideration. This selective approach differs from a search among all materials in the periodic table that requires thousands of experiments. We call this approach selective combinatorial catalysis (SCC). We start with an exhaustive study of the existing literature that is synthesized into a reaction model that is used to select families of materials to be studied. Fig. 1 shows schematically the SCC approach as an inverted pyramid showing various levels of experimentation that we feel is the most efficient way to utilize combinatorial and HTE methodologies in catalytic research in an academic environment. The main difference from the conventional HTE approach is that the parameter space is restricted based on the existing knowledge of the reaction.

The first level of experimentation is the use of an in situ, spatially-resolved technique to obtain an indication of catalytic activity of an array of materials in a single experiment. In the second level of experimentation we use a parallel flow reactor that can measure the activity of the 10 most active samples found in the first level of experimentation. Finally, the most active and selective catalyst found in the parallel reactor is studied in a single flow recycle reactor to get the reaction rate parameters, and is characterized to determine its bulk and surface structure. The knowledge gained from these results is used to formulate a revised model of the surface and the reaction pathway. The revised model is used in a second round of experiments to optimize the catalyst.

The spatially resolved technique used in our work as an indicator of activity is infrared thermography (IRT). This technique was first introduced at Notre Dame by Pawlicki and Schmitz [14]. In our group we used IRT to display the formation of temperature patterns during auto-oscillations occurring during CO oxidation in Rh/SiO$_2$ supported catalysts [15,16]. We introduced a further advance in spatially resolved techniques by using a band pass filter in combination with the IRT camera to obtain what we believe are the first infrared images of CO adsorption and desorption on a supported catalyst [17]. In the area of combinatorial catalysis Willson and co-workers [18] used infrared thermography to evaluate the catalytic activity of an array of 16 metal-supported catalysts for the oxidation if hydrogen. Maier and co-workers [19] used emissivity corrected IRT to detect activity in a library of 37 mixed oxides for the hydrogenation of isooctane and the oxidation of isooctane to toluene.

The parallel reactor used in the second stage of experimentation was designed and developed by ISRI Inc. ([20], COMBI Reactor^{TM}) and tested in our group. This parallel flow microreactor increases the productivity of the acquisition of catalytic activity results by a factor of 10 compared to the sequential analysis with a single reactor. The catalyst that gives the best results in the parallel reactor is then tested in a single flow recycle reactor to confirm the results from the parallel reactor and obtain kinetic information.

The reaction under study is the preferential oxidation of carbon monoxide (PROX) in the presence of hydrogen. CO is a poison for the Pt electrodes in a fuel cell and must be removed from the hydrogen containing feed with a minimum of hydrogen oxidation. In the preferential oxidation of CO the desired reaction is the oxidation of CO to CO_2 without oxidizing valuable hydrogen to water. Each separate oxidation reaction has been intensively studied from a fundamental standpoint [21,22], so there is plenty of literature to select materials that are potential active for each separate reaction, albeit not necessarily selective in the combined reaction. Activity results for the PROX reaction have been reported by Oh and Sinkevitch [23], Korotkikh and Farrauto [24], and Matralis and co-workers [25].

2. Experimental

2.1. IRT reactor

The experimental system employed in the IRT studies has been described elsewhere [5,6]. It includes electronic flow controllers to provide gases at specific flow rates, temperature control, the IR-cell reactor and the IR camera. The IR-cell reactor has a 2.5 cm diameter sample holder designed to hold an array with nine catalysts. A new IR reactor that has an array containing up to 50 wells is commercially available [9]. The signal collected from the IRT camera is proportional to the object temperature with ±0.1 °C of accuracy. During reaction, the temperature of the reactor is increased in 10 °C steps and the IR intensity is recorded after the image does not change with time. Based on a careful temperature calibration with blank experiments, the temperature difference with the blank experiment on each spot of the catalysts array is obtained as a function of the reactor temperature and it is used as an indicator of catalytic activity. A typical loading of catalyst on each spot is 10 mg and the flow rate used in the IRT runs is about 250 cm^3/min. It should be noted that that the gases flow over the plate supporting the array and not through each spot.

2.2. Parallel reactor

The activity of the best catalysts obtained from the IRT studies is re-evaluated in the 10-port COMBI reactor. The separate effluent from each well is interfaced with an on line fast gas chromatograph (GC) which provides composition analysis from which conversion and selectivity results are obtained for each catalyst. The system also has programmable electronic flow controllers to meter various gases to the reactor and a temperature control to maintain the reactor temperature constant. The reactant flow through each well in the COMBI reactor is 40 cm^3/min and the mass loading, 100 mg.

3. Model of the ideal catalyst

Literature results indicate that noble metals (Pt, Pd, Rh) are the most active catalysts for both the CO and H_2 oxidation reactions and that they follow a Langmuir–Hinshelwood mechanism. Unfortunately, most of the metals that adsorb CO also adsorb H_2. Therefore a selective catalyst would be one where CO adsorption and reaction take place al low temperature, in this way CO adsorption would be favored against H_2 adsorption minimizing further H_2 oxidation. Thus, we propose that a successful catalyst for the PROX reaction must have sites that promote CO adsorption and sites that provide oxygen so that reaction can occur at low temperature. On this basis we propose two hypothetical models of the PROX catalysts (Fig. 2) leading to the selection of two families of materials that, based on the literature, have the highest potential to oxidize CO to CO_2 without oxidizing H_2. This does not mean that this is the actual reaction pathway, but rather the model provides an approach to selecting a small subset of materials that has a good chance of giving successful results.

In one family the active sites of CO oxidation (1% M, M = Pt and Pd) are assumed to be separated from those that can provide adsorbed oxygen (CeO_2). Two supports (S) were selected: alumina and titania, and the concentration of CeO_2 was 1, 5 and 15% (i.e. family I: M/S, M-1% Ce/S, M-5% Ce/S, M-15% Ce/S, total 16 catalysts). In the second family the active metal sites (1% Pt, 1% Pd) are inter-dispersed in the oxygen bearing sites consisting of oxides of 1% Co,

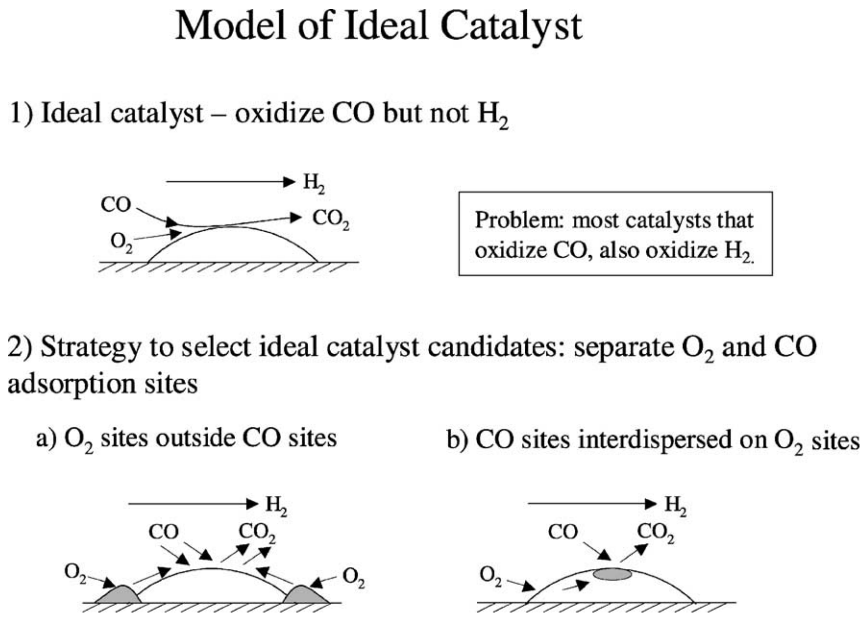

Fig. 2. Hypothetical model of the ideal catalyst and the two strategies selected to achieve the ideal behavior used to select the families of catalysts.

Cu, Cr, Zr, V, Mn, and Fe supported on alumina and titania (family II: M-CoO/S, M-CuO/S, M-Cr_2O_3/S, M-ZrO_2/S, M-VO_2/S, M-MnO_2/S, M-Fe_2O_3/S $=$ 14 catalysts). The supported oxides activities without Pt and Pd were also measured.

3.1. Catalysts preparation

The Pt/Al_2O_3 catalyst was prepared by impregnation of γ-Al_2O_3 support (Alfa Aesar) with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$. After drying in air at 110 °C for 8 h the sample was reduced in a hydrogen-containing atmosphere at 300 °C for 12 h before reaction.

To prepare Pt-Ce/Al_2O_3 catalysts, Ce/Al_2O_3 samples were prepared first by impregnation of γ-Al_2O_3 support with an aqueous solution of $Ce(NO_3)_3\cdot 6H_2O$ (Sigma–Aldrich). The sample was then dried in air at 110 °C for 8 h, and calcined in air at 600 °C for 2 h. The sample thus obtained was impregnated with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ and dried in air at 110 °C for 8 h. Finally the catalysts was reduced at 300 °C for 12 h. Palladium supported catalysts were prepared using $Pd(NO_3)_2$ as precursor following the same impregnation method used for platinum catalysts.

Similar procedures used for the preparation of metal supported Al_2O_3 catalysts were followed for the preparation of metal supported TiO_2 catalysts. The TiO_2 support used in this study was Degussa Co. P25, which is a mixture of approximately 70% anastase and 30% rutile. Since the Degussa material is primarily in the anastase form, it was used without pretreatment as an anastase TiO_2 support.

The Pt-oxide supported catalysts were prepared by co-impregnation of $Pt(NH_3)_4(NO_3)_2$ or $Pd(NO_3)_2$ with the corresponding oxide precursor salt on γ-Al_2O_3 and TiO_2. The precursors used were $Co(NO_3)_3\cdot 6H_2O$, $Cr(NO_3)_3\cdot 9H_2O$, $Zn(NO_3)_2\cdot xH_2O$, $VO(C_5H_7O_2)$ (Sigma–Aldrich), $Fe(C_5H_7O_2)_3$ (Strem Chemicals Inc.), and $Cu(NO_3)_2\cdot 2.5H_2O$ (Fisher Scientific).

4. Results and discussion

A total of 36 catalysts were examined by IRT in only four experiments. The IRT images of Pt supported

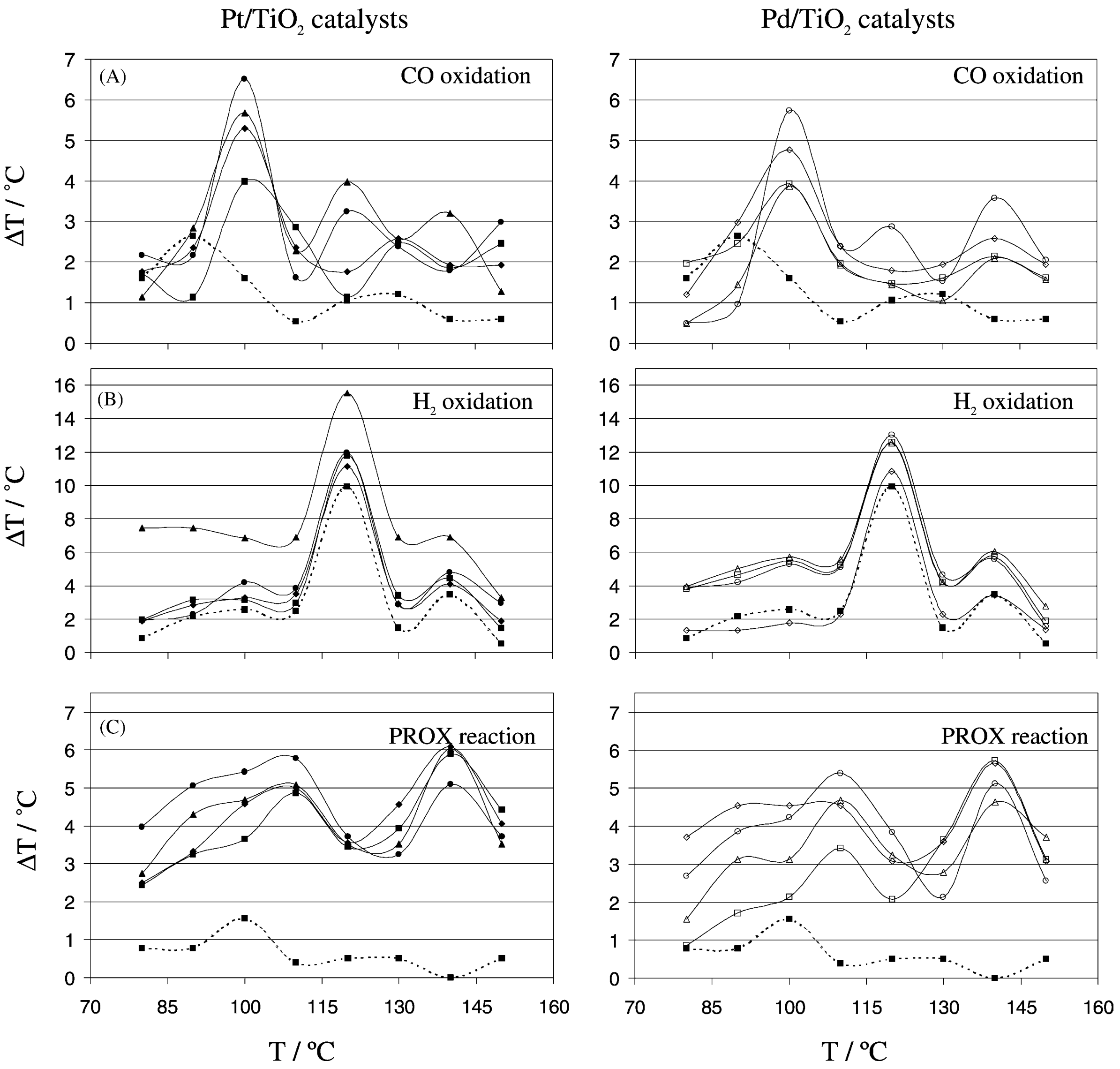

Fig. 3. Temperature differences for the separate CO (3A) and hydrogen (3B) oxidation, and for the PROX reaction (3C) on TiO_2 supported catalysts. Reactant ratio $CO:O_2:H_2 = 1:2:30$, balance He. Total flow 250 cc/min. (- -■- -) TiO_2; (◆) 1% Pt/TiO_2; (◇) 1% Pd-1% Ce/TiO_2; (●) 1% Pt-1% Ce/TiO_2; (○) 1% Pd-1% Ce/TiO_2; (▲) 1% Pt-5% Ce/TiO_2; (△) 1% Pd-5% Ce/TiO_2; (–■–) 1% Pt-15% Ce/TiO_2; (□) 1% Pd-15% Ce/TiO_2.

on TiO_2 and Al_2O_3 catalysts were obtained at various temperatures in the IR cell-reactor with an array of nine spots. Fig. 3A–C displays the temperature difference for Pt/TiO_2 and Pd/TiO_2 catalysts when the same temperature ramps are run with and without reaction (no oxygen present). This ΔT is indicative of additional heating at each reaction's light-off temperature due to the reaction exothermicity and thus is a good indicator of catalytic activity. The results for the separate CO and H_2 reaction show a maximum ΔT with the CO maximum occurring at lower temperature than the H_2 maximum ΔT (Fig. 3A and B). In the case of the PROX reaction there are two maxima; the one at lower temperature corresponding to CO oxidation and the one at higher temperature corresponding to hydrogen oxidation. There are several factors involved in these observations involving the interplay of heat and mass transfer in the IRT reactor. The IRT reactor is a boundary-layer reactor with a flow pattern that does not go through the catalysts particles so the heat transfer effects are not obvious. It is well known that in oxidation reactions during the transition from the low-activity to the high-activity regime there is a temperature range at which the heat generated by the reaction is much greater than the removal of heat in the system. At this point the surface temperature rises well above of that of the reactor temperature and ΔT increases. It should be noted that in the IRT reactor CO conversion is not 100% since only very small amounts of catalysts are used in each well. In the boundary layer configuration a concentration gradient limits the rate of mass transfer and the CO coverage, and additional heat is not released as the reactor temperature increases resulting in a decrease in ΔT. Further increases in reactor temperature increases CO desorption, which allows hydrogen adsorption and reaction, and thus additional heating effect due to the hydrogen reaction results in the second temperature increase leading to a ΔT. This reaches a maximum that then decreases for the same reason than it does for the CO reaction. The ΔT observed for CO and H_2 run separately further demonstrate this point. A similar ΔT versus T behavior would be observed in a flow reactor but it will be quite broad in such case. The reactor and catalysts temperatures equilibrate at low temperature and low conversion, and at high temperatures when there is 100% conversion and mass transfer limits the rate of reaction.

IRT results shown in Fig. 4 show that that the catalysts supported on TiO_2 are more active than those supported on alumina, hence we decided to concentrate studying only the titania supported catalysts. We also found that Pd was less active than Pt in accord with results reported by Oh and Sinkevitch [23]. IRT results obtained on the catalyst containing ceria (family I) are more active and selective that those containing oxides (family II). As seen in Figs. 3 and 4, the small ΔT values from the IRT results were indicative of the major trends between families, but they are not sufficiently accurate to differentiate among the activities within each family. Hence further work proceeded using the parallel flow COMBI reactor to verify the IRT results within each family using direct measurements of the concentrations instead of the indirect ΔT indication provided by IRT.

The results for CO conversion and selectivity for the titania supported catalysts obtained in the parallel COMBI reactor are presented in Fig. 5. Similar results obtained with Pt and Pd inter-dispersed on oxides (family of catalysts II) are shown in Fig. 6, confirming the IRT results that they are less active than Pt and Pd promoted with ceria catalysts.

The selectivity and conversion of CO to CO_2 exhibit the usual inverse correlation, i.e. the higher the conversion the lower the selectivity. This is clearly seen in Fig. 7, where selectivity is plotted as a function of CO conversion. A linear interpolation is shown for each catalyst to demonstrate these well known trends. It can be observed that the 1% Pt-5% Ce/TiO_2 catalyst departs from the general trend showing high activity (85%) along with high selectivity (80%). While it is encouraging that the activity–selectivity trend is altered by promotion by ceria, further enhancement in selectivity is needed to achieve the required removal of CO with minimum hydrogen consumption.

Finally, the activity of the most active catalyst observed in the parallel reactor was studied in a single recycle reactor. While the results in the recycle reactor showed similar conversion-selectivity results than those obtained in the parallel-flow reactor, there are some differences in the light-off temperature in each reactor. This is due to the fact that heat transfer in the recycle flow reactor operating at a high recycle flow is different from that of the parallel reactor. Reactor design considerations to decrease heat transfer effects are needed to decrease heat accumulation leading to a high steady state yield.

It should be emphasized that the results presented here were obtained in a fast track experimental program comprising four weeks of experiments. A similar program using a sequential approach would have taken several months to complete. At this writing we have not completed the loop yet including the surface characterization and simulation studies. These studies will involve characterization (XPS, TPD, chemisorption) of those catalysts showing the highest activity and selectivity as well as detailed Monte Carlo simulations, considering the kinetics of each reaction separately [26], that are currently underway. The interpretation proposed by Oh and Sinkevitch [23] explains in general the temperature trends observed in

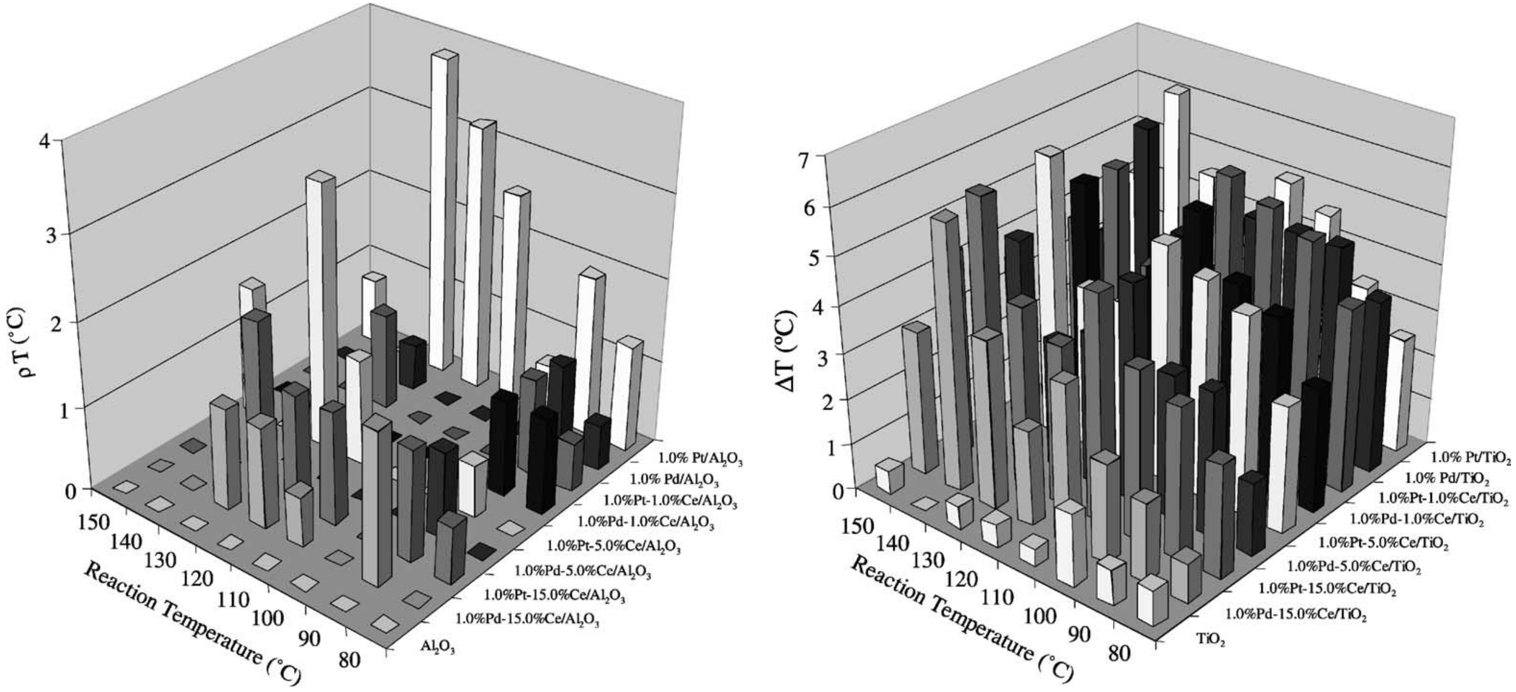

Fig. 4. IRT results for the catalyst supported on Al_2O_3 and TiO_2.

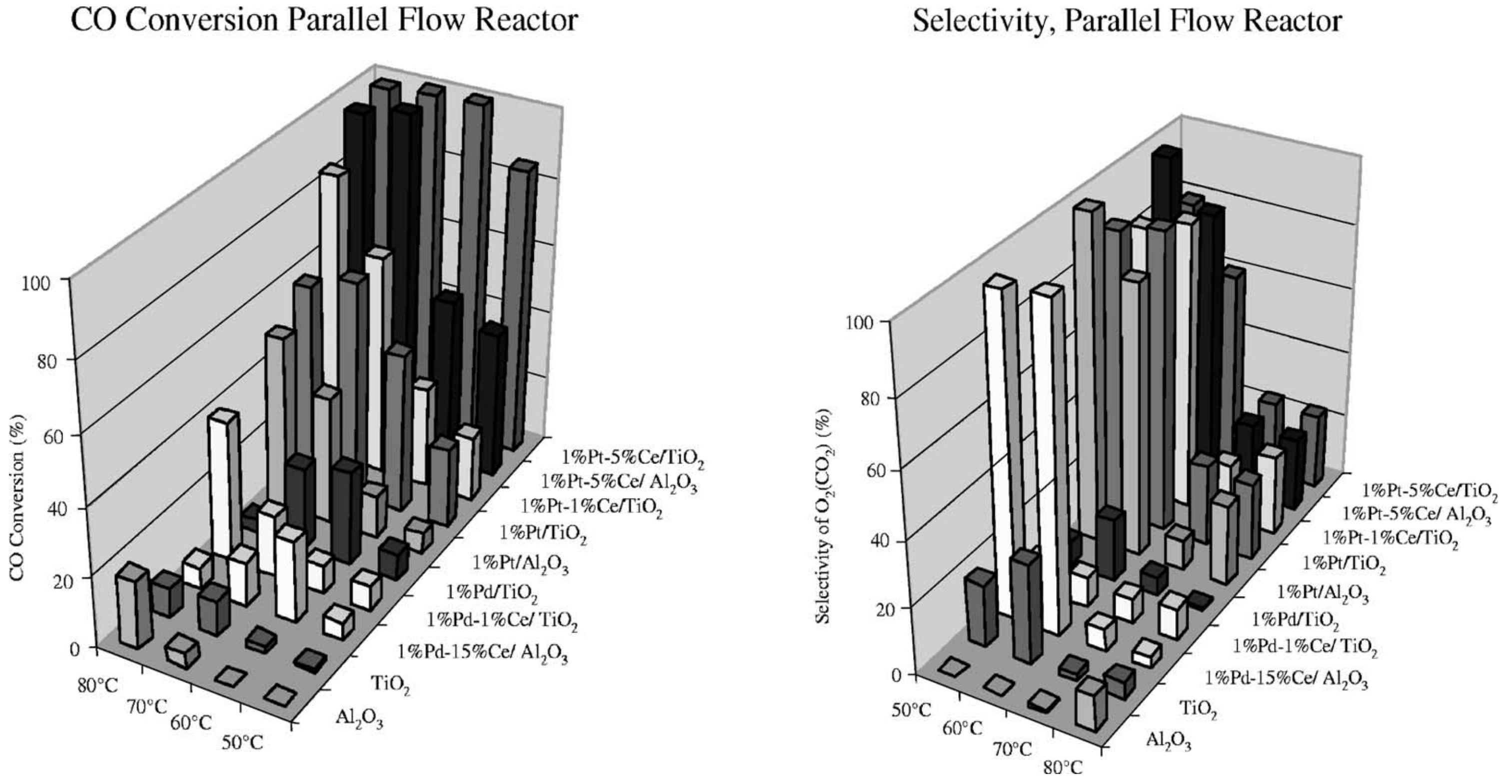

Fig. 5. Conversion and selectivity obtained on the COMBI reactor on family I catalysts supported on TiO_2 and Al_2O_3.

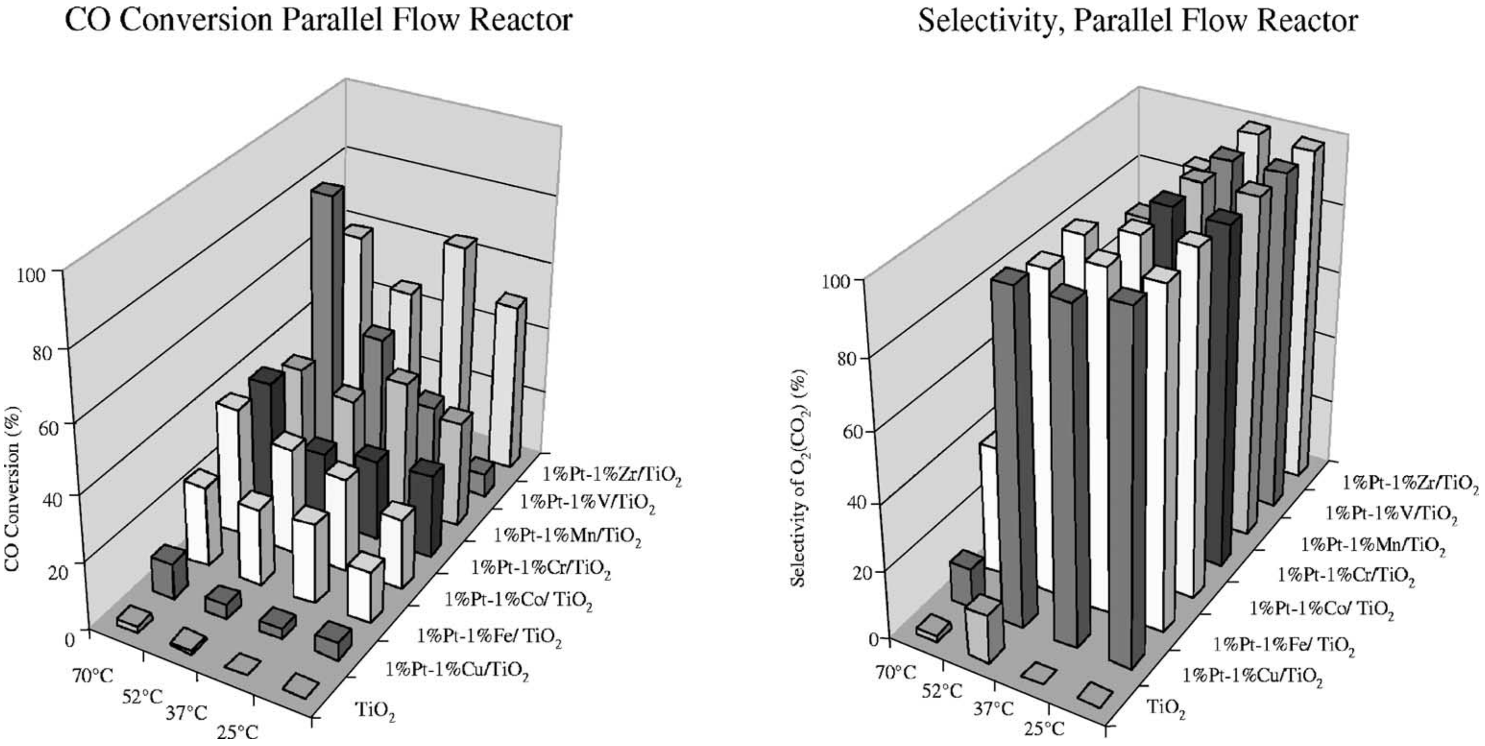

Fig. 6. Conversion and selectivity obtained on the COMBI reactor on family II catalysts of Pt and Pd interdispersed on oxides supported on TiO_2.

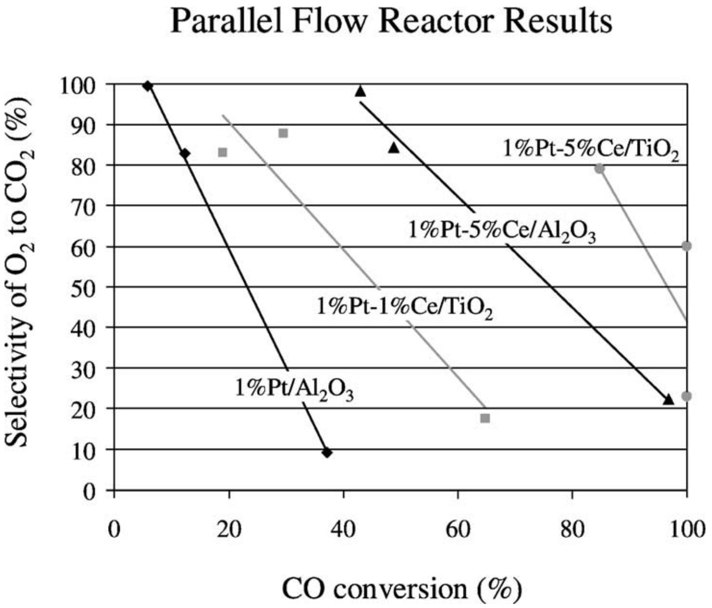

Fig. 7. Parallel flow COMBI reactor results in terms of selectivity vs. CO conversion for various catalysts.

our work as well. At low temperature, adsorbed CO covers the Pt surface inhibiting hydrogen adsorption. As the temperature increases, empty sites are created due to desorption and reaction, thus increasing hydrogen adsorption and dissociation leading to its oxidation, which explains the decrease in selectivity as temperature increases. Work is under way using multiple characterizations to explain the effect of ceria promotion observed in the results presented here. There is plenty of literature, however, showing that ceria plays a role as promoter due to its oxygen storage capacity [27] operating under the tree way catalysts conditions in the catalytic converter. According to this mechanism oxygen adsorbs and dissociates on ceria and then reacts at the periphery of the Pt particles where CO is adsorbed as shown in Fig. 2. Korotkikh and Farrauto [24] reported a very selective Pt catalysts promoted with an undisclosed metal oxide that is very selective and active for the PROX reaction and speculate that it operates according with the above mechanism.

The lower activity and selectivity of Pt inter-dispersed in oxides, while not totally unexpected, needs further examination and characterization to ascertain if the reason resides in the lower dispersion of Pt on the oxides or it is due to the less active nature of the oxides to dissociate oxygen. Oh and Sinkevitch [23] also examined the activity of various base metals and found that it was lower than that of the noble metals. Recently, Liu and Flytzani-Stephanopoulos [28], reported a very active Cu-CeO_2 catalysts for the total oxidation of CO. Matralis and co-workers [25] studied a similar Cu-CeO_2 catalyst for the PROX reaction. These authors claim that these mixed oxides are very active and exceptionally selective for this reaction with good resistance to CO_2 and H_2O poisoning. The oxides used in this study were not bulk oxides but they were dispersed on the TiO_2 and Al_2O_3 supports, which may have limited their oxygen activity. Further work with varying oxides is needed to verify the activity and selectivity of the inter-dispersed catalysts.

Clearly, from an academic standpoint, the bottleneck of the SCC studies is the availability of multiple characterization tools that can lead to the understanding of the activity–selectivity trends obtained from the selective combinatorial catalysis experimentation. Work is under way using IR imaging and a combination of a parallel reactor with a multiple characterization chemisorption unit to determine adsorbed species and the degree of Pt dispersion on the catalysts studied in this work [20].

5. Summary and conclusions

In this work we have shown that a knowledge-based combinatorial approach is an effective tool to accelerate the discovery of new catalytic phenomena and catalytic materials. This methodology has been demonstrated through an inverted pyramidal approach using simple and tested analytical techniques using the PROX oxidation of CO as a probe reaction.

Based on literature results we studied two families of catalysts comprising 36 samples in a period of about four weeks. The IRT results showed the existence of two temperature regimes on the catalysts with separated sites (family I). The low temperature corresponded to CO oxidation and the high temperature to H_2 oxidation. In general the TiO_2 supported catalysts showed higher activity than the alumina supported catalysts, and promotion by Ce increased the selectivity towards CO oxidation over hydrogen oxidation. The second family of catalysts (Pt co-supported on transition metals) was less active and selective than family 1. Parallel reactor studies confirmed the trends observed in the IRT results and showed that the most active and selective catalyst is the 1% Pt-5% Ce/TiO_2. The results are in line with the assumed model and suggest that CO adsorption on Pt inhibits hydrogen adsorption at low temperature. The addition of Ce provided oxygen for the CO oxidation to occur at lower temperature preferentially over hydrogen oxidation. As the temperature increases, and Pt sites for H_2 adsorption become available, the selectivity to CO oxidation decreases. The selectivity–activity trends of the PROX reaction on the best catalyst studied were 80–85%, better that on the Pt/Al_2O_3 catalyst. Higher selectivity is required, however, to meet the target of CO reduction in a hydrogen stream used in the fuel conversion train of a fuel cell.

Further work is underway to characterize and verify the working hypothesis of the selected families of catalysts and optimize the catalysts for even higher selectivity.

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