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The preferential oxidation of CO: selective combinatorial activity and infrared studies

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The activity and selectivity for the preferential oxidation of CO (PROX), on Pt- and Pd-supported catalysts, have been studied using a high-throughput method of screening and analysis of catalysts. Two families of catalysts were selected on the basis of existing literature results: one family consisted of platinum and palladium supported on alumina and titania promoted with ceria, and the other family of the same metals interdispersed in various oxides. The activity of these materials was first screened using *in situ* infrared thermography (IRT). The samples with the higher activity were selected for study in a parallel reactor with 10 microreactors and in a single recycle reactor. Platinum supported on titania promoted with ceria showed the highest activity and selectivity, in particular, the 1%Pt–15%CeO_2/TiO_2 catalyst appears to be a suitable candidate for the PROX reaction at temperatures below 90 °C.

KEY WORDS: selective combinatorial catalysis; infrared thermography; preferential oxidation of CO; platinum; ceria; titania.

1. Introduction

Over the last decade, there has been a great interest in using combinatorial methods and high-throughput experimentation (HTE) for studies in heterogeneous catalysis. Thermographic imaging was initially used as a screening technique [1–4], and lately, the use of mass spectroscopy has improved the quality of the information obtained by combinatorial methods [5–11]. If applied judicially, these methods hold great promise to accelerate the discovery of new catalysts, reaction pathways, and catalytic processes. Several companies offer services to conduct combinatorial studies in heterogeneous catalysis, and this methodology is now being used by several research groups [5,7,9,12]. The approach to combinatorial catalysis taken in our group, as well as others [7,9,12–14] is a knowledge-based approach emphasizing the previous knowledge of materials that have shown the fundamental characteristics that can lead to catalytic activity for the reaction under consideration. This selective approach, which we call *selective combinatorial catalysis* (SCC) [15], differs from an extensive search among all materials in the periodic table that requires thousands of experiments. Instead, we start with an extensive study of the literature and the available information is synthesized into a reaction model that is used to select the families of materials to be studied. Then we use several levels of experimentation in which the number of experiments decreases as the yield increases.

At the first level of experimentation, wherein the largest data set is obtained, an array of various samples under model reaction conditions is analyzed by *in situ* infrared thermography (IRT). This spatially resolved technique allows us to measure simultaneously the temperature of the catalysts' array as an indication of catalytic activity. In a second level of experimentation, a 10-channel parallel-flow reactor (COMBI Reactor^{TM} [16]) is used to measure sequentially the activity of 10 of the most active samples. In the final step, the most active and selective catalyst is studied in a single-flow recycle reactor to determine the reaction-rate parameters and is characterized in detail 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. Currently, we are using a Monte Carlo simulation that includes particle-size dependence to correlate quantitatively the reaction-rate parameters with the catalyst's characteristics that fit the experimental results [17,18].

We have been studying the preferential oxidation of carbon monoxide (PROX) in the presence of hydrogen [15]. In the last years, there has been a growing interest on the PROX process due to its relevance in fuel cell technology. When H_2 is produced by the water–gas shift reaction, the resulting H_2-rich gas stream still has about 1% CO, which at low temperature poisons the platinum anodes, reducing the energy conversion efficiency. Thus, CO must be removed with minimum H_2 oxidation. Among several possible methods for CO removal (adsorption, reduction, oxidation), the selective oxidation is recognized to be the most promising alternative

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[19–21]. While CO and H_2 oxidation reactions have been extensively studied and there is plenty of literature for each separate reaction [22–27], most of the attention is now focused on the PROX reaction to identify its catalytic mechanism and develop catalysts with both high CO conversion and selectivity toward CO_2 formation. Oh and Sinkevitch [19] were among the first to report the activity results for the PROX reaction showing that Ru/Al_2O_3 and Rh/Al_2O_3 were more active and selective than Pt/Al_2O_3 at temperatures as low as 100 °C. More recently, Korotkikh and Farrauto [28] have reported improved activity on Pt/Al_2O_3 catalysts promoted with an undisclosed metal oxide. Au-supported catalysts have also shown to exhibit high activity and selectivity at 80 °C [29,30], while CuO–CeO_2-mixed oxides catalysts are less active but significantly more selective [21,31]. Schubert *et al.* [32] have indicated that this difference on selectivity may be due to lower CO coverage on gold particles compared to near saturation on platinum surface at various temperatures. This low reactant concentration would allow O_2 and H_2 to adsorb and react, thus decreasing the selectivity.

In our previous studies of this reaction, we have published preliminary results to demonstrate the combinatorial methodology. In this work, we have used a new pretreatment procedure that resulted in a slightly different sequence of activity selectivity among the various catalysts studied. This shows that the combinatorial approach is critically dependent on the catalyst preparation method, i.e., the precursors used and pretreatment. Furthermore, new characterization results are presented here showing that dispersion is an important variable in considering the design of the next combinatorial iteration. *In situ* FTIR studies also show that the interaction between adsorbed CO and hydrogen modifies the reaction kinetics during selective oxidation compared with the separate oxidation of CO and H_2.

2. Experimental

IRT reactor

The experimental system employed in the IRT studies has been described elsewhere [15,33,34] and will not be described here in detail. It includes an *in situ* IR-cell reactor with a sample holder designed to hold an array of catalysts and an IRT camera. The signal collected from the IRT camera is proportional to the object temperature with ±0.1 °C of accuracy. On the basis of a careful temperature calibration with blank experiments, the temperature difference with a blank experiment on each spot of the catalysts array is obtained as a function of the reactor temperature and it is used as a descriptor of catalytic activity. A typical loading of catalyst on each spot is 20 mg and the flow rate used in the IRT runs is about 250 cc/min. It should be noted that that the gases flow over the plate supporting the array and not through each spot.

Parallel reactor

The activity of the best 10 catalysts obtained from the IRT studies is reevaluated in a flow reactor with 10 wells. The separate effluent from each well is interfaced with an on-line fast gas chromatograph (GC) that provides composition analysis from which the conversion and selectivity results are obtained for each catalyst. Each well in the COMBI reactor has a capacity of up to 1 g of catalyst, thus representing a more representative result than the ones obtained from the catalyst array that only uses a few milligram of the material. The GC provides sequential analysis of the effluent trapped from each reactor. Both the IRT and COMBI reactors have 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 was 60 cc/min and the mass loading, 100 mg.

FTIR spectroscopy

In situ FTIR results were obtained in an IR cell used in previous studies [18,35], which is also commercially available [16]. Transmission IR spectra of pressed disks (~14 mg) of Pt/SiO_2 were collected in an FTIR spectrometer (Mattson, Galaxy 6020) at a resolution of $2\,cm^{-1}$ and 30 scans/spectrum. The IR cell is equipped with NaCl windows and with flow and temperature control as the IRT and COMBI reactor. The spectra were obtained in absorbance mode after substraction of the background spectrum of the catalyst's disk under helium atmosphere at the corresponding temperature. The samples were pretreated in hydrogen at 200 °C prior to studying CO adsorption and desorption.

3. Results and discussion

3.1. Catalysts selection

Literature results show that noble metals are the most active catalysts for both reactions, and that each reaction follows a Langmuir–Hinshelwood mechanism. We hypothesized that a successful catalyst for the PROX reaction must have sites that promote CO adsorption and reaction at low temperature. On this basis, we formulated two models of the PROX catalysts leading to the selection of two families of materials that have the highest potential to oxidize CO to CO_2 without oxidizing H_2 [15].

According to the first model, the active sites of CO oxidation (platinum and palladium) are assumed to be separated from those that can provide adsorbed oxygen (CeO_2). Two supports were selected: alumina and titania

Table 1
Families of Pt- and Pd-supported catalyst

Family I	Family II
1. 1.0% Pt/S	1. 1.0% M–1.0% Ce/TiO_2
2. 1.0% Pd/S	2. 1.0% M–1.0% Co/TiO_2
3. 1.0% Pt–1%Ce/S	3. 1.0% M–1.0% Cu/TiO_2
4. 1.0% Pd–1.0%Ce/S	4. 1.0% M–1.0% Cr/TiO_2
5. 1.0% Pt–5%Ce/S	5. 1.0% M–1.0% Zr/TiO_2
6. 1.0% Pd–5%Ce/S	6. 1.0% M–1.0% V/TiO_2
7. 1.0% Pt–15%Ce/S	7. 1.0% M–1.0% Mn/TiO_2
8. 1.0% Pd–15%Ce/S	8. 1.0% M–1.0% Fe/TiO_2
9. S	9. TiO_2

and the concentration of CeO_2 was 1, 5 and 15%. This led to the selection of catalyst's family I consisting of combinations of platinum or palladium and CeO_2, as shown in table 1 (total 16 catalysts). In the second model, the active metal sites are assumed to be interdispersed on oxygen-bearing sites. This model led to the selection of a combination of platinum or palladium with oxides of transition metals supported on TiO_2 (table 1, 14 catalysts). The supported oxides activities without platinum and palladium were also measured.

3.2. Catalyst preparation

The $Pt/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnating $\gamma\text{-}Al_2O_3$ (Aluminum oxide Alfa Aesar, surface area: $220\,m^2/g$; pore diameter: 70 Å; Pore volume: 0.66 cc/g) with an aqueous solution of $Pt(NH_3)_4\,(NO_3)_2$. Then, the sample was dried in air at 110 °C for 8 h.

A different reduction procedure was used than in the studies reported here. In this case, to ensure reducibility, each sample was first reduced in a flow reactor under 120 cc/min of hydrogen at 300 °C for 2 h. This large flow could not be achieved in the COMBI reactor when the total flow is divided in the 10 wells. Reduction at low flow rates can result in the readsorption of water in the support, which can limit the extent of reduction, resulting in partially reduced catalysts. Finally, to stabilize the catalysts before running each reaction, the catalysts were pretreated *in situ* with a mixture of 50% H_2 in helium for 3 h at 200 °C. The flow in each well was 40 cc/min.

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

Similar procedures used for the preparation of metal-supported $\gamma\text{-}Al_2O_3$ catalysts were applied to the preparation of metal-supported TiO_2 catalysts. The TiO_2 support material used in this study was Degussa Co. P25.

Family II catalysts were prepared by coimpregnation of platinum or palladium salt with the corresponding oxide on $\gamma\text{-}Al_2O_3$ and TiO_2. The precursors used were $Co(NO_3)_3 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot xH_2O$, $VO(C_5H_7O_2)_2$ (Sigma-Aldrich Inc.), $Fe(C_5H_7O_2)_3$ (Strem Chemicals Inc.), and $Cu(NO_3)_2 \cdot 2.5H_2O$ (Fisher Scientific).

3.3. Results and discussion

A total of 36 catalysts were examined by IRT in only four experiments (each array contained 9 spots). We observed that the difference between the spot temperature with and without reaction reached a maximum for the separate CO oxidation reaction and hydrogen oxidation reaction when run separately. A detailed explanation of the maximum ΔT has been discussed previously [15]. Table 2 shows the maximum temperature

Table 2
Maximum temperature difference for each reaction. In parenthesis, the temperature at which each maximum occurred

Catalyst	Reaction			
	CO oxidation (100 °C) ΔT (°C)	H_2 oxidation (120 °C) ΔT (°C)	PROX reaction	
			CO oxidation (110 °C) ΔT (°C)	H_2 oxidation (140 °C) ΔT (°C)
1%Pt/TiO_2	5.3	11.1	5.0	6.1
1%Pt–1%Ce/TiO_2	6.5	11.9	5.8	5.1
1%Pt–5%Ce/TiO_2	5.7	15.5	5.1	6.0
1%Pt–15%Ce/TiO_2	3.9	11.8	4.9	5.9
1%Pd/TiO_2	4.8	10.8	4.5	5.6
1%Pd–1%Ce/TiO_2	5.7	13.0	5.4	5.1
1%Pd–5%Ce/TiO_2	3.9	12.5	4.7	4.6
1%Pd–15%Ce/TiO_2	3.9	12.6	3.4	5.7

difference between the catalysts when the temperature ramps are run with and without reaction (no oxygen present) for the separate CO and H_2 oxidation and for the PROX reaction on an array made of family I catalysts supported on TiO_2. The values in parenthesis correspond to the reactor temperature at which each maximum occurs for each reaction.

As anticipated from adsorption results, the maximum for CO oxidation ($\sim$100 °C) occurs at a lower temperature than that required for H_2 oxidation ($\sim$120 °C), thus showing a temperature window wherein the reactions might not overlap. The results for the combined PROX reaction show two maxima; the one at lower temperatures corresponding to CO oxidation ($\sim$110 °C) and one at higher temperature due to H_2 oxidation ($\sim$140 °C). Each maximum occurs at a higher temperature than that required for the separate CO and H_2 oxidation reaction, indicating that some interaction between adsorbed species occurs when both the gases are present. Evidence for this interaction is presented later by *in situ* FTIR experiments. The results suggest that a selective catalyst could be designed if the CO oxidation reaction occurs at low temperature.

The first set of IRT results (not shown) indicated that the catalysts supported on TiO_2 were more active than those supported on alumina [15], hence we decided to concentrate our study only on the titania-supported catalysts. We also found that palladium was less active than platinum, in agreement with results reported by Oh and Sinkevitch [19]. IRT results also indicated that the catalyst containing ceria (family I) were more active and selective than those containing oxides (family II). Thus, the IRT results consisting of four runs quickly showed that ceria-promoted platinum catalysts supported on TiO_2 were the most promising among the 36 materials initially selected. Recent results on CO oxidation [36] confirmed that Pd/TiO_2 catalysts promoted with CeO_2 are more active than individual Pd/CeO_2 and Pd/TiO_2 catalysts, indicating that a synergism between both oxides occurs. Owing to the small range of ΔT observed in the IRT results, they are not sufficiently accurate to ascertain which one among them all is the most active catalyst; hence we moved to the second level of experimentation to obtain such a result.

At the second level of experimentation, we proceeded using the parallel reactor to measure directly the activity of a subgroup of catalysts selected according to the IRT results. In this study, the reaction conditions used were 100 mg of catalysts and a flow rate of 60 cc/min in each well. These new results were obtained, with each sample being previously reduced in a separate flow reactor. Prior to reaction, the catalysts were pretreated *in situ* in a mixture H_2/He (0.5 : 0.5) during 3 h at 200 °C.

The results for CO conversion and selectivity for the ceria-promoted platinum catalysts supported on titania and alumina at various temperatures obtained in the parallel COMBI reactor are presented in figure 1. The results show that CO conversion increased with the amount of ceria on the Pt–titania samples with 15% ceria being the most active one (90% CO conversion at 71 °C). In the case of the Pt–alumina catalysts, the enhancing effect of ceria is observed at temperatures above 80 °C.

The selectivity to CO_2 formation, however, decreases with temperature or conversion. As expected, high selectivities are seen at low temperature i.e. low conversion. It should be emphasized here that the parallel-flow reactor operates as a standard microreactor exhibiting a characteristic ignition behavior leading to a loss of selectivity beyond ignition. The combination of activity and selectivity for each catalyst, expressed as yield for CO_2 formation, was plotted versus temperature

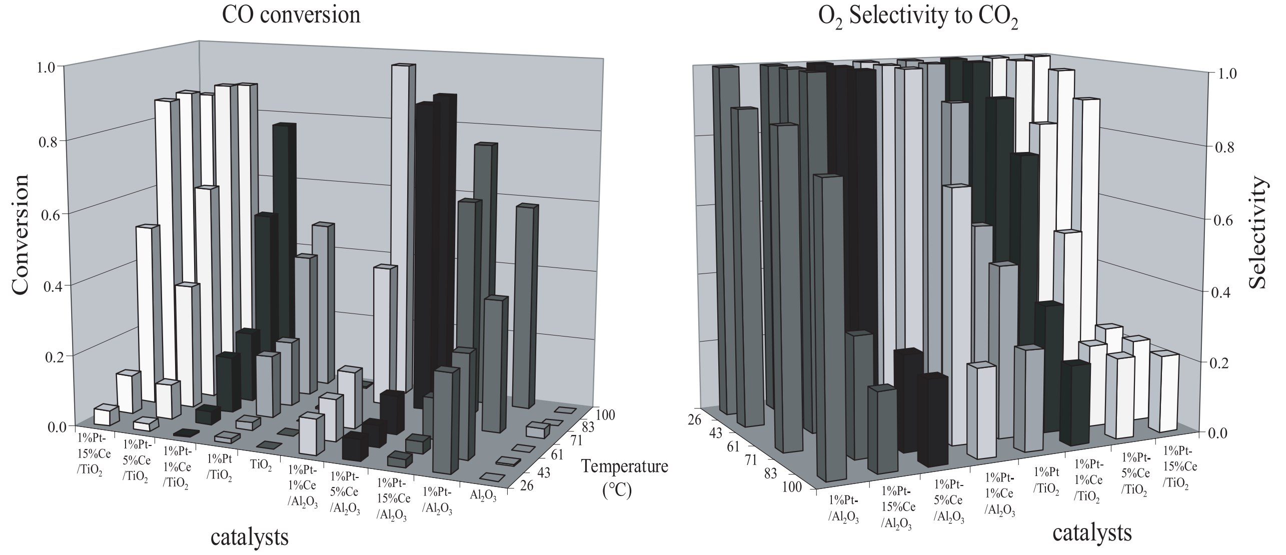

Figure 1. Conversion and selectivity versus temperature obtained on the COMBI reactor on family I: platinum catalysts supported on TiO_2 and Al_2O_3. Reactant composition: $CO : O_2 : H_2 = 1 : 2 : 40$, balance helium. Total flow: each well 60 cc/min.

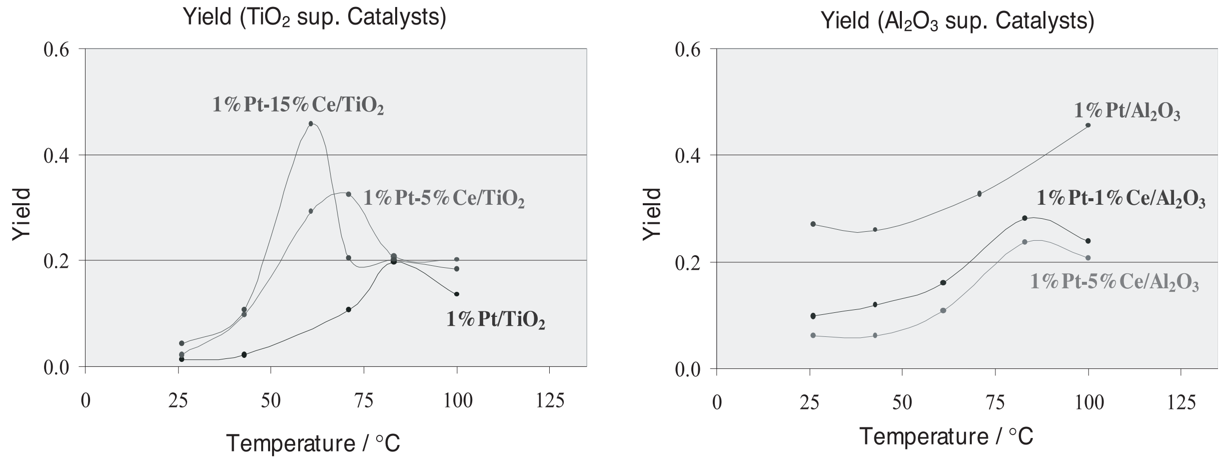

Figure 2. Yield versus temperature for various supported family I catalysts.

as shown in figure 2. The catalysts exhibiting highest yields are the 15% Ce-promoted platinum supported on titania, and the unpromoted platinum supported on alumina. The former shows the highest yield at low temperature (~60 °C), whereas the latter shows it above 100 °C. This activity sequence is slightly different than our previous results, in which we found that the 1%Pt–5%CeO_2/TiO_2 catalysts were more active than the other samples in that family. Furthermore, the unpromoted Pt/Al_2O_3 catalysts did not show high activity and selectivity in our previous studies, based on chemisorption measurements. It appears that when the catalysts were initially reduced in the COMBI reactor they were not completely reduced. Nonetheless, apart from the small discrepancy on the percentage of cerium and the activity of Pt/Al_2O_3 catalysts, the main trends are very similar with our previous results [15]. The discrepancy, nonetheless, shows that pretreatment procedures in multitube reactors may be different than those in single reactors changing to some extent the hierarchy of the results obtained. The result also confirms the findings of Dong *et al.* [36], about a strong synergism between CeO_2 and TiO_2 enhancing the catalytic activity of platinum for CO oxidation at low temperature.

The conversion-temperature and selectivity-temperature results for the family II catalysts obtained in the parallel COMBI reactor are shown in figure 3. It can be seen at once that most of these oxides are less active than those obtained with the family I catalysts. The vanadium and iron oxides containing catalysts, however, are as active at the higher temperatures as the most active catalysts of family I. Their CO_2 selectivity at the higher temperatures is, however, much lower than those of family I at similar temperatures. It should be noted, however, that the preparation procedure used in preparing these oxides was not optimized, and may not have resulted in the interdispersed catalysts envisioned in the model, i.e., metal sites on top of the oxides sites.

Finally, in the last experimentation step in the selective combinatorial approach, before a new iteration is designed, the most active catalyst was studied in a

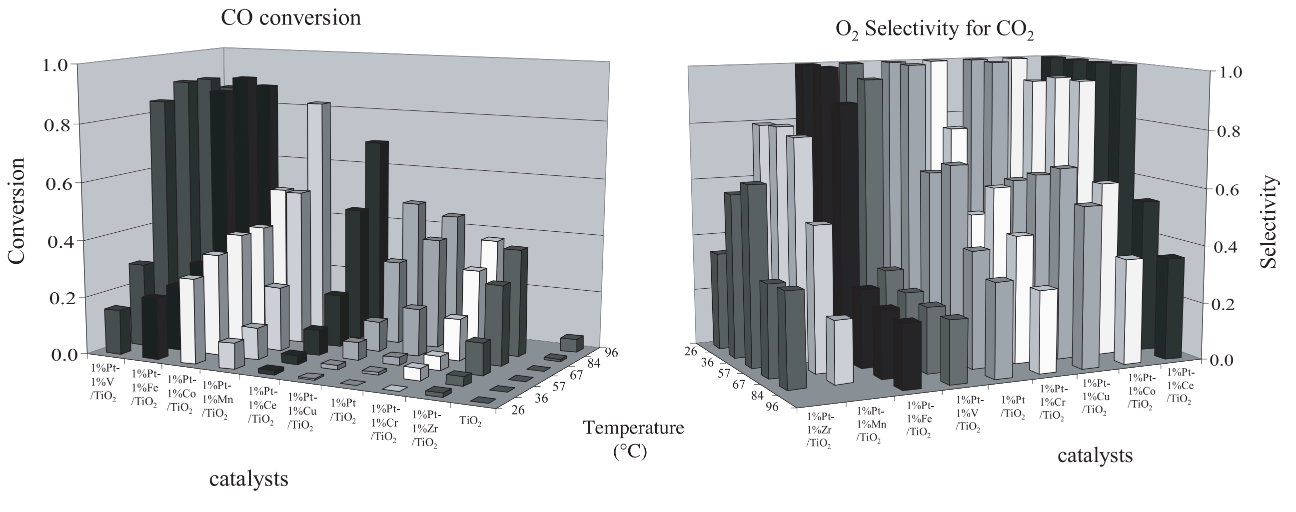

Figure 3. Conversion and selectivity for the family II catalysts obtained on the COMBI reactor. All active components supported on TiO_2. Reactant composition: $CO:O_2:H_2 = 1:2:40$, balance helium. Total flow: each well 60 cc/min.

Table 3
H_2 chemisorption results

Catalyst	Dispersion value (H/Pt)
1% Pt/Al_2O_3	0.73
1% Pt–15%Ce/Al_2O_3	0.35
1% Pt/TiO_2	0.28
1% Pt–15%Ce/TiO_2	0.50

single-recycle reactor and its surface structure and the adsorbed species were studied by H_2 chemisorption and FTIR spectroscopy, respectively.

The results in the recycle reactor (not shown) were similar to the conversion-selectivity results obtained in the COMBI parallel-flow reactor, but with 20 °C increase in the light off temperature in each reactor. This is due to the improved heat transfer in the recycle reactor operating at high flow rates different from those of the parallel reactor. This results in the suppression of sudden ignition seen in flow reactors and to the gradual increase of conversion with temperature.

Results of hydrogen chemisorption at room temperature (table 3) indicate that the samples with highest yields (1%Pt–15%Ce/TiO_2 and 1%Pt/Al_2O_3) exhibit platinum dispersion values two times larger than other catalysts within the same family. Thus, the smaller the platinum particle size, the higher the yield for CO_2 formation. This shows that the metal dispersion is an important parameter in controlling the selectivity of the catalyst. In the case of the 1%Pt–15%Ce/TiO_2, the capacity of CeO_2 for providing atomic oxygen to react with CO is more effective when platinum is highly dispersed on the surface of TiO_2 support.

The interaction of CO and H_2 on the platinum surface at 75 °C was studied by FTIR spectroscopy. Figure 4 shows two spectra taken under 1%CO in helium atmosphere and after adding 40%H_2 to the gas phase. There are two distinctive peaks besides the doublet at 2180 and 2100 cm^{-1} characteristic of CO in the gas phase. The first one at 2077 cm^{-1} corresponds to CO linearly adsorbed on platinum, and the second one at 1800 °cm^{-1} is typical of bridge-bonded CO on platinum. The height of the linearly adsorbed CO peak band changes slightly in the presence of H_2, but the integrated absorbance (IA) is similar in helium and H_2. In the case of the bridge-bonded CO, however, the integrated absorbance increases almost two times (from 2.8 to 5.2) when H_2 is added to the gas phase. This increase indicates the possible presence of adsorbed aldehyde moieties $\{-CH = O\}$ originated from the interaction between adsorbed CO and H_2 dissociated on platinum.

To further verify the CO–H_2 interaction on the platinum surface, the desorption of the CO-adsorbed species was followed in time. Once the maximum absorbance was reached under both atmospheres, 1% CO in helium and 1%CO–40%H_2 in helium, the CO flow was stopped and the absorbance of the signals at 2077 and 1800 cm^{-1} was monitored for 70 min (figure 5). It is clear that the presence of hydrogen accelerates the desorption of both CO species, indicating that indeed CO and H_2 are competing for the Pt-adsorption sites that support the IRT and activity results.

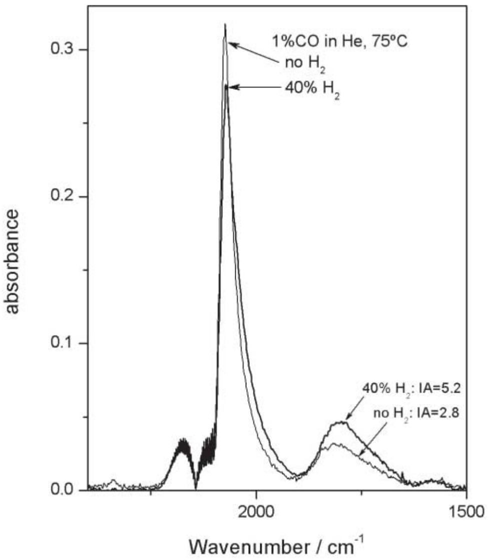

Figure 4. FTIR spectra of the effect of H_2 in the CO adsorption on Pt/SiO_2 catalyst.

The interpretation proposed by Oh and Sinkevitch [19] and Schubert *et al.* [32] is consistent with the general trends observed in our work and confirmed by the above FTIR results. At low temperatures, the CO oxidation reaction occurs in the *low-rate branch* of the reaction [30]. At these conditions, the adsorbed CO covers almost completely the platinum surface inhibiting oxygen and hydrogen adsorption; thus the dissociative oxygen adsorption is the rate-limiting step for both the oxidation reactions [22]. This regime is characterized for low CO conversion and high CO_2 selectivity. As the temperature increases, empty sites are created because of reaction and CO desorption. The FTIR results show that this process is further accelerated by the presence of hydrogen. This increases hydrogen dissociative adsorption leading to its oxidation, which explains the higher CO and H_2 oxidation rates and the decrease in selectivity as temperature increases.

In both supports, Al_2O_3 and TiO_2, the presence of ceria enhances CO conversion at low temperature. The Pt/TiO_2 catalyst reaches the highest activity with 15% CeO_2, whereas for the Pt/Al_2O_3 catalyst the optimum promoter concentration is only 1%. There is plenty of literature demonstrating the role of ceria on the basis of its oxygen storage capacity [21,31,37–40,41 and references therein]. According to this mechanism, oxygen adsorbs and dissociates on ceria, reacting later at the periphery of the platinum particles where CO is adsorbed. This interaction allows the promoted catalyst

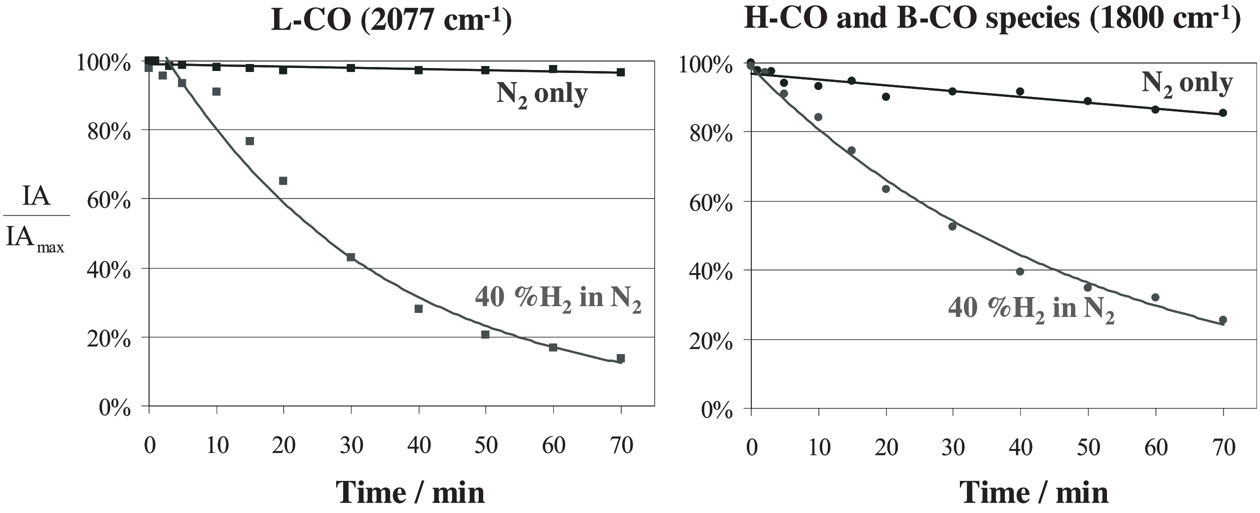

Figure 5. Effect of the presence of H_2 in the CO desorption on Pt/SiO_2 catalyst.

to be active at conditions of high CO coverage on the noble metal surface where few or no oxygen is present, contributing also to a high selectivity. The difference in the $\%CeO_2$ on the alumina-supported catalysts might be due to the higher dispersion (chemisorption) measured in the former catalyst. Work by Andersson and coworkers [42,43] on the interaction of platinum and ceria during CO oxidation shows that in a reduced catalyst, ceria is also partially reduced, which lowers significantly the reduction temperature. These authors also report that oxygen transport from platinum to ceria is fast in comparison to oxygen adsorption and desorption, and bulk diffusion [44]. All these literature reports clearly point out to Pt–Ce interactions, which are responsible for the observations reported here for the selective PROX reaction. It is also clear that these interactions are critically dependent on the method of preparation, and further work is underway to optimize the preparation procedures.

The low activity and selectivity of platinum interdispersed in oxides is a result that needs further examination and characterization. Previous studies of various base metals showed that their activity was lower than that of noble metals [19]. Liu and Flytzani-Stephanopoulos [37], on the other hand, reported a very active $CuO\text{-}CeO_2$ catalyst for the total oxidation of CO. Matralis and coworkers [21] studied a similar $CuO\text{-}CeO_2$ 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 our study were not bulk oxides, but they were dispersed on the TiO_2 and Al_2O_3 supports, which may have originated that platinum (or palladium) was not in close contact with the oxides, thus limiting their oxidation activity. Further work and characterizations with varying oxides loadings will be carried out to analyze the modest activity of the interdispersed oxides catalysts, and ascertain whether the reason for this low activity resides in a low dispersion of platinum on the oxides or whether it is due to the less active nature of the oxides to dissociate oxygen.

4. Conclusions

The application of combinatorial and high-throughput methods in catalysis is rather recent and in development, so is the research on the selective oxidation of CO in H_2-rich atmospheres. In this work, we have shown that a knowledge-based selective combinatorial approach is an effective tool to accelerate the discovery of new catalytic materials. Nonetheless, the fundamental characterization and single reactor kinetic studies for the most active samples are still needed to iterate to further optimize the activity and selectivity of the catalysts.

We have found that in a few runs we could obtain activity trends that show that, for the PROX reaction at low temperature, platinum supported on TiO_2 is more active than platinum supported on Al_2O_3. Furthermore, the promotion of Pt/TiO_2 catalysts with ceria provides sites that enhance CO conversion and selectivity at low temperature. $1\%Pt–15\%CeO_2/TiO_2$ catalyst showed the highest activity and selectivity at temperatures below 100 °C, whereas the unpromoted Pt/Al_2O_3 appears to be the best catalyst at 100 °C and higher temperatures. We also found that catalyst pretreatment in multitube reactors needs to be carefully evaluated to get the proper reduction and high metal dispersion.

In situ FTIR result showed that coadsorbed H_2 and CO interacted on the surface accelerating the rate of CO desorption. This explains the activity trends showing that the combined reaction have different kinetics than the separate CO and H_2 oxidation reaction.

Acknowledgments

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References

[1] F.C. Moates, M. Somani, J. Annamalai, J.T. Richardson, D. Luss and R.C. Willson, Ind. Eng. Chem. Res. 35 (1996) 4801.

[2] A. Holzwarth, H. Schmidt and W.F. Maier, Angew. Chem. Int. Ed. 37(19) (1998) 2644.

[3] M.T. Reetz, M.H. Becker, K.M. Kühling and A. Holzwarth, Angew. Chem. Int. Ed. 37(19) (1998) 2647.

[4] S.J. Taylor and J.P. Morken, Science 280 (1998) 267.

[5] P. Cong, R.D. Doolen, Q. Fan, D.M. Giaquinta, S. Guan, E.W. McFarland, D.M. Poojary, K. Self, H.W. Turner and W.H. Weinberg, Angew. Chem. Int. Ed. 38(4) (1999) 484.

[6] M. Orschel, J. Klein, H. Schmidt and W.F. Maier, Angew. Chem. Int. Ed. 38(18) (1999) 2791.

[7] P.P. Pescarmona, J.C. van der Waal, I.E. Maxwell and T. Maschmeyer, Catal. Lett. 63 (1999) 1.

[8] S. Senkan, K. Krantz, S. Ozturk, V. Zengin, and I. Onal, Angew. Chem. Int. Ed. 38(18) (1999) 2794.

[9] C. Hoffmann, H. Schmidt and F. Schüth, J. Catal. 198 (2001) 348.

[10] S. Senkan, Angew. Chem. Int. Ed. 40 (2001) 312.

[11] Y. Yamada, A. Ueda, Z. Zhao, T. Maekawa, K. Suzuki, T. Takada and Kobayashi, Catal. Today 67 (2001) 379.

[12] J. Holmgren, D. Bem, M. Bricker, R. Gillespie, G. Lewis, D. Akporiaye, I. Dahl, A. Karlsson, M. Plassen and R. Wendelbo, in *Studies in Surface Science and Catalysis*, A. Galarneau, F. Di Renzo, F. Fajula and J. Vedrine (eds), Vol. 135 (2001) p. 461.

[13] R. Schlögl, Angew. Chem. Int. Ed. 37 (1998) 2333.

[14] R.J. Berger, J. Pérez-Ramírez, F. Kapteijn and J.A. Moulijn, Appl. Catal. A: Gen. 227 (2002) 321.

[15] W. Li, F.J. Gracia and E.E. Wolf, Catal. Today (2003) in press.

[16] http://www.in-situresearch.com

[17] F. Gracia and E.E. Wolf, Chem. Eng. J. 82(1–3) (2001) 291.

[18] F.J. Gracia, L. Bollmann, E.E. Wolf, J.T. Miller and A.J. Kropf, J. Catal. (2003) in press.

[19] S.H. Oh and R.M. Sinkevitch, J. Catal. 142 (1993) 254.

[20] M.J. Kahlich.H.A. Gasteiger and R.J. Behm, J. Catal. 171 (1997) 93.

[21] G. Avgouropoulos, T. Ioannides, H.K. Matralis, J. Batista and S. Hocevar, Catal. Lett. 73(1) (2001) 33.

[22] T. Engel and G. Ertl, in *Advances in Catalysis*, D.D. Eley, H. Pines and P.B. Weisz (eds), Vol. 28 (Academic Press, New York, 1979) p. 2.

[23] S.H. Oh, G.B. Fisher, J.E Carpenter and D.W. Goodman, J. Catal. 100(2) (1986) 360.

[24] P. Aghalayam, Y.K. Park and D.G. Vlachos, Proc. Comb. Inst. 25 (2000) 1331.

[25] S. Ljungström, B. Kasemo, A. Rosén, Y. Wahnström and E. Fridell, Surf. Sci. 216 (1989) 63.

[26] W.R. Williams, C.M. Marks and L.D. Schmidt, J. Phys. Chem. 96 (1992) 5922.

[27] N.E. Fernandes, Y.K. Park and D.G. Vlachos, Combust. Flame 118 (1999) 164.

[28] O. Korotkikh and R. Farrauto, Catal. Today 62 (2000) 249.

[29] R.M. Torres-Sanchez, A. Ueda, K. Tanaka and M. Haruta, J. Catal. 168 (1997) 125.

[30] M.J. Kahlich, H.A. Gasteiger and R.J. Behm, J. Catal. 182 (1999) 430.

[31] J.B. Wang, S. Lin and T. Huang, Appl. Catal. A: Gen. 232 (2002) 107.

[32] M.M. Schubert, M.J. Kahlich, H.A. Gasteiger and R.J. Behm, J. Power Sources 84 (1999) 175.

[33] J. Kellow and E.E. Wolf, Chem. Eng. Sci. 45 (1990) 2597.

[34] F. Qin and E.E. Wolf, Chem. Eng. Sci. 49 (1994) 4263.

[35] F.J. Gracia, J.T. Miller, A.J. Kropf and E.E. Wolf, J. Catal. 209 (2002) 341.

[36] G. Dong, J. Wang, Y. Gao and S. Chen, Catal. Lett. 58 (1999) 37.

[37] W. Liu and M. Flytzani-Stephanopoulos, J. Catal. 153 (1995) 304, 317.

[38] M. Luo, Z. Hou, X. Yuan and X. Zheng, Catal. Lett. 50 (1998) 209.

[39] P. Larsson and A. Andersson, J. Catal. 179 (1998) 72.

[40] S. Bedrane, C. Descorme and D. Duprez, Catal. Today 75 (2002) 401.

[41] M. Shelef, G.W. Graham and R.W. McCabe, in *Catalysis by Ceria and Related Materials*, A. Trovarelli (ed.) (Imperial College Press, London, 2002) p. 343.

[42] A. Holmgren, B. Andersson and D. Duprez, Appl. Catal. B: Environ. 22 (1999) 215.

[43] A. Holmgren, F. Azarnoush and E. Fridell, Appl. Catal. B: Environ. 22 (1999) 49.

[44] A. Holmgren, D. Duprez and B. Andersson, J. Catal. 182 (1999) 441.