

Catalytic Conversion of Ethanol to Hydrogen Using Combinatorial Methods

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Ethanol is a globally available renewable source for hydrogen production for fuel cell applications. Prior research in this area focused on steam reforming of ethanol at relatively high temperatures ($T > 500$ °C), where carbon deposition and heat integration create operational problems. Combinatorial catalysis, an effective methodology for the accelerated discovery and optimization of functional materials, has been applied for the discovery of low-temperature catalysts for the production of hydrogen from ethanol. Libraries of catalytic materials were prepared by impregnating porous pellets of γ -Al₂O₃, SiO₂, TiO₂, CeO₂, and Y–ZrO₂ with individual aqueous salt solutions of 42 elements from the periodic table at 4 different loadings in the range 0.5–5 wt %. Ethanol steam reforming activities and H₂ selectivities of these 840 distinct materials were then evaluated using a computerized array channel microreactor system and mass spectrometry. Catalysts were screened under identical operating conditions of 300 °C, 1 atm, and a GHSV of 60 000 h⁻¹ using a feed gas composition of 2% C₂H₅OH and 12% H₂O in a helium carrier gas. This systematic investigation, completed over a period of several months, both provided confirmatory results and produced new leads of superior catalytic materials. Pt/TiO₂ and Pt/CeO₂ were the most significant new leads, both of which gave the highest ethanol conversions (+90%) and hydrogen selectivities (~30%) at 300 °C among all the single component catalytic materials explored.

Introduction

Due to their high energy conversion efficiencies and low pollutant emissions, fuel cells are becoming increasingly attractive as a power source, especially for the transportation industry.¹ The direct use of hydrogen clearly is the preferred mode of operation of fuel cells. However, the absence of a hydrogen distribution network and the risk and difficulties associated with the storage and transportation of hydrogen impede the broad utilization of this direct approach. On the other hand, the successful implementation of fuel cells in the near term can be accomplished via hydrocarbon processing, that is, production of hydrogen from liquid fuels using steam reforming. Methane, methanol, and gasoline, all of which are derived from fossil fuels, have long been studied as possible liquid feedstocks to produce hydrogen for automotive fuel cell applications.^{2–4} In contrast, ethanol steam reforming has been studied to a much more limited extent.

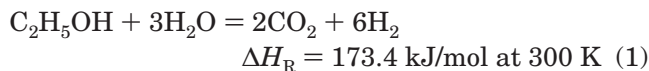
Ethanol has several advantages over fossil-fuel-derived hydrocarbons as a source for hydrogen production in fuel cell applications. First, it represents a *renewable and CO₂-neutral* source that can readily be obtained from biomass fermentation.⁵ The use of ethanol as a liquid fuel in the U.S. had a difficult start because of the initial high cost (about \$5.00/gal) of production relative to inexpensive petroleum prices. This necessitated substantial government subsidies to allow producers to remain in the business. However, the cost of production has now been reduced to about \$1.20/gal,⁵ and projected cost ranges of \$0.50–0.60/gal create considerable optimism regarding the future utility of ethanol as a sustainable energy source without any

government subsidies.⁵ The economic future of ethanol production looks even more favorable when one considers the likely increases in the price of petroleum and other fossil fuels as the world's reserves are depleted. Although ethanol has only 65–70% of the energy density of hydrocarbon fuels, it represents a reliable and sustainable energy source which is decoupled from geopolitical developments and will result in a significant net reduction in CO₂ emissions when it replaces fossil fuels. All these considerations render ethanol an economically, environmentally, and strategically attractive energy source. In addition, ethanol can be a particularly attractive energy and hydrogen source for countries that lack fossil fuel resources but have a significant agricultural economy. This is feasible because virtually any biomass can now be converted into ethanol as a result of recent advances in biotechnology. For example, most agricultural residues, such as sugar cane waste, corn cobs and stalks, wheat and rice straw, forestry and paper mill byproducts, as well as the organic portion of municipal waste, can be converted into ethanol.⁵

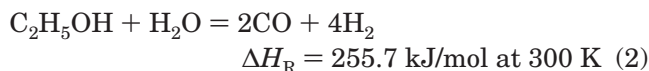
Second, because it is a functionalized hydrocarbon, ethanol reforming proceeds at temperatures in the range 300–600 °C, which is significantly lower than those required for CH₄ or gasoline reforming. This is an important consideration for the improved heat integration of fuel cell vehicles. Third, ethanol is significantly less toxic than methanol and, as such, provides less risk to the population. The fact that methanol is derived from fossil fuel resources also renders it an unreliable energy source in the long run.

The thermodynamics of steam reforming of ethanol has been extensively studied.^{6–9} The preferred ethanol steam reforming process is represented by the following endothermic reaction with the formation of CO₂ as the desired product.

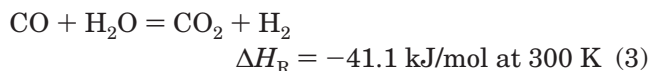
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On the basis of the thermodynamic considerations of the above reaction, it is possible to convert over 90% of $\text{C}_2\text{H}_5\text{OH}$ into the above products at a temperature as low as 350 °C. In addition, the formation of CO, which is undesirable, as it poisons the Pt catalyst of the electrochemical cell, must also be considered under steam reforming conditions.



Furthermore, some steam reforming catalysts can also catalyze the following water gas shift reaction



which, at high steam concentrations, enhances CO_2 production over CO. The formation of other byproducts such as CH_4 , C_2H_4 , and CH_3CHO has also been observed in ethanol reforming processes.¹⁰ An important byproduct that must be considered in the design and operation of all reforming catalysts is solid carbon formation. Because of its accumulative nature, carbon formation can lead to catalyst deactivation and, at its limit, can even result in the plugging of the reforming reactors with potentially catastrophic consequences. Carbon formation is a problem at high temperatures and at low $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ ratios. Consequently, the discovery and development of new catalytic materials that can efficiently convert ethanol to hydrogen at *low temperatures* and at *low $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ ratios* is crucial for the practical utilization of fuel cells in the transportation industry.

Previously, a variety of oxide support materials and metals have been considered for the steam reforming of ethanol.¹¹ Most of the catalysts investigated earlier were Ni-based materials, with the addition of Cu, Cr, Zn, or K.^{12–17} This was due to the generally accepted belief that nickel promotes C–C bond rupture^{13–15} and, thus, should be a good ethanol reforming catalyst. Marino et al.^{15,16} studied ethanol steam reforming on Cu/Ni/K/ γ - Al_2O_3 at a temperature of 300 °C, as a function of Cu loading, Ni loading, and calcination temperature. They concluded that Cu was the active agent while Ni acted as a promoter. Klouz et al.¹³ obtained product streams with H_2 concentrations of about 40% at 600 °C using Ni–Cu/ SiO_2 , but carbon formation and subsequent catalyst deactivation was a serious problem. In related studies, Freni et al.¹⁸ and Cavallaro¹⁹ examined Rh-based catalytic materials, which led to the formation of about 30% H_2 at 650 °C. More recently, cobalt supported on ZnO has also been determined to be a promising catalytic material for the conversion of ethanol to hydrogen.²⁰ However, despite excellent initial results, carbon deposition remained a persistent problem in Co/ZnO at the 450–500 °C temperatures associated with these catalysts, necessitating the use of dopants, such as alkali metals, to suppress coke formation.²¹ In summary, there exists a need for the development of low-temperature catalytic materials for the efficient synthesis of hydrogen by the steam reforming of ethanol.

In this article, we present the results of a systematic application of the tools and methods of combinatorial catalysis or high-throughput experimentation for the discovery and optimization of low-temperature (300 °C) ethanol steam reforming catalysts. In combinatorial heterogeneous catalysis, large and diverse libraries of inorganic materials are prepared, processed, and screened for desired catalytic activity and selectivity in a high-throughput fashion.^{22–24} Consequently, the pace of research in catalyst discovery and development is significantly increased.

The implementation of combinatorial methods generally entails a two-phase approach.^{22,23} In the first, that is, primary, screening phase, libraries of catalytic materials are rapidly evaluated to identify “leads” or “hits” exhibiting superior activities and, equally desirable, superior product selectivities. In the secondary screening phase, new leads are thoroughly evaluated, characterized, and optimized using traditional catalysis research methods and tools. It is also in the secondary screening phase that issues related to durability and resistance to poisoning are addressed in order to develop industrially significant catalysts. Here we report the results of the primary screening phase as applied to the title reaction.

Experimental Section

Since ethanol steam reforming catalysis has not been studied broadly, our initial studies were aimed to remedy this situation by systematically exploring the activities of a large number of elements from the periodic table together with diverse porous support materials and establishing trends in their reactivity and selectivity. This clearly is an essential first step in any discovery program. Catalyst synthesis and testing were performed using the standardized experimental systems described previously.²² All of the catalytic materials were prepared using the following procedure: First, single component libraries of metal salt solutions were prepared by dispensing predetermined volumes of stock solutions into arrays of glass tubes. Standard porous pellets (4 mm diameter by 1 mm high cylinders) of support materials of γ - Al_2O_3 , TiO_2 , CeO_2 , SiO_2 , and Y– ZrO_2 were then introduced into each glass tube to affect impregnation. These supports were chosen as each offers different levels of acidity and surface area and provides different levels of metal support interactions and, thus, reactivity. In Table 1, the properties of the support pellets and metal salts used are presented. Following 12 h of impregnation, the libraries were heated at a rate of 2 °C/min to 110 °C and dried at 110 °C overnight. After drying, the library was heated to 500 °C at a rate of 2 °C/min and calcined at 500 °C for 5 h. Both the drying and calcination processes were performed at ambient pressure. Synthesis and evaluation of bimetallic and higher order catalytic materials are currently underway, and these results will be reported in the future. Prior to catalytic testing, the catalysts were reduced *in situ* under the flow of a 10% H_2 and 90% He gas mixture for 3 h at 450 °C. After reduction, the catalysts were cooled to the reaction temperature of 300 °C.

Catalyst testing was accomplished using a fully computer-controlled catalyst performance analyzer system (CPA).²⁵ The CPA had 4 array channel microreactor banks, each consisting of 20 channels; thus, it was possible to evaluate 80 catalysts simultaneously. How-

Table 1. Support Materials and Metal Salt Precursors Used

support	pellet wt, mg	area, m ² /g	support	pellet wt, mg	area, m ² /g
γ-Al ₂ O ₃	23	128	TiO ₂	11.6	268
CeO ₂	60	17	SiO ₂	9.2	325
Y-ZrO ₂	31	36.5			

group	metal	precursor	group	metal	precursor
[IA]	Li	LiNO ₃	[IIIB]	Sc	Sc(NO ₃) ₃
	Na	NaNO ₃		Y	Y(NO ₃) ₃
	K	KNO ₃		La	La(NO ₃) ₃
	Rb	RbNO ₃		Ce	Ce(NO ₃) ₃
[IIA]	Mg	Mg(NO ₃) ₂		Nd	Nd(NO ₃) ₃
	Ca	Ca(NO ₃) ₂		Sm	Sm(NO ₃) ₃
	Sr	Sr(NO ₃) ₂	[IVB]	Ti	(NH ₄) ₂ TiO(C ₂ O ₄) ₂
	Ba	Ba(NO ₃) ₂		Zr	ZrCl ₂ O
[IIIA]	B	H ₃ BO ₃	[VB]	V	NH ₄ VO ₃
	Al	Al(NO ₃) ₃		Nb	NbCl ₅
	Ga	Ga(NO ₃) ₃	[VIB]	Cr	CrCl ₂
	In	In(NO ₃) ₃		Mo	(NH ₄) ₆ Mo ₇ O ₂₄
[IVA]	Ge	(NH ₄) ₂ GeF ₆		W	W(NO ₃) ₂
	Sn	(NH ₄) ₂ SnCl ₆	[VIIB]	Mn	MnCl ₂
	Pb	Pb(NO ₃) ₄	[VIII]	Fe	Fe(NO ₃) ₃
[VA]	Bi	Bi(NO ₃) ₂		Ru	(NH ₄) ₂ RuCl ₆
[IB]	Cu	Cu(NO ₃) ₂		Co	Co(NO ₃) ₂
	Ag	AgNO ₃		Ni	Ni(NO ₃) ₂
	Au	HAuCl ₄		Rh	RhCl ₃
[IIB]	Zn	Zn(NO ₃) ₂		Pd	PtCl ₂
				Ir	IrCl ₆
				Pt	PtCl ₆

ever, the actual number of catalysts tested at any given time was less than this number due to the use of duplicates and blank pellets placed in some channels. Each channel possessed a cylindrical well to hold the catalyst pellet. The array reactors were placed inside a temperature-controlled heating block, the temperature of which was regulated by the computer using PID controllers. The reactor block was placed on a computer-controlled robotic motion system (Newmark Systems, Irvine, CA); thus, it was possible to sequentially analyze the exhaust streams of each reactor channel. Gas analysis was accomplished by using an on-line quadrupole mass spectrometer (QMS, SRS Systems, Sunnyvale, CA). The QMS had a detection sensitivity of 50–100 ppm (parts per million) under the scan parameters used in the experiments. We also conducted a series of experiments to determine the reproducibility of our measurements. These investigations indicated that site-to-site variations of mass spectrometric intensity measurements were well within $\pm 10\%$ during a given experiment. To account for experiment-to-experiment variations, QMS intensities were ratioed to blank sites. Reactor effluents were withdrawn to a QMS using a 50 μm diameter capillary sampling probe and analyzed in real time. The mass spectrum covering the 2–50 amu range was scanned 4 times for each reactor channel and averaged to improve the signal-to-noise ratio. Consequently, it was possible to screen the entire 80-site library at one temperature in about 1 h. The preparation and primary screening of the set of 840 catalytic materials were completed in a time period of less than two months.

Flow rates of feed gases were controlled by digital mass flow controllers (MKS, Andover, MA), whereas flow rates of feed liquid mixtures were controlled by high-precision liquid syringe pumps (Newmark Systems, Irvine, CA). Liquid ethanol–water mixtures were evaporated in the preheater section of the reactor block. Catalysts were evaluated under identical operating

conditions of 300 °C, 1 atm, and a GHSV of 60 000 h⁻¹, using a feed gas composition of 2% C₂H₅OH and 12% H₂O in a helium carrier gas. The use of a large excess of helium was deliberate in order to maintain near-isothermal conditions in the reactor channels. Catalytic screening was accomplished by monitoring mass 31 for ethanol together with mass 2 for hydrogen at the reactor exit. Masses 16, 28, and 44 were also monitored for CH₄, CO, and CO₂ levels, respectively, while contributions from other species were taken into account. The individual reactor signals were referenced to an empty site in each reactor array to remove the influence of possible homogeneous reactions, blank reactor activity, and block-to-block and experiment-to-experiment variations.

It should be noted that the major emphasis of this primary screening study was to determine new leads of catalytic materials that can efficiently convert ethanol to hydrogen at 300 °C, a temperature significantly lower than those reported by other investigators indicated above. Clearly, other byproducts such as CH₄, C₂H₄, and CH₃CHO can also form under the reaction conditions investigated over some catalytic materials. However, the quantification of all byproducts for all of the 840 catalytic materials is unnecessary at the primary screening phase as reported here. Once promising new leads are found, all the relevant byproducts can and must be quantified, using, for example, gas chromatography or gas chromatography/mass spectrometry (GC/MS), in the secondary screening phase. Surface characterization of superior lead materials, as well as their durability and resistance to poisoning, can be evaluated during the secondary screening phase as well.

Results and Discussion

The initial discovery library was prepared by impregnating pellets of 5 different porous support materials with the salt solutions of 42 metals from the periodic table shown in Table 1. Metal loading levels were kept at 0.5%, 1%, 2.5%, and 5% by adjusting the concentrations of the salt solutions. This range of metal loading should create a good diversity of catalytic materials, from well-dispersed small-metal/metal-oxide ensembles at 0.5% loading to large clusters at 5% loading. As noted earlier, promising catalytic materials, once identified, can be thoroughly characterized in the secondary screening phase.

In Figure 1, ethanol conversion activities of all 840 different catalytic materials are presented in the form of bar charts. As indicated in the legend, the horizontal subdivisions in each element cell correspond to the support materials, while the divisions that appear perpendicular to the reader represent metal loadings as indicated. Ethanol conversions (X) were calculated from the following equation:

$$X_{\text{EtOH}} = [(C_{\text{EtOH,in}} - C_{\text{EtOH,out}})/C_{\text{EtOH,in}}] \times 100 \quad (4)$$

where C_{EtOH} represents the measured ethanol concentrations determined from the intensities of mass signal 31 and the calibration standards. All our mass spectrometric measurements were reproducible within $\pm 10\%$ under all the conditions investigated.

Similarly in Figure 2, the reactor exit concentrations of H₂, expressed in mole percent, are presented using the mass signal at 2 amu. It should be noted that the ideal maximum H₂ concentration under the feed condi-

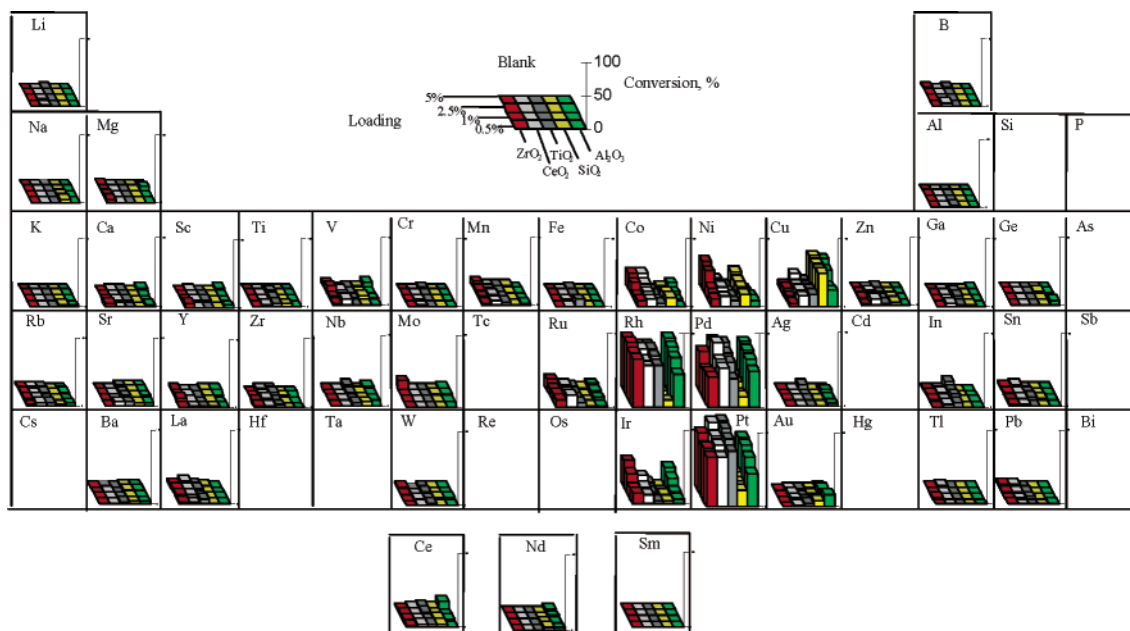


Figure 1. Ethanol conversions on supported single-component catalysts at 300 °C, 60 000 h⁻¹ of GHSV, and a 1:6 ethanol/H₂O molar ratio, diluted in 86% He.

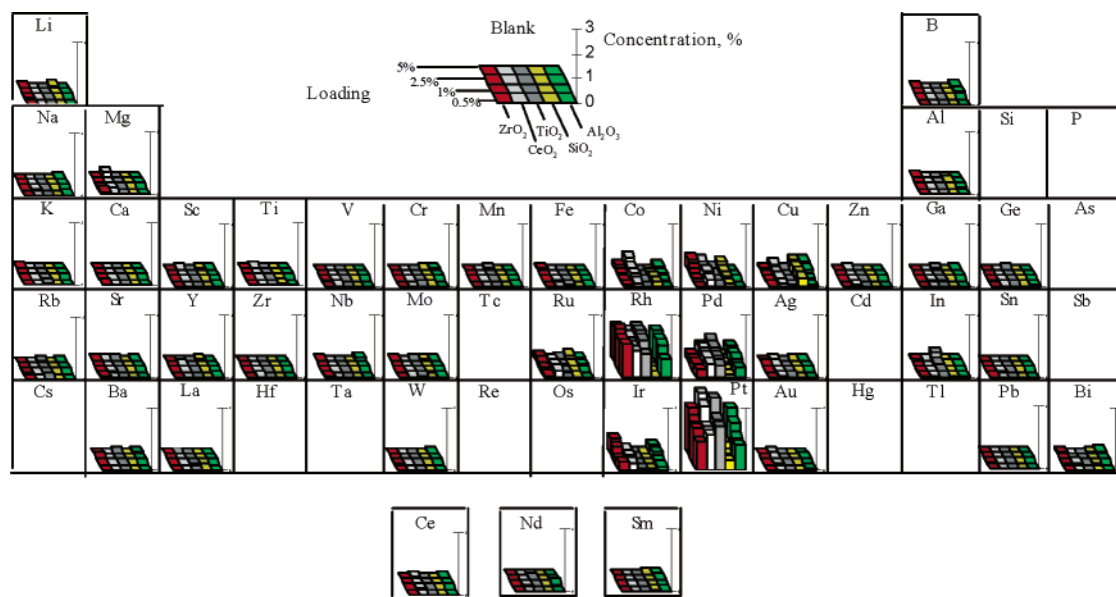


Figure 2. Reactor exit H₂ concentrations (mole %) on supported single component catalysts at 300 °C, 60 000 h⁻¹ of GHSV, and a 1:6 ethanol/H₂O molar ratio, diluted in 86% He.

tions stated above will be about 11% (100% selectivity) based on the desired ethanol steam reforming reaction (eq 1).

As evident from Figure 1, most metals and support materials were inactive for ethanol conversion except the group VIII and group IB elements. The approximate activity ranking of these elements was Pt > Pd, Rh > Cu, Ni > Co, Ir, although this order was strongly dependent on the support material being used. For hydrogen production, a similar ranking of Pt > Rh > Pd > Co, Ni, Cu, Ir was observed (Figure 2). A close inspection of Figure 1 reveals that Pt/TiO₂ and Pt/CeO₂ provided the highest ethanol conversions, concomitant with the highest hydrogen levels (Figure 2). Ethanol conversions also increased with increased Pt loading. At 5% Pt loading, both TiO₂ and CeO₂ provided over 90% ethanol conversion and about 3% hydrogen produc-

tion. In contrast, the performance of Pt/SiO₂ was significantly inferior, leading to less than 50% conversion of ethanol, irrespective of the metal loadings. This result can be attributed to the well-known poor dispersion characteristics of Pt over silica.²⁶ The performances of Pt/Y–ZrO₂ and Pt/Al₂O₃ were intermediate between those of Pt/CeO₂, Pt/TiO₂, and Pt/SiO₂.

It is important to note that, despite its substantially lower surface area of 17 m²/g, Pt/CeO₂ performed as well as the higher surface area Pt/TiO₂ (268 m²/g) with regard to ethanol conversion and hydrogen production. In fact, 5% Pt/CeO₂ resulted in the production of the highest levels of H₂ among all 840 catalytic materials explored, reaching levels as high as 3.0%, corresponding to about 30% selectivity. As an important component in auto emission control catalysts, CeO₂ is known to provide oxygen storage capacity,²⁷ as well as to help

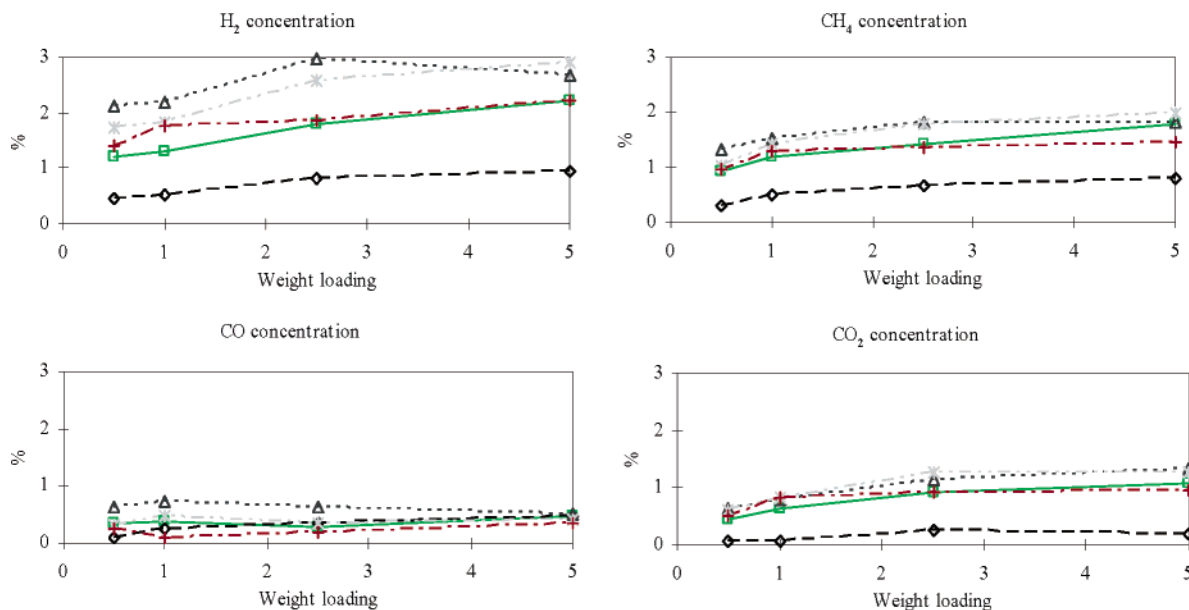


Figure 3. Reactor exit concentrations (mole %) of H₂, CH₄, CO, and CO₂ as a function of Pt loading at 300 °C, 60 000 h⁻¹ of GHSV, and a 1:6 ethanol/H₂O molar ratio, diluted in 86% He: γ -Al₂O₃, green square; SiO₂, diamond; TiO₂, triangle; CeO₂, asterisk; Y-ZrO₂, plus sign.

maintain the high dispersion of precious metals during the repeated oxidation–reduction cycles. Our results clearly demonstrate the presence of strong metal support interactions in Pt/CeO₂ during the catalytic steam reforming of ethanol. Pt/Y–ZrO₂ and Pt/Al₂O₃ also produced substantial levels of H₂ in the reactor exit as shown in Figure 2, with H₂ levels increasing with increased Pt loadings. Maximum hydrogen levels were about 2.2% for both Pt/Y–ZrO₂ and Pt/Al₂O₃.

As seen in Figures 1 and 2, both Pd and Rh provided ethanol conversions in excess of 80%. However, their performances with regard to H₂ production were substantially different. Most importantly, Rh-based catalysts exhibited higher H₂ levels, reaching about 1.8%, relative to Pd-based materials, which produced peak hydrogen concentrations of only 1.0% (See Figure 2). Hydrogen production levels over zirconia- and silica-supported Pd and silica-supported Rh were particularly poor.

Although not as effective as the precious metals noted above, less expensive Co, Ni, and Cu were also active catalytic materials for the steam reforming of ethanol, allowing the production of maximum hydrogen levels of about 0.5% (See Figures 1 and 2). These findings are in total harmony with the earlier literature summarized above. Most notably, Figure 1 shows that SiO₂ is a superior support for Cu when compared to the other supports studied, a result consistent with those reported by Klouz et al.¹³ Zirconia and ceria were the preferred supports for Ni and Co, respectively, with regard to hydrogen production (Figure 2). These confirmatory results clearly demonstrate the utility of combinatorial or high-throughput experimentation tools in the discovery and optimization of catalytic materials.

It should be noted that no evidence of carbon deposition was observed in the present experiments based on the visual inspections of used catalytic pellets. Limited numbers of extended-time experiments (i.e., 5–6 h duration) with Pt/TiO₂ and Pt/CeO₂ also did not result in any measurable decrease in their catalytic activities, again supporting the notion that carbon deposition was not a significant problem. If present, carbon deposition

could be quantified simply by an ex situ gravimetric technique, by simply weighing the pellets before and after carbon burn off. Alternately, one can use oxygen-bearing feed gas to burn off the carbon deposits in situ at a high reactor temperature and monitor the CO₂ emissions over a period of time.

Due to the superior performance of Pt-based materials, some of their reaction products were further investigated with MS. In particular, the reactor exit concentrations of CH₄, CO, and CO₂ were quantified and are presented in Figure 3. As evident from this figure, substantial amounts of CH₄ (i.e. 1.5–2.0%) were produced, reaching levels that were comparable with those of H₂. Clearly, CH₄ ties up substantial amounts of hydrogen, thereby lowering the selectivity for H₂ production. Therefore, significant reductions in CH₄ will be necessary to render these leads commercially viable. In addition, substantial levels of CO (i.e. 0.5%) were also formed as a byproduct over supported Pt catalysts. This is also undesirable, since even trace levels of CO adversely impact the current generation of electrocatalysts used in fuel cells. Consequently, we are presently exploring binary and higher order combinations of Pt-based and other catalytic metals, together with other supports in order to increase H₂ production rates and to decrease the levels of byproducts. The results of these investigations will be presented in a future communication.

In conclusion, the systematic application of the tools of combinatorial catalysis or high-throughput experimentation to a *low-temperature* ethanol steam reforming reaction resulted in the discovery of Pt/CeO₂ and Pt/TiO₂ as promising new leads. Although these catalytic materials were highly active, converting over 90% of ethanol at 300 °C, their H₂ production levels require further improvement. Therefore, future studies must focus on increasing the selectivities for H₂ production, while decreasing the same for CH₄, CO, and other byproducts. This could be accomplished, for example, by considering binary, ternary, and higher order combinations of Pt on these supports, using the genetic algorithm approach.²²

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