High Throughput Discovery of Families of High Activity WGS Catalysts: Part I - History and Methodology

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Abstract: State-of-art water gas shift catalysts (FeCr for high temperature shift and CuZn for low temperature shift) are not active enough to be used in fuel processors for the production of hydrogen from hydrocarbon fuels for fuel cells. The need for drastically lower catalyst volumes has triggered a search for novel WGS catalysts that are an order of magnitude more active than current systems. Novel catalytic materials for the high, medium and low temperature water gas shift reactions have been discovered by application of combinatorial methodologies. Catalyst libraries were synthesized on 4 inch wafers in 16x16 arrays and screened in a high throughput scanning mass spectrometer in the temperature range 200ºC to 400ºC. More than 200 wafers were screened under various conditions and more than 250,000 experiments were conducted to comprehensively examine catalyst performance for various binary, ternary and higher-order compositions.

Keywords: Water-gas shift, combinatorial, high throughput screening.

1. INTRODUCTION

Renewed interest in the WGS reaction and the demand for more efficient WGS catalysts was triggered by the development of stationary as well as mobile fuel cell systems for power generation. Currently, many research programs are directed toward the development of superior water-gas-shift catalysts for use in fuel processors that convert gasoline into a hydrogen-rich gas for automotive PEM fuel cells. One of the major technical hurdles to PEM fuel cell commercialization is the need for a fuel processing system that is light and small enough to fit into the confined spaces of a consumer's home. The system must also be able to perform reliably under highly variable power loads, be capable of rapid start-up, and deliver a gas stream containing very low levels of carbon monoxide. Carbon monoxide is a poison to all existing electrocatalysts employed in PEM fuel cells, and its presence results in rapid degradation of performance.

The water-gas shift reactor is a critical component of the fuel processor. Its function is to reduce the carbon monoxide concentration to intermediate levels, which can then be further reduced in a subsequent preferential oxidation step or with the use of different types of gas separation, such as PSA or membrane. Conventional Cu based and Fe based catalysts used for the water-gas shift reaction are unsuitable for use in mobile fuel processors. This is due to their insufficient reactivity (in terms of total volume), as well as their tendency to degrade under the severe conditions encountered in non-industrial settings. Furthermore, conventional Cu and Fe WGS systems require activation by *in-situ* reduction, and can lose this activity upon exposure to air. Finally, they suffer from transportation issues related to the catalysts' pyrophoric nature ultimately leading to decomposition. Meeting these challenges in the design of water-gas shift catalysts is critical to the commercial success of automotive PEM fuel cell systems.

The water gas shift reaction (Equation **1**) is commonly used to adjust the CO/H_2 ratio in syngas in order to generate pure hydrogen or to remove CO from gas streams [1-25]. Depending on the CO conversion required, commercial processes are carried out in two distinct temperature ranges: An upstream high temperature shift stage (HTS, 300-350°C, Fe/Cr-oxide catalysts) and a second downstream low temperature shift stage (LTS, 200-300°C, Cu/ZnO catalysts) [26-73].

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad \Delta H_{600} = -38.9\ \text{kJ/mol},\ K_p = 27$$
$$\Delta H_{700} = -38.1\ \text{kJ/mol},\ K_p = 9$$

Equation 1. Water-gas shift reaction.

Various alternative catalyst systems have been proposed [74-88] including supported precious metals [89-156] that offer some advantages. These include elimination of the *in*

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situ activation step, increased tolerance to temperature excursions, the reduction of size/weight of shift reactors, and extended lifetimes of the catalyst. Precious metal WGS catalysts that have been described in the literature involve Pt, Pd, and Rh supported on a wide range of materials including ceria, zirconia, various mixed valence and rare earth oxides, ceria primed alumina, and titania [89-149]. Other systems that contain supported Ru have also been reported [150-156]. Deactivation issues have been addressed by Sokolovskii and Farrauto for Pt/CeO_2 [157,158], Flytzani-Stephanopouls and Thompson for Au/CeO_2 [159, 160], and Gorte for Pd/CeO_2 [161]. Surface contamination as well as loss of metallic surface area are seen as the major sources of deactivation, but can be managed by control of reaction conditions.

With cost/weight/volume modeling of WGS reactors based on ceramic monoliths washcoated with Pt/ceria catalysts (Table **1**), it was confirmed that the Partnership for a New Generation of Vehicle (PNGV) cost target ($150) will be met with reactors of less than six liters in volume and three kilograms in weight. These calculations were based upon on-board reforming and the targets may be slightly less for off-board. Also noteworthy are innovative concepts applied to the WGS reactor fabrication [162-183], such as the use of heat-recycling, improved thermal efficiency, and more compact design.

Table 1. Comparsion of Washcoated Pt/Ceria Cataytic Monnliths with State-of-Art Water-Gas-Shift Reactors, for a 50-kWatt Fuel Processor

Criterion	Pt/Ceria	State-of-Art
Cost	< $ 150	$ 300 to $ 500
Weight	< 3 kg	20-40 kg
Volume	5 to 6 liters	20-40 liters
CO Content	0.3 to 0.6%	<0.50

Novel LTS systems based on supported precious and base metal nanoparticles have also been synthesized, in particular Au on reducible metal oxides, that are highly active at very low temperatures - well below 200°C [184-213].

Combinatorial and high throughput methods have become popular with the demand for developing more novel materials. This demand has been further driven by research applying concepts of synergy to metal combinations in catalyst systems. A combinatorial search by secondary screening for novel WGS catalysts incorporating Pt and Cu systems has also been carried out by Mirodatos [214, 215].

We have applied combinatorial and high throughput methodologies [216-228] to the discovery of novel and highly active families of high, medium, and low temperature water-gas shift catalysts. The discovery program started with primary screening, where wafer-formatted thick-film libraries were analyzed in Symyx' scanning mass spectrometer (SMS) [229-241]. Secondary screening involved the confirmation of hits and elimination of false positives, as well as scale up of leads, using the Celero^{TM} 8x1 multi channel fixed bed reactors [242-247]. In this paper, we review the history that guides the direction of the combinatorial screening and will report on the methodology used to examine the water-gas shift reaction utilizing combinatorial methods. HTS, MTS, LTS, full-range shifters, rare earth systems, and non-noble metal systems will be discussed in forthcoming publications.

2. EXPERIMENTAL

An integrated synthesis and screening workflow has been developed and applied to WGS catalyst development [248, 249], using wafers formatted as thick film libraries.

2.1. Screening Strategy and Library Design

Libraries were synthesized on round 3 inch or 4 inch quartz wafers in an 11x11 or 16x16 element format (Fig. **1**). Gradients of precursor solutions were chosen in order to obtain an array of solution mixtures within a single microtitre plate. A catalyst library substrate (wafer) is defined with an array of wells to which a portion of the premixed solutions from the microtitre plate will be transferred, and these libraries are designed using proprietary Symyx software. If precursor solutions are incompatible, gradients of the individual solutions are prepared in different microtitre plates, and transferred sequentially to the wafer. Once the library design is complete, the software generates a text file containing instructions that control liquid dispensing robots, which physically prepare the libraries.

The methodology for catalyst synthesis that is based on carrier impregnation with noble metal or base metal precursor solutions is well established at Symyx. This work used proprietary robotic slurry dispensing technology for transferring the carrier powders (e.g., silica, alumina, titania, zirconia, ceria, niobia, magnesia) to the wafer-formatted pre-coated arrays (Fig. **2**). Once these arrays are loaded with the desired amount of support they then can be subsequently impregnated with metal solutions. The carrier slurries were prepared by combining the finely ground powders into an ethylene glycol/water/methoxyethanol mixture (e.g., 1.0 g ZrO_2 powder would be mixed into 4ml 30% ethylene glycol/30% water/40% methoxyethanol). Master batches of commercial Pt/CeO_2 shift catalysts, commercial Pt/ZrO_2 catalysts or pre-synthesized Pt/TiO_2 catalysts can also be doped with modifiers and promoter metal solutions using the robotic liquid dispensing unit for use in the wafer-formatted primary screen libraries. The wafers are then optionally calcined in air and reduced *ex-situ* in tubular ovens using a continuous flow of hydrogen.

Rapid broad screening was carried out with 3-point, 5-point, or 10-point binaries or ternaries, where the compositional space was mapped out by 3, 5, or 10 points of varying compositions of metal precursor solution (i.e. 10PB means 10-point binary, 5PT means 5-point ternary, etc). Active hits (samples that give high CO_2 production) that were identified in the discovery libraries were re-synthesized for confirmation and further optimization into a "focus" library. In this library, more shallow compositional gradients are used, for example, 56 points (compositions) were tested per ternary. These focus libraries more clearly reveal the trends from the conversion profiles, and give some indication as to which metal ratios to choose for scale up and further optimization. For example, a broad screen may be a

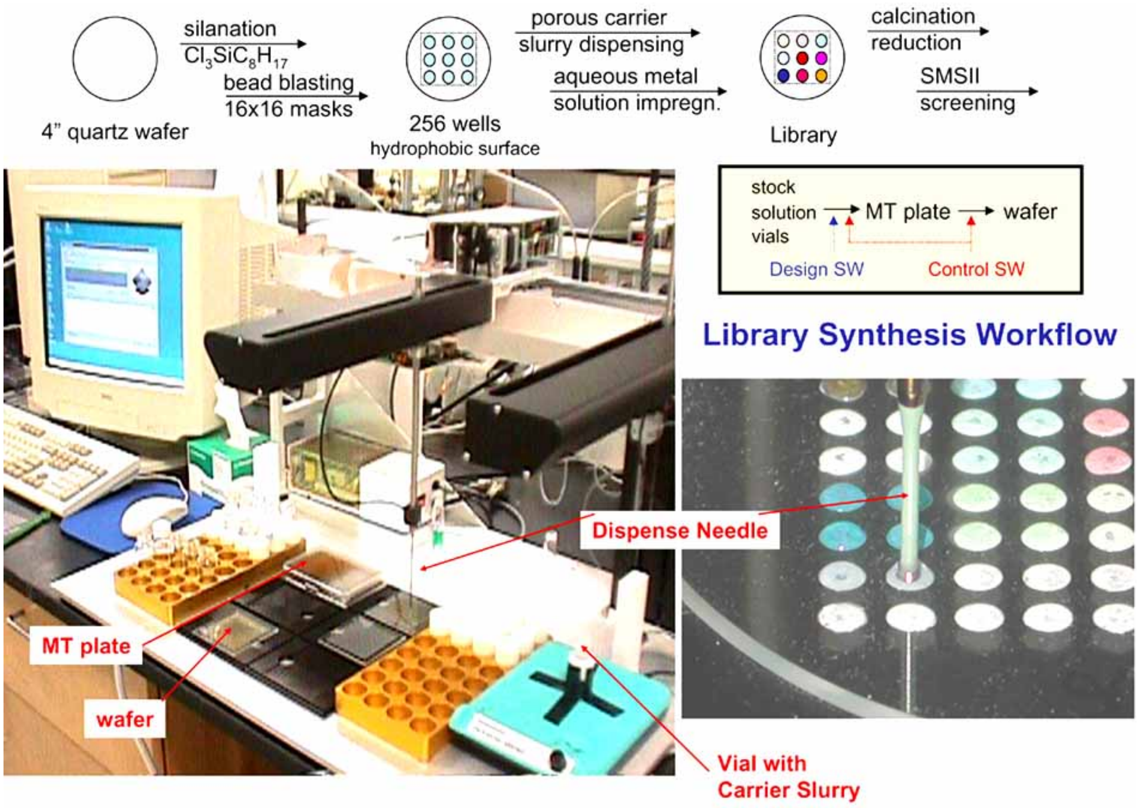

Fig. (1). Primary synthesis workflow. Catalysts can be prepared by impregnation or incipient wetness.

5-point binary (5PB) that consists of Pt metal with a transitional metal (Mn, Co, Fe, Ni, or Cr) supported on alumina, which would be depicted as Pt-(Mn-Co-Fe-Ni-Cr)/Al_2O_3. A subsequent focus library may be simplified to two metal system of Pt -Mn/Al_2O_3, with the amounts of Pt and Mn varied much more broadly. Note that in our formulas, elements within parentheses ( ) are to be selected from.

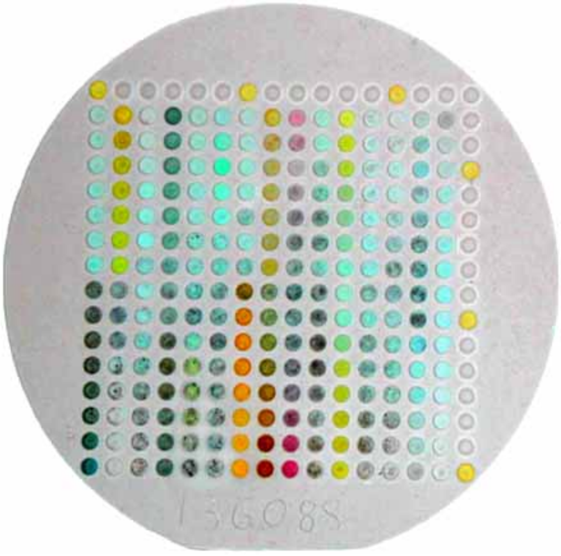

Fig. (2). Example of 4 inch quartz wafer with thirty 8-point binaries on gamma-alumina carrier.

2.2. Precursor Stock Solutions

Commercially available as well as proprietary recipes were used for metal precursor solutions in the synthesis of the catalysts. For the WGS relevant metals, the following is a non-inclusive list of examples of the ligands and anions used in precursor solutions: amines, nitrates, nitrites, chlorides, hydroxides, acetates, formates, and citrates. In general, more that a hundred different precursor solutions were used, however sulfur containing anions were specifically not used as metal precursors.

2.3. SMSII Screening

Scanning mass spectrometry version 2 (SMS-II) is a primary screening tool that uses a flat wafer catalyst surface, a scanning/sniffing nozzle, and a mass spectrometer to compare relative catalytic activities (Fig. **3**). Quartz wafers are mounted on a standard wafer holder that allows movement in the XY plane. The scanning/sniffing nozzle moves in the Z direction, and is designed to 'touch down' on the surface of the wafer. The nozzle surrounds each independent catalyst element and delivers the feed gas, and then transmits the product gas stream to a quadrupole mass spectrometer. Each element is heated locally using a CO_2 laser, allowing a screening temperature range of approximately 200-600 °C. The product signals from each element are analyzed for a given time period (generally 1-2 minutes), where the average of the last 6 data points is calculated and reported for each signal. The mass spectrometer can be programmed to monitor up to a total of

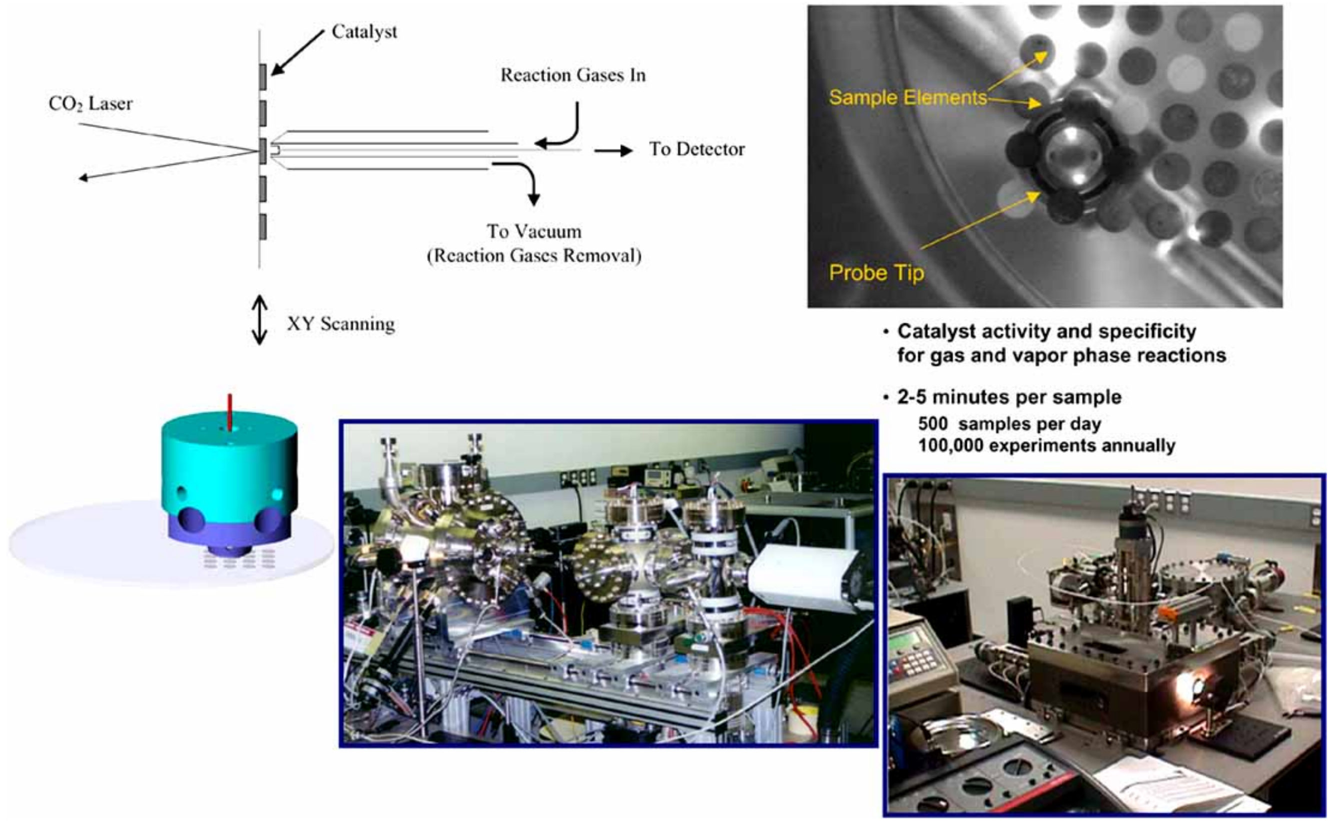

Fig. (3). Scanning Mass Spectrometer.

20 individual masses. Each additional mass adds 20% to the total analysis time, therefore minimizing the number of analysis channels is important for a reasonable analysis time. For our WGS screening purposes we analyzed seven masses: 2, 16, 18, 28, 40, 44, and 84, corresponding to hydrogen, methane, water, CO, argon, CO_2 and krypton. This resulted in a screening time of approximately 3.5 hours per 11x11 catalyst grid, and we have recently upgraded our SMSII software to allow for automated temperature ramping on an individual wafer. Therefore, the researcher only interacts with the apparatus to load the wafer, which is then analyzed typically for temperatures of 250, 300, 350, and 400℃. Since time-on-stream is short for SMS primary screening, no information on deactivation or long-term stability of catalysts can be retrieved.

2.4. Reaction Conditions

Krypton was used as an internal standard and all the raw data for CO, CO_2, and H_2O gases were normalized to the Kr signal. The reactor was operated in the temperature regime of 250 - 450℃, with the transfer lines and reactor head temperatures at 180℃. The pressure inside the reactor was 30 psi of argon gas, and the following gas mixtures was added during analysis, 51.6 % H_2, 7.4 % Kr, 7.4 % CO, 7.4 % CO_2 (premixed tank), 26.2 % H_2O. The approximate total analysis time (on stream) was 160 sec., with the signal being averaged from the final 40 sec. A 3” wafer took about 3.5 hours to fully screen.

3. RESULTS AND DISCUSSION

3.1. Data Processing and Data Analysis

A proprietary, custom software program running on a dedicated Windows computer controls the SMSII instrument. This program, in addition to controlling the hardware, also creates a set of data files that contain setup parameters and the collected data for each SMSII run for an 11x11 or 16x16 element matrix. On a regular schedule (currently nightly), the data from these files are automatically uploaded to the Symyx Oracle Database, where they are written to tables. The Symyx Database is a centrally managed data repository through which data can be accessed from a variety of in-house sources.

For this project, extraction of data from the Symyx Database was performed by custom data-extraction web pages. Written as a Java Server Page, they communicate with Oracle using standard Java Database Connectivity (JDBC) routines. Specialized SQL statements were written to extract both raw and computationally processed values from the database tables. All of the normalizations, statistical scores and other computed values, as discussed in the Data Analysis section below, were implemented in SQL. The extracted data records that were written to files are of two types, which can be easily downloaded to the user's computer. One of these is a comma-separated-value (csv) file that can be read by, for example, Microsoft Excel, and the other is a visualization file (sfs file) that can be opened in Spotfire^{TM}. The extraction

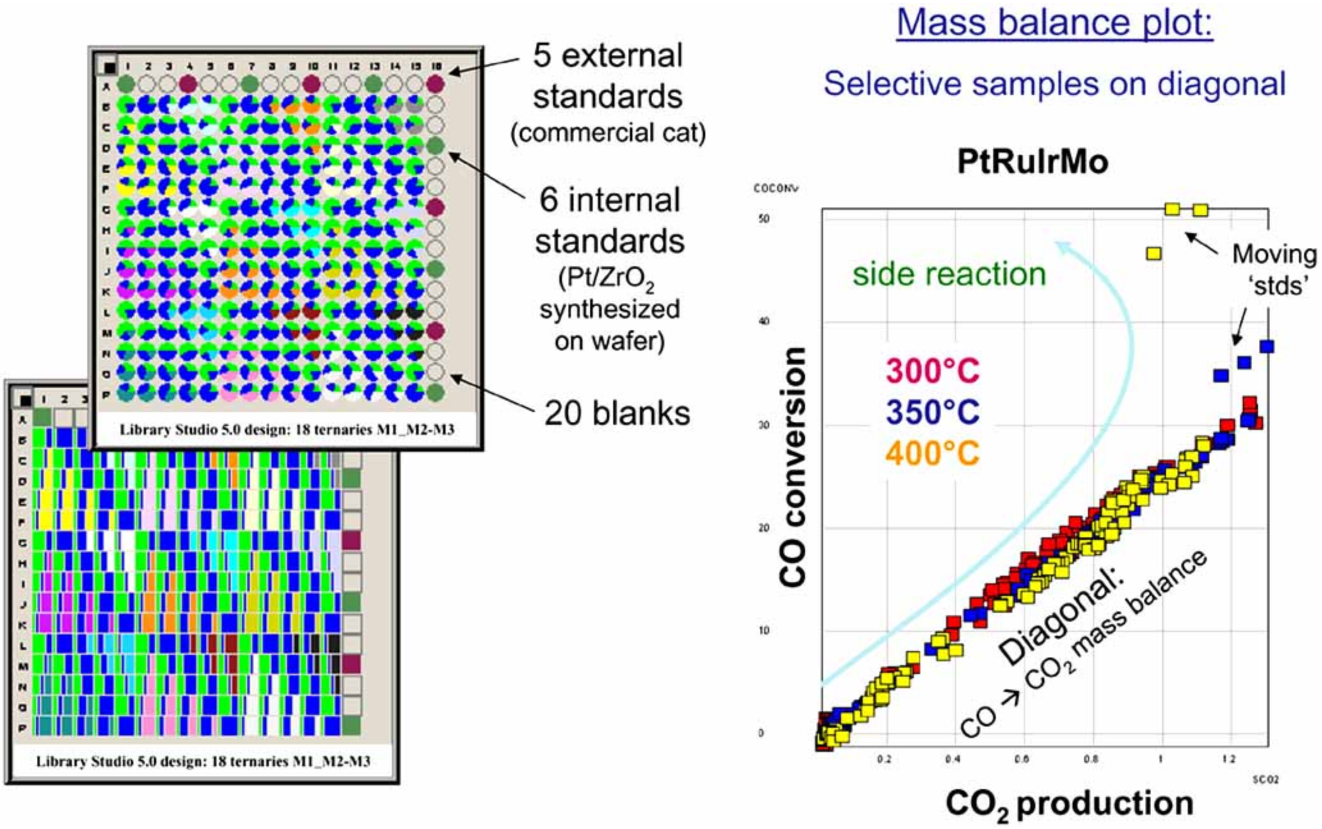

Fig. (4). Data analysis by mass balance plots.

and downloading could be initiated from any computer, requiring only a reasonably up-to-date web browser.

Chemical compositions for all libraries were also entered into the Database, starting from the library designs. The SMSII-data extracts were augmented with columns showing mole fractions of participating metals, and the identity of the support material (Fig. **4**).

3.2. Data Analysis

The raw data were first normalized to the Kr signal (internal standard) by the following equation:

Norm CO_2 = raw CO_2/raw Kr (repeated for all masses).

The normalization of each mass to the Kr internal standard compensates for systematic errors (e.g., pressure fluctuations, gas flow fluctuations, varying wafer-nozzle gap) and improves the wafer-to-wafer reproducibility. Next, the signals of Pt/CeO_2 (commercial obtain sample) or Pt/ZrO_2 (internally synthesized) standards, found in first row and last column of wafer, and all blank elements were averaged. The commercial standard was deposited after the thermal processing of the wafer and prior to screening, which allowed checking of the 'wafer to wafer' reproducibility. Conversely, the internal standard was synthesized on the wafer, where it underwent all the thermal pretreatments of the wafer and allowed for checking the uniformity across the wafer. This procedure was apart from providing a benchmark for relative comparisons with the library elements.

A quality factor was also calculated from the average standard signal, the average blank signal (background) and the standard deviations of the distribution functions for the standards and blanks, respectively. This calculation is expressed as:

Quality = (ave std-ave backgr)/(stddev std + stddev backgr)

where ave is the average of the standard (std) and background (backgr), and stddev is the standard deviation. With this expression it can be observed good quality data with a high S/N ratio and good uniformity across the wafer would result in a large quality factor.

The data analysis of the library screens was based on "mass balance plots", where the CO_2 production is plotted versus the CO conversion. The CO_2 production is uncalibrated so Kr is used to normalize the mass spectrometry signals. Since the WGS reaction converts one CO molecule into one CO_2 molecule, the selective shifters would lie on a straight line with a slope of unity, which is called the "WGS diagonal", and any deviation from the WGS diagonal is indicative of unselective side reactions. In this case with the methanation side reaction, the catalyst's performance would result in CO consumption far greater than its CO_2 production and would deviate from the WGS diagonal.

3.3. Trajectory Mapping

The SMS screening results demonstrate that dispersed noble metals can catalyze both WGS and methanation

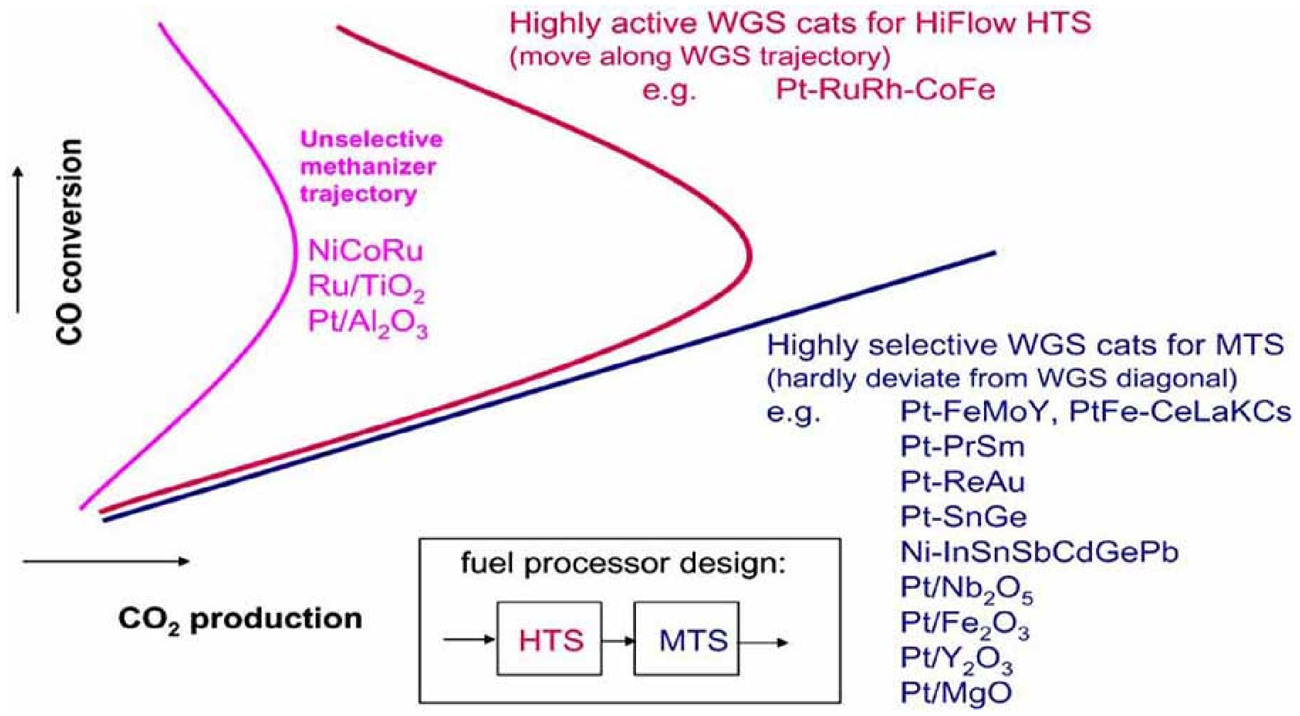

Fig. (5). Trajectories for active and selective WGS catalysts.

reactions, which compete with each other. Here, the selectivity of the WGS reaction strongly depends on temperature of the reaction, the type of noble metal (NM) used, as well as the NM dispersion. In the case of choosing the proper NM, Pt metal favors the WGS reaction, whereas Ru and Rh tend to favor methanation. The dispersion, which is a function of NM loading, will depend on the nature of the dispersant and the pretreatment. Therefore, highly active, well-dispersed NM's will catalyze the WGS reaction in the middle temperature shift region (MTS) while promoting methanation at high temperature shift (HTS). The metal loading of the libraries (i.e. the compositional metal gradients) was purposely chosen to achieve CO conversion between 10 and 70 %, in order to avoid experimental error while also staying away from WGS equilibrium. This facilitates the discrimination of catalysts and allows for better analysis of the metal and dopant effects on the activity and selectivity of a particular catalyst family. For each family (metals that are the same but have different composition or metal loadings), data points from the catalysts are mapped out on a smooth curve or "trajectory" when plotting the CO_2 production versus CO conversion. Fig. (**5**) shows the unselective methanation trajectory that is characterized by a high CO conversion but negligible CO_2 production, as seen for Ru/TiO_2. The highly selective WGS trajectory shows hardly any deviation from the WGS mass balance diagonal, as with Pt-Fe and Pt-Mo, even at high temperatures or at high metal loadings. Typically for many of the trajectories, the crossover from the WGS reaction to methanation was observed at higher temperatures or higher metal loadings, as seen for Pt-Ru-Ce. The longer the catalysts stay on the WGS diagonal and the later they deviates into the methanation reaction branch, the more selective is the catalyst family and indicative of how synergistic the combination of metals are for the catalyst.

Figs. (**6**, **7**) demonstrate this principal further. In Fig. (**6**), the binary system Pt-(Ir-Ag-Au) shows a single trajectory at 250 C, while PtRu-Fe deviates more from the WGS diagonal. However, Pt-Ru-Fe is still more selective and synergistic than Ru-Fe alone (Fig. **7**), which is more selective and synergistic than such methanizers as Ru-Ti. Furthermore, Pt-Ru-Co-Fe also demonstrates improvement in selectivity and synergistics performance over Ru-Co-Fe catalyst (Fig. **6**). These plots are the foundation for how subsequent data is analyzed and interpreted for the other catalyst families.

4. CONCLUSION

New advanced noble metal WGS catalysts have been discovered as cost effective components in fuel processor systems for fuel cell and hydrogen generation applications. The development of time efficient and reliable combinatorial technologies for discovery and exploration of these new novel materials was paramount. Also, the development of software and database for the cataloging and interpreting extremely large data sets was a necessity.

As a result of the development of a novel NM WGS catalyst, reactors can be very compact and cost competitive compared to base metal reactors, being 10 times smaller with a similar cost for a same capacity unit. The new proprietary catalysts will be safer and easier to handle since they do not have the self-heating and handling issues associated with the

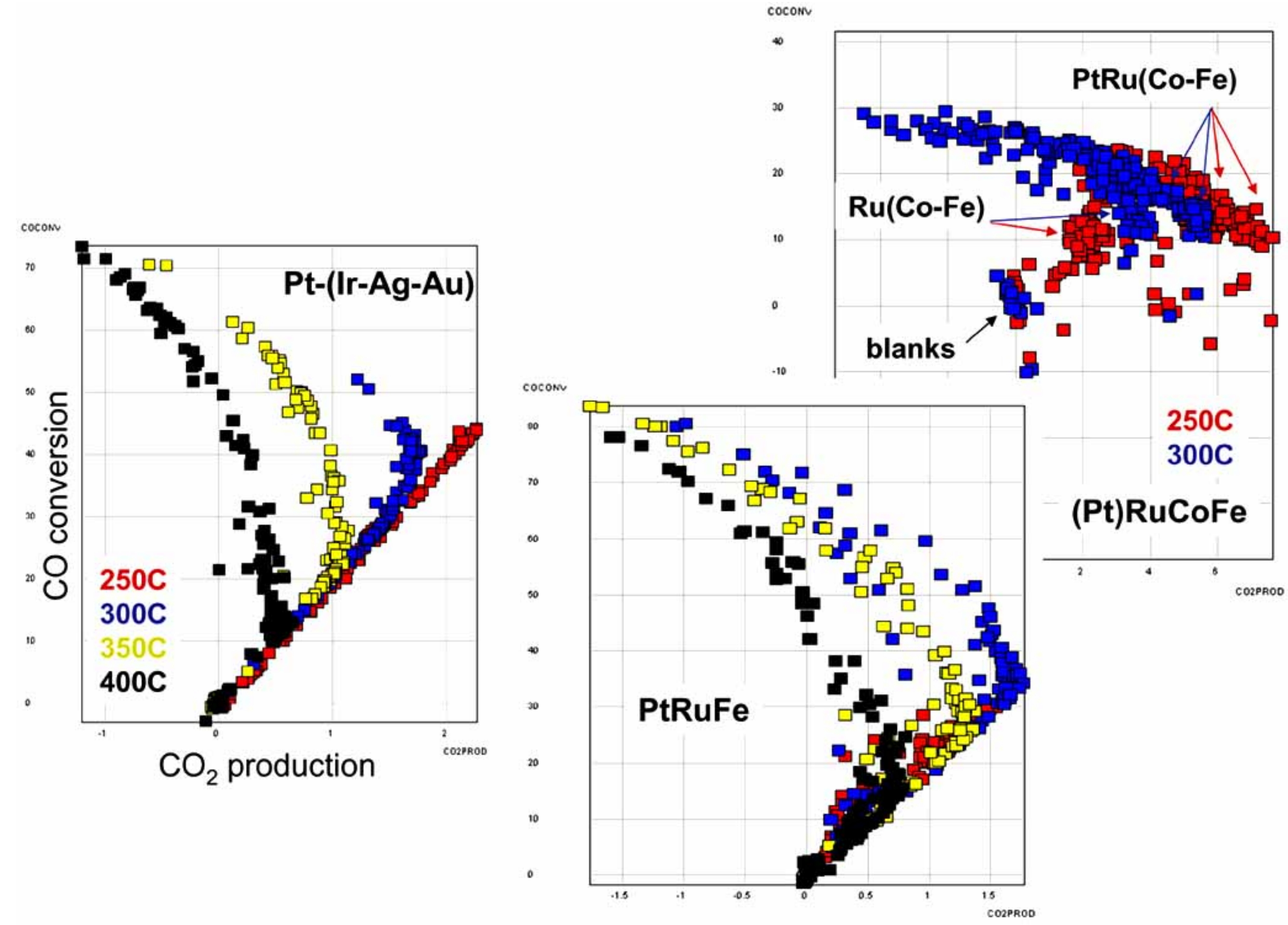

Fig. (6). Examples of single and multiple trajectories.

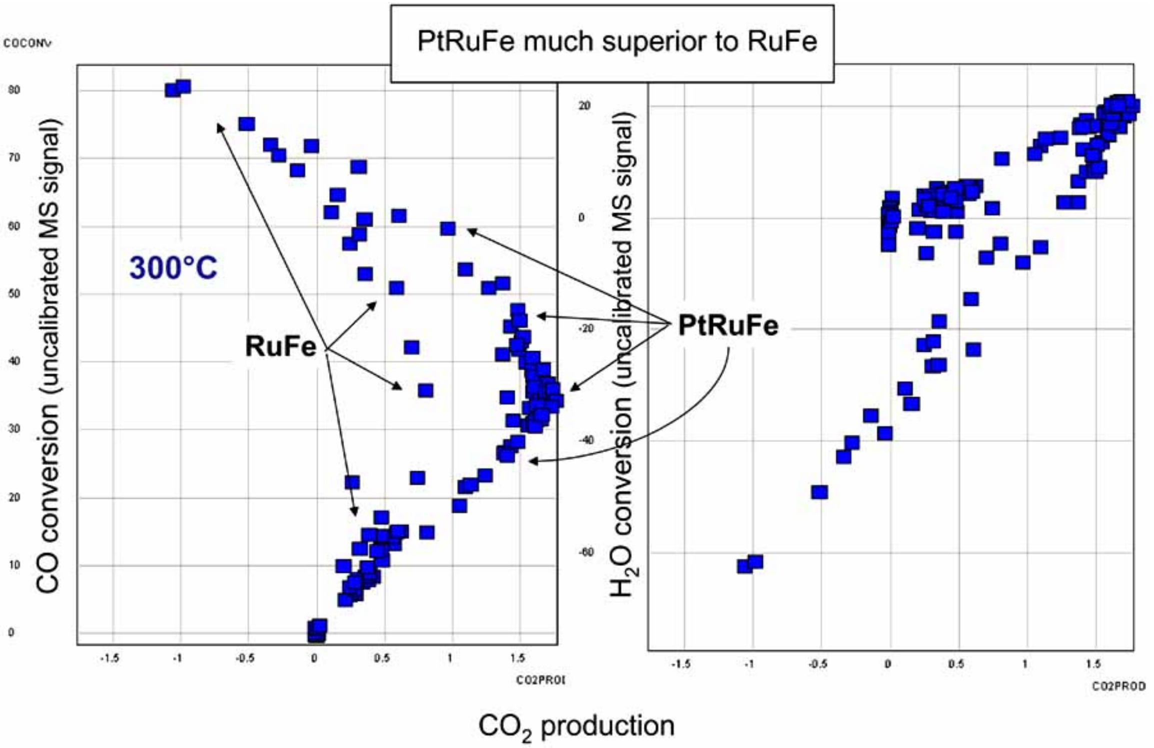

Fig. (7). Trajectories of Pt-Ru-Fe and Ru-Fe.

base metal catalysts. Newly designed novel catalysts will allow for the expansion of WGS technology to new applications or at least greatly improve the performance in current uses.

In the coming months we will report details on the range of WGS catalysts developed using the methods described in this paper. They encompass HTS-LTS and include full range shifters as well. Compositions include RE and non-NM catalysts. A portion of this work has appeared in recent patents and patent applications [250-257].

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REFERENCES

[1] Weissermel, K.; Arpe, H.J. Industrial organic chemistry, Wiley-VCH: Weinheim, **1993**.

[2] Rase, H.F. Handbook of commercial catalysts: heterogeneous catalysts, CRC Press: Boca Raton, **2000**.

[3] Grenoble, D.C.; Estadt, M.M. The chemistry and catalysis of the water gas shift reaction. *J. Catal*., **1981**, *67*, 90-102.

[4] Rhodes, C.; Hutchings, G.J.; Ward, A.M. Water-gas shift reaction: finding the mechanistic boundary. *Catal. Today*, **1995**, *23*, 43-58.

[5] Shido, T.; Iwasawa, Y. Regulation of reaction intermediate by reactant in the water-gas shift reaction on CeO2, in relation to reactant-promoted mechanism. *J. Catal*., **1992**, *136*, 493-503.

[6] Trimm, D.L.; Onsan, Z.I. On-board fuel conversion for hydrogen fuel cell driven vehicles. *Catal. Rev*., **2001**, *43*(1&2), 31-84.

[7] Gray, P.G.; Petch, M.I. Advances with HotSpot fuel processing. *Platinum Metals Rev*., **2000**, *44*(3), 108-111.

[8] Senetar, J.J.; Towler, G.P.; Harness, J.R. Multistage combustion for fuel processing for use with fuel cell. U.S. Patent 6,342,197, January 29, **2002**.

[9] Schiodt, N.C.; Aasberg-Petersen, K.; Nielsen, P.E.H.; Lehrmann, P. Process for manufacture of hydrogen rich gas. EP Patent 1,149,799, October 31, 2001.

[10] Bentley, J.M.; Clawson, L.G.; Mitchell, W.L.; Dorson, M.H. Integrated reformer and shift reactor. EP Patent 1,181,241, February 27, 2002.

[11] Stevens, J.F.; Krause, C.F.; Naa, D. Method and apparatus for catalytic reducing carbon monoxide content of hydrogen-rich gas for fuel cells. WO Patent 02/45836, June 13, 2002.

[12] Van Nisselrooy, P.F.M.T.; De Jongh, W.R.; Scholten, A.; Stokman, J. Thermal regulating catalyst composition for use in fuel processor for a fuel cell system. WO Patent 01/37990, May 31, 2001.

[13] Sevenhuijsen, E.; Wentinck, H.M. Fuel processor. WO Patent 01/079112, October 25, 2001.

[14] Deshpande, V.A. Nested compact fuel processor for producing hydrogen rich gas. U.S. Patent 20020090328, June 20, 2002.

[15] Krause, C.; Wolfenbarger, J.K.; Martin, P. Compact fuel processor for producing hydrogen rich gas for fuel processor. U.S. Patent 20020094310, June 13, 2002.

[16] Wieland, S.; Baumann, F.; Starz, K.A. New powerful catalysts for autothermal reforming of hydrocarbons and water-gas shift reaction for on-board hydrogen generation in automotive PEMFC applications. *Soc. Automot. Eng*., Spec. Publ. SP (Fuel Cell Power for Transportation), **2001**, SP-1589, 17-21.

[17] Baumann, F.; Wieland, S. Precious and noble metal catalysts with oxidation catalysts for water gas shift reaction for manufacture of hydrogen from carbon monoxide. EP Patent 1,136,442, September 26, 2001.

[18] Baumann, F.; Wieland, S.; Docter, A.; Himmen, M. Procedure for operating a fuel cell system with improved cold start behaviour. WO Patent 03/015200, February 20, 2003.

[19] Godat, J.; Marechal, F. Optimization of a fuel cell system using process integration techniques. *J. Power Sources*, **2003**, *118*(1-2), 411-423.

[20] Ahmed, S.; Lee, S.; Carter, J.; Krumpelt, M. Fuel processor and method for generating hydrogen for fuel cells. U.S. Patent 6,713,040, March 30, 2004.

[21] Bortoff, S.A.; Eborn, J.; Varigonda, S. Multivariable control design for the water gas shift reactor in a fuel processor. *Proc. Am. Control Conf*., **2004**, *1*, 840-844.

[22] Crewdson, B.J.; Process for producing hydrogen including a water gas shift reaction. EP Patent 1,525,153, April 27, 2005.

[23] Baumann, F.; Wieland, S.; Britz, P.; Heikrodt, K. Combined power/heat plant for fuel cells with fuel gas manufacturing by steam reforming in combination with water gas shift reaction and methanation for carbon monoxide removal. U.S. Patent 6,923,948, August 02, 2005.

[24] Trimm, D.L. Minimization of carbon monoxide in a hydrogen stream for fuel cell applications. *Appl. Catal. A*, **2005**, *296*(1), 1-11.

[25] Crewdson, B.J. Process for producing hydrogen including a water gas shift reaction. WO Patent 04/013040, February 12, 2004.

[26] Muenger, J.R. Water gas shift conversion process. U.S. Patent 3,666,682, May 30, 1972.

[27] Gruendler, K.H.; Irgang, M.; Neth, N.; Sprague, M.J.; Zirker, G. Copper-containing catalysts for hydrogen manufacture. EP Patent 0,205,130, December 17, 1986.

[28] Ray, J.A.; Huang, D.C.; Dienes, E.K. Low-temperature water gas shift reaction catalyst, and its use in the manufacture of ammonia and hydrogen. EP Patent 0,371,526, June 06, 1989.

[29] Mesters, C.M.A.M.; Geus, J.W.; Kuijpers, E.G.M. Hydrogen produced with simultaneous formation of carbon dioxide. U.S. Patent 4,711,773, December 08, 1987.

[30] Klier, K.; Herman, R.G.; Vedage, G.A. Catalyst and method for production of alkylamines. U.S. Patent 5,021,233, June 04, 1991.

[31] Cai, Y.; Davies, S.; Wagner, J. Water gas shift catalyst. U.S. Patent 6,627,572, September 30, 2003.

[32] Adachi, T.; Sato, Y.; Fukuyama, T. Copper-zinc type catalyst for water gas shift reaction. JP Patent 3,236,382, August 26, 2003.

[33] Eguchi, K.; Yano, S.; Utaka, T.; Sekizawa, K.; Arai, H. Removal of CO from methanol reforming gas by low temperature shift reaction. *Sci. Technol. Catal*., **1998**, 445-448.

[34] Utaka, T.; Sekizawa, K.; Eguchi, K. CO removal by oxygen-assisted water gas shift reaction over supported Cu catalysts. *Appl. Catal. A*, **2000**, *194-195*, 21-26.

[35] Eguchi, K.; Kikuchi, R.; Sasaki, K.; Tanaka, Y.; Utaka, T. Water gas shift reaction over Cu-based mixed oxides for CO removal from the reformed fuels. *Appl. Catal. A*, **2003**, *242*(2), 287-295.

[36] Tanaka, Y.; Utaka, T.; Kikuchi, R.; Takeguchi, T.; Sasaki, K.; Eguchi, K. Water gas shift reaction for the reformed fuels over Cu/MnO catalysts prepared *via* spinel-type oxide. *J. Catal*., **2003**, *215*, 271-278.

[37] Tanaka, Y.; Takeguchi, T.; Kikuchi, R.; Eguchi, K. Influence of the preparation method and additive for Cu-Mn spinel oxide catalyst on water gas shift reaction of reformed fuels. *Appl. Catal. A*, **2005**, *279* (1-2), 59-66.

[38] Du, X.; Wang, S.; Xu, W.; Yuan, Z.; Zhang, C. Low temperature water gas shift catalysts for onboard hydrogen production. *Huagong Xuebao*, **2004**, *55*, 99-102.

[39] Nomura, K.; Yamazaki, K. Catalyst for water gas shift reaction containing Al Zn oxide, Cu and alkali, or alkali earth metal co-catalyst. JP Patent 4,321,924, November 18, 2004.

[40] Faur-Ghenciu, A.; Mallapudi, S.; Feaviour, M.R.; Trusty, N.E.; Reinkingh, J.G. High activity water gas shift catalysts with no methane formation. U.S. Patent 20050207958, September 22, 2005.

[41] Tanaka, Y.; Takeguchi, T.; Kikuchi, R.; Eguchi, K. Influence of preparation method and additive for Cu-Mn spinel oxide catalyst on water gas shift reaction of reformed fuels. *Appl. Catal. A*, **2005**, *279*(1-2), 59-66.

[42] Hutchings, G.J.; Copperthwaite, R.G.; Gottschalk, F.M.; Hunter, R.; Mellor, J.; Orchard, S.W.; Sangiorno, T. A comparative evaluation of cobalt chromium oxide, cobalt manganese oxide, and copper manganese oxide as catalysts for the water-gas shift reaction. *J. Catal*., **1992**, *137*, 408-422.

[43] de Souza, T.R.O.; Brito, S.M.D.; Andrade, H.M.C. Zeolite catalysts for the water gas shift reaction. *Appl. Catal. A*, **1999**, 178, 7-15.

[44] Chen, C.-S.; Cheng, W.-H. Study on the mechanism of CO formation in reverse water gas shift reaction over Cu/SiO2 catalyst by pulse reaction, TPD and TPR. *Catal. Lett*., **2002**, *83*(3-4), 121-126.

[45] Chen, C.-S.; Cheng, W.-H.; Lin, S.-S. Study of reverse water gas shift reaction by TPD, TPR and CO2 hydrogenation over potassium-promoted Cu/SiO2 catalyst. *Appl. Catal. A*, **2003**, *238*, 55-67.

[46] Chen, C.-S.; Cheng, W.-H.; Lin, S.-S. Study of iron-promoted Cu/SiO2 catalyst on high temperature reverse water gas shift reaction. *Appl. Catal. A*, **2004**, *257*, 97-106.

[47] Cai, Z.; Huang, W.; Jiang, L.; Li, Y.; Pan, Y.; Sun, Y.; Wang, G.; Xie, K.; Zhao, X.; Zhong, B. Surface structure sensitivity of the water-gas shift reaction on Cu(hkl) surfaces: a theoretical study. *J. Phys. Chem. B*, **2003**, *107*(2), 557-562.

[48] Callaghan, C.; Carpenter, M.; Chmielewski, M.; Datta, R.; Fishtik, I.; Lugo, A. An improved microkinetic model for the water gas shift reaction on copper. *Surf. Sci.*, **2003**, *541*(1-3), 21-30.

[49] Koryabkina, N.A.; Phatak, A.A.; Ruettinger, W.F.; Farrauto, R.J.; Ribeiro, F.H. Determination of kinetic parameters for the water-gas shift reaction on copper catalysts under realistic conditions for fuel cell applications. *J. Catal.*, **2003**, *217*, 233-239.

[50] Choi, Y.; Stenger, H.G. Kinetics, simulation and optimization of methanol steam reformer for fuel cell applications. *J. Power Sources*, **2003**, *124* (2), 432-439.

[51] Fukuhara, C.; Gonohe, K.; Igarashi, A.; Ohkura, H. Low-temperature water-gas shift reaction of plate-type copper-based catalysts on an aluminum plate prepared by electroless plating. *Appl. Catal. A*, **2005**, *279* (1-2), 195-203.

[52] Haukka, M.; Pakkanen, T.A. Preparation of supported heterogeneous catalysts by pulse impregnation: application to Ru3(CO)12/2,2´-bipyridine/SiO2 catalyst. *J. Catal.*, **1994**, *148*, 315-322.

[53] Jozwiak, W.K.; Maniecki, T.P.; Basinska, A.; Goralski, J.; Fiedorow, R. Reduction requirements for Ru/(K)Fe2O3 catalytic activity in water-gas shift reaction. *Kinet. Catal.*, **2004**, *45*(6), 879-889.

[54] De Andrade, H.M.C.; Fierro, J.L.G.; Figueiredo, R.T.; Ramos, A.L.D. Effect of low steam/carbon ratio on water gas shift reaction. *Catal. Today*, **2005**, *107-108*, 671-675.

[55] Schneider, M.; Kochloefl, K.; Pohl, J.; Bock, O. Iron oxide-chromium oxide catalyst for high temperature carbon monoxide conversion. U.S. Patent 4,598,062, July 01, 1986.

[56] Huang, D.C.; Braden, J.L. High-temperature shift catalyst and its manufacture. U.S. Patent 4,861,745, August 29, 1989.

[57] Ladebeck, J.; Kochloefl, K. Cr-free iron-catalysts for water gas shift reaction. *Stud. Surf. Sci. Catal*., **1995**, *91*, 1079-1083.

[58] Ward, A.M. Shift reaction catalysts. U.S. Patent 5,656,566, August 12, 1997.

[59] Schneider, M.; Kochloefl, K.; Maletz, G.J.; Ladebeck, J.; Heinisch, C. Chromium-free catalyst based on iron oxide for converting carbon monoxide. EP Patent 0,634,990, May 21, 1997.

[60] Koy, J.; Ladebeck, J.; Hill, J.R. Role of Cr in Fe based high temperature shift catalysts. *Stud. Surf. Sci. Catal.*, **1998**, *119*, 479-484.

[61] Carneiro de Araujo, G.; do Carmo Rangel, M. An environmental friendly dopant for the high-temperature shift catalysts. *Catal. Today*, **2000**, *62*, 201-207.

[62] Hu, Y.; Jin, H.; Liu, J.; Hao, D. Reactive behaviors of iron-based shift catalyst promoted by ceria. *Chem. Eng. J.*, **2000**, *78*, 147-152.

[63] Do Carmo Rangel, M.; Marchetti, G.S.; Rangel Costa, J.L. A thorium-doped catalyst for the high temperature shift reaction. *Catal. Today*, **2002**, *77*(3), 205-213.

[64] ICI, Manufacture of hydrogen by steam reforming. U.S. Patent 5,030,440, July 09, 1991.

[65] Ward, A.M. Process for the production of hydrogen from a carbonaceous feedstock. WO Patent 00/017096, March 30, 2000.

[66] Chang, L.; Ma, H.; Tan, X.; Zhang, J.; Zhu, H. Preparation and high-temperature water-gas shift catalytic features of La1-xCexFeO3 perovskite. *J. Rare Earth*, **2004**, 22(3), 357-360.

[67] Rangel, M.D.C.; Aouine, M.; Junior, I.L.; Millet, J.-M.M. The role of vanadium on the properties of iron based catalysts for the water gas shift reaction. *Appl. Catal. A*, **2005**, *283*(1-2), 91-98.

[68] Teng, B.T.; Chang, J.; Yang, J.; Wang, G.; Zhang, C.-H.; Xu, Y.-Y.; Xiang, H.-W.; Li, Y.-W. Water gas shift reaction kinetics in Fischer-Tropsch synthesis over an industrial Fe-Mn catalyst. *Fuel*, **2005**, *84*(7/8), 917-926.

[69] He, R.; Liu, Q.; Ma, W.; Mu, Z. Reaction and characterization studies of an industrial Cr-free iron-based catalyst for high-temperature water gas shift reaction. *Catal. Today*, **2005**, *106*(1-4), 52-56.

[70] Sato, Y.; Terada, K.; Soma, Y.; Miyao, T.; Naito, S. Marked addition effect of Re upon the water gas shift reaction over TiO2 supported Pt, Pd and Ir catalysts. *Catal*. *Commun*., **2006**, *7*, 91-95.

[71] Cant, N.W.; Lei, Y.; Trimm, D.L. Activity patterns for the water gas shift reaction over supported precious metal catalysts. *Catal. Lett.*, **2005**, *103*(1-2), 133-136.

[72] Stone, F.S.; Waller, D. Cu-ZnO and Cu-ZnO/Al2O3 catalysts for the reverse water-gas shift reaction. The effect of the Cu/Zn ratio on precursor characteristics and on the activity of the derived catalysts. *Topics Catal.*, **2003**, *22*(3-4), 305-318.

[73] Ronning, M.; Huber, F.; Meland, H.; Venvik, H.; Chen, D.; Holmen, A. Relating catalyst structure and composition to the water-gas shift activity of Cu-Zn-based mixed-oxide catalysts. *Catal. Today*, **2005**, *100*, 249-254.

[74] BASF, Catalysts for the conversion of carbon monoxide to carbon dioxide by steam. U.S. Patent 3,529,935, September 22, 1970.

[75] Aldridge, C.L.; Kalina, T. Hydrogen manufacture. U.S. Patent 3,850,841, November 26, 1974.

[76] Michel, A.; Henkel, H.J.; Koch, C.; Kostka, H. Oxide catalyst for conversion of water gas. GB Patent 1,540,668, February 14, 1979.

[77] Park, J.N.; Kim, J.H.; Lee, H.I. A study on the sulfur-resistant catalysts for water gas shift reaction. I. TPR studies of Mo/Al2O3 catalysts. *Bull. Korean Chem. Soc.*, **1998**, *19*(12).

[78] Schiodt, N.C.; Aasberg-Petersen, K.; Nielsen, P.E.H.; Lehrmann, P. Process for manufacture of hydrogen rich gas. U.S. Patent 20010055560, December 27, 2001.

[79] Park, S.W.; Joo, O.S.; Jung, K.D.; Kim, H.; Han, S.H. Development of ZnO/Al2O3 catalyst for reverse-water-gas-shift reaction of CAMERE (carbon dioxide hydrogenation to form methanol *via* reverse-water-gas-shift reaction) process. *Appl. Catal. A*, **2001**, *211*, 81-90.

[80] Hu, C.; Qin, S.; Su, Z.; Yang, H. Theoretical study of the reaction mechanism of the gas-phase H2/CO2/Ni(3D) system. *J. Phys. Chem. A*, **2005**, *109*(29), 6498-6502.

[81] Thompson, L.T.; Patt, J.; Moon, D.J.; Phillips, C. Transition metal carbides, nitrides and borides and their oxygen containing analogs useful as water gas shift catalysts. WO Patent 01/074484, October 11, 2001.

[82] Darujati, A.R.S.; laMont, D.C.; Thomson, W.J. Oxidation stability of Mo2C catalysts under fuel reforming conditions. *Appl. Catal. A*, **2003**, 253 (2), 397-407.

[83] Moon, D.J.; Ryu, J.W. Molybdenum carbide water-gas shift catalyst for fuel cell-powered vehicles applications. *Catal. Lett.*, **2004**, *92*(1-2), 17-24.

[84] Nishikiori, H.; Takahashi, H.; Matsumoto, S.; Nagai, M. Catalyst, fuel cell electrode catalyst, and water gas shift catalyst. JP Patent 05/138006, June 02, 2005.

[85] El-Shobaky, G.A.; Mohamed, M.M.; Othman, A.I.; Salama, T.M. Low-temperature water-gas shift reaction on cerium containing mordenites prepared by different methods. *Appl. Catal. A*, **2005**, *279*(1-2), 23-33.

[86] Klier, K.; Herman, R.G.; Deemer, M. Ethanol synthesis and water gas shift over bifunctional sulfide catalysts. Technical progress report DOE/PC/91301-1-12, **1994**.

[87] Klier, K.; Herman, R.G.; Deemer, M. Technical Report Ethanol synthesis and water gas shift over bifunctional sulfide catalysts, Report Nos DOE/PC/91301, **1991-1993**.

[88] Mhadeshwar, A.B.; Vlachos, D.G. Hierarchical, multiscale surface reaction mechanism development: CO and H2 oxidation, water-gas shift, and preferential oxidation of CO on Rh. *J. Catal.*, **2005**, *234*, 48-63.

[89] Mendelovici, L.; Steinberg, M. Methanation and water-gas shift reactions over Pt/CeO2. *J. Catal.*, **1985**, *96*, 285-287.

[90] Kalakkad, D.S.; Datye, A.K.; Robota, H.J. Pt-CeO2 contact and its effect on CO hydrogenation selectivity. *J. Catal.*, **1994**, *148*, 729-736.

[91] Swartz, S.L.; Seabaugh, M.M.; Holt, C.T.; McCormick, B.E.; Dawson, W.J. Pt/ceria water-gas-shift catalysts, 17th NACS Meeting, Toronto, June 3-8, **2001**.

[92] Swartz, S.L.; Seabaugh, M.M.; McCormick, B.E.; Dawson, W.J. Nanoscale water-gas-shift catalysts, 222nd ACS National Meeting, Chicago, August 26-30, **2001**.

[93] Swartz, S.L. Nanoscale water-gas-shift catalysts, 230th ACS National Meeting, Washington, DC, United States, Aug. 28-Sept. 1, **2005**.

[94] Choung, S.Y; Ferrandon, M.; Krause, T. Water-gas shift catalysis on Pt bimetallic catalysts. Preprints of Symposia - American Chemical Society. *Div. Fuel Chem*., **2003**, *48*(2), 808-809.

[95] Swartz, S.L.; Seabaugh, M.M.; McCormick, B.E.; Dawson, W.J. Pt/ceria WGS catalysts for PEM fuel cell systems, ACS Preprints. *Fuel Chem. Div. Preprints*, **2001**, *46*(2), 674-675.

[96] Swartz, S.L.; Seabaugh, M.M.; Holt, C.T.; Dawson, W.J. Water gas shift catalysts. *Fuel Cell Bull.*, **2001**, *4*, 7.

[97] www.nextechmaterials.com/products.htm.

[98] Myers, D.J.; Krebs, J.F.; Krause, T.R.; Carter, J.D. Water-gas shift catalysts with improved durability for automotive fuel cell applications. *Fuel Chem. Div. Preprints*, **2001**, *46*(2), 676-677.

[99] Igarashi, A.; Higashi, H.; Mizobuchi, M.; Hashimoto, M.; Kinugawa, K. Catalyst used in water gas shift reaction for removing carbon monoxide from hydrogen gas for fuel cell. WO Patent 00/54879, September 21, 2000.

[100] Sharma, S.; Hilaire, S.; Vohs, J.M.; Gorte, R.J.; Jen, H.W. Evidence for oxidation of ceria by CO2. *J. Catal.*, **2000**, *190*, 199-204.

[101] Hilaire, S.; Sharma, S.; Gorte, R.J.; Vohs, J.M.; Jen, H.W. Effect of SO2 on the oxygen storage capacity of ceria-based catalysts. *Catal. Lett.*, **2000**, *70*, 131-135.

[102] Hilaire, S.; Wang, X.; Luo, T.; Gorte, R.J.; Wagner, J. A comparative study of water-gas-shift reaction over ceria supported metallic catalysts, *Appl. Catal. A*, **2001**, *215*, 271-278.

[103] Wang, X.; Gorte, R.J. The effect of Fe and other promoters on the activity of Pd/ceria for the water-gas shift reaction. *Appl. Catal. A*, **2003**, *247*, 157-162.

[104] Zhao, S.; Gorte, R.J. The activity of Fe-Pd alloys for the water-gas shift reaction. *Catal. Lett*., **2004**, *92*(1-2), 75-80.

[105] Bunluesin, T.; Gorte, R.J.; Graham, G.W. Studies of the water-gas shift reaction on ceria-supported Pt, Pd, and Rh: implications for oxygen-storage properties. *Appl. Catal. B*, **1998**, *15*, 107-114.

[106] Gorte, R.J.; Zhao, S. Studies of the water-gas shift reaction with ceria-supported precious metals. *Catal. Today*, **2005**, *104*, 18-24.

[107] Barbier, J.; Duprez, D. Hydrogen formation in propane oxidation on Pt-Rh/CeO2/Al2O3 catalysts. *Appl. Catal. A*, **1992**, *85*, 89-100.

[108] Shido, T.; Iwasawa, Y. Reactant-promoted reaction mechanism for water-gas shift reaction on Rh-doped CeO2. *J. Catal.*, **1993**, *141*, 71-81.

[109] Cordatos, H.; Bunluesin, T.; Stubenrauch, H.; Vohs, J.M.; Gorte, R.J. Effect of ceria structure on oxygen migration for Rh/ceria catalysts. *J. Phys. Chem.*, **1996**, *100*, 785-789.

[110] Dettling, J.C.; Lui, Y.K. Palladium-containing, ceria-supported platinum catalyst for three-way exhaust gas treatment. EP Patent 0,393,612, October 24, 1990.

[111] Xue, E.; O'Keeffe, M.; Ross, J.R.H. Water-gas shift conversion using a feed with a low steam to carbon monoxide ratio and containing sulphur. *Catal. Today*, **1996**, *30*, 107-118.

[112] Korotkikh, O.; Ruettinger, W.F.; Farrauto, R.J. Suppression of methanation activity by a water gas shift reaction catalyst. U.S. Patent 6,562,315, May 13, 2003.

[113] Tanaka, Y.; Utaka, T.; Kikuchi, R.; Sasaki, K.; Eguchi, K. CO removal from reformed fuel over Cu/ZnO/Al2O3 catalysts prepared by impregnation and coprecipitation methods. *Appl. Catal. A*, **2003**, *238*, 11-18.

[114] Ruettinger, W.F.; Korotkikh, O.; Farrauto, R.J. Non-pyrophoric water-gas shift reaction catalysts for hydrogen generation by reaction of CO and H2O in fluid media. U.S. Patent 20020061277, May 23, 2002.

[115] Silver, R.G. Shift converter having an improved catalyst composition for processing hydrogen-rich gas streams for fuel cells. WO Patent 02/090247, November 14, 2002.

[116] Zhu, T.; Silver, R.G.; Emerson, S.C.; Bellows, R.J. Oxygen-assisted water gas shift reactor having a supported catalyst, and method of its use. U.S. Patent 6,821,494, November 23, 2004.

[117] Nomura, K.; Yamamoto, S.; Yamazaki, K. Catalyst for water gas shift reaction with suppressed methanation. JP Patent 04/358323, December 24, 2004.

[118] Faur-Ghenciu, A.; Trusty, N.E.; Feaviour, M.E.; Reinkingh, J.G.; Shady, P.; Andersen, P.J. High-activity water gas shift catalysts consisting of noble metals, a metal oxide support, a promoter, and a support dopant. U.S. Patent 20050005520, January 13, 2005.

[119] Davis, B.H.; Jacobs, G. In situ DRIFTS investigation of the steam reforming of methanol over Pt/ceria. *Appl. Catal. A*, **2005**, *285*(1-2), 43-49.

[120] Crawford, A.C.; Burton, B.H.; Graham, U.M.; Jacobs, G.; Patterson, P.M. Low temperature water gas shift: the link between the catalysis of WGS and formic acid decomposition over Pt/ceria. *Int. J. Hydrogen Energy*, **2005**, *30*(11), 1265-1276.

[121] Buglass, J.; Desjardins, J.; Liu, K.; Sun, J. Noble metal water gas shift catalysis: kinetics study and reactor design. *Int. J. Hydrogen Energy*, **2005**, *30*(11), 1259-1264.

[122] Burch, R.; Goguet, A.; Meunier, F.C.; Reid, D.; Tibiletti, D. On the reactivity of carbonate species on a Pt/CeO2 catalyst under various reaction atmospheres: application of the isotopic exchange technique. *Appl. Catal. A*, **2005**, *289*(1), 104-112.

[123] Jacobs, G. Developing structural property relationships of Pt/ceria catalysts for low temperature water gas shift, AIChE Spring Natl. Meet. Conf. Proc., Atlanta, GA, **2005**, 2099.

[124] Cordatos, H.; Dardas, Z.; Feng, F.; Newman, C.A.; Opalka, S.M.; Radhakrishnan, R.; She, Y.; Tang, X.; Vanderspurt, T.H.; Wijzen, F.; Willigan, R.R. Water gas shift activity of noble metals and promoted noble metals supported on ceria-zirconia oxides, *AIChE Annu. Meet. Conf. Proc*., Austin, TX, **2004**, *505-506*, 9075-9076 and 9485-9486.

[125] Sato, Y.; Soma, Y.; Miyao, T.; Naito, S. The water-gas-shift reaction over Ir/TiO2 and Ir-Re/TiO2 catalysts. *Appl. Catal. A*, **2006**, *304*, 78-85.

[126] Jacobs, G.; Graham, U.M.; Chenu, E.; Patterson, P.M.; Dozier, A.; Davis, B.H. Low-temperature water-gas shift: impact of Pt promoter loading on the partial reduction of ceria and consequences for catalyst design. *J. Catal.*, **2005**, *229*, 499-512.

[127] Bispo, J.R.C.; Querino, P.S.; Rangel, M.D.C. The effect of cerium on the properties of Pt/ZrO2 catalysts in the WGSR. *Catal. Today*, **2005**, *107-108*, 920-925.

[128] Davis, B.H.; Graham, U.M.; Jacobs, G.; Patterson, P.M.; Ricote, S. Low temperature water gas shift: type and loading of metal impacts forward decomposition of pseudo-stabilized formate over metal/ceria catalysts. *Catal. Today*, **2005**, *106*(1-4), 259-264.

[129] Cordatos, H.; Dardas, Z.; Feng, F.; Newman, C.A. ; Opalka, S.M.; Radhakrishnan, R.; She, Y.; Tang, X.; Vanderspurt, T.H.; Wijzen, F.; Willigan, R.R. *AIChE Annu. Meet. Conf. Proc*., Austin, TX, **2004**, 505-506, 9075-9076, 9485-9486.

[130] Mhadeshwar, A.B.; Vlachos, D.G. Is the water-gas shift reaction on Pt simple ? Computer-aided microkinetic model reduction, lumped rate expression, and rate-determining step. *Catal. Today*, **2005**, *105*, 162-172.

[131] Goguet, A.; Meunier, F.; Breen, J.P.; Burch, R.; Petch, M.I.; Faur Ghenciu, A. Study of the origin of the deactivation of a Pt/CeO2 catalyst during reverse water gas shift (RWGS) reaction. *J. Catal.*, **2004**, *226*, 382-392.

[132] Jacobs, G. *AIChE Spring Natl. Meet. Conf. Proc*., Atlanta, GA, **2005**, 2099.

[133] Crawford, A.C.; Davis, B.H.; Graham, U.M.; Jacobs, G.; Patterson, P.M. Low temperature water gas shift: the link between the catalysis of WGS and formic acid decomposition over Pt/ceria. *Int. J. Hydrogen Energy*, **2005**, *30*(11), 1265-1276.

[134] Burch, R.; Goguet, A.; Meunier, F.C.; Reid, D.; Tibiletti, D. On the reactivity of carbonate species on a Pt/CeO2 catalyst under various reaction atmospheres: application of the isotopic exchange technique. *Appl. Catal. A*, **2005**, *289*(1), 104-112.

[135] Davis, B.H.; Jacobs, G. Reverse water-gas shift reaction: steady state isotope switching study of the reverse water-gas shift reaction using in situ DRIFTS and a Pt/ceria catalyst. *Appl. Catal. A*, **2005**, *284*, 31-38.

[136] Jacobs, G.; Crawford, A.C.; Davis, B.H. Water-gas shift: steady state isotope switching study of the water-gas shift reaction over Pt/ceria using in-situ DRIFTS. *Catal. Lett*., **2005**, *100*(3-4), 147-152.

[137] Moon, D.J.; Ryu, J.W.; Kim, D.H.; Lee, S.D.; Lee, B.G. Preparation of high performance water gas shift catalyst. U.S. Patent 20050238574, October 27, 2005.

[138] Trimm, D.L. Minimisation of carbon monoxide in a hydrogen stream for fuel cell application. *Appl. Catal. A*, **2005**, *296*(1), 1-11.

[139] Jacobs, G.; Ricote, S.; Patterson, P.M.; Graham, U.M.; Dozier, A.; Khalid, S.; Rhodus, E.; Davis, B.H. Low temperature water-gas shift: examining the efficiency of Au as a promoter for ceria-based catalysts prepared by CVD of a Au precursor. *Appl. Catal. A*, **2005**, *292*, 229-243.

[140] Chenu, E.; Jacobs, G.; Crawford, A.C.; Keogh, R.A.; Patterson, P.M.; Sparks, D.E.; Davis, B.H. Water-gas shift: an examination of Pt promoted MgO and tetragonal and monoclinic ZrO2 by *in situ* drifts. *Appl. Catal. B*, **2005**, *59*, 45-56.

[141] Igarashi, A.; Iida, H. Characterization of a Pt/TiO2 (rutile) catalyst for water gas shift reaction at low temperature. *Appl. Catal. A*, **2006**, *298*(1-2), 152-160.

[142] Mizobuchi, M.; Kinugawa, K.; Hashimoto, M.; Igarashi, A.; Iida, H. Method of preparation of catalyst for removing carbon monoxide in hydrogen rich gas for fuel cell. U.S. Patent 6,713,032, March 30, 2004.

[143] Walsh, T.L.; Rogers, D.B.; Balakos, M.W.; Madden, M.R. Water gas shift catalyst for fuel cells application. U.S. Patent 20050119118, June 02, **2005**.

[144] Rogers, D.B.; Walsh, T.L.; Madden, M.R.; Balakos, M.W. Water gas shift catalyst on a lanthanum-doped anatase titanium dioxide support for fuel cells application. WO Patent 2005061108, July 07, 2005.

[145] Liu, K.; Buglass, J.G.; Preston, J.L.; Zhu, T.; Schoonebeek, R.J. Hybrid water gas shift system to produce hydrogen-rich fuel for fuel cells. U.S. Patent 20050268553, December 08, 2005.

[146] Jacobs, G.; Williams, L.; Graham, U.; Thomas, G.A.; Sparks, D.E.; Davis, B.H. Low temperature water-gas shift: *in situ* DRIFTS-reaction study of ceria surface area on the evolution of formates on Pt/CeO2 fuel processing catalysts for fuel cell applications. *Appl. Catal. A*, **2003**, *252*, 107-118.

[147] Copperthwaite, R.G.; Gottschalk, F.M.; Sangiorgio, T.; Hutchings, G.J. Cobalt chromium oxide: a novel sulphur tolerant water-gas shift catalyst. *Appl. Catal.*, **1990**, *63*, L11-L16.

[148] Iida, H.; Igarashi, A. Difference in the reaction behavior between Pt-Re/TiO2 (rutile) and Pt-Re/ZrO2 catalysts for low-temperature water gas shift reactions. *Appl. Catal. A*, **2006**, *303*, 48-55.

[149] Correia dos Santos, D.; Oliveira, A.C.; Morais, P.C.; Garg, V.K.; de Oliveira, A.C.; Santos Corrrea, M.L.; do Carmo Rangel, M. Evaluation of Fe/MCM-41 catalysts in the water gas shift reaction. *Stud. Surf. Sci. Catal.*, **2004**, *154*, 2417-2424.

[150] Basinska, A.; Domka, F. Chlorine-free iron-ruthenium catalyst for the water-gas shift reaction. *Catal. Lett.*, **1993**, *22*, 327-331.

[151] Basinska, A.; Kepinski, L.; Domka, F. The effect of support on WGSR activity of ruthenium catalysts. *Appl. Catal. A*, **1999**, *183*, 143-153.

[152] Tonkovich, A.Y.; Zilka, J.L.; LaMont, M.J.; Wang, Y.; Wegeng, R.S. Microchannel reactors for fuel processing applications. I. water gas shift reactor. *Chem. Eng. Sci.*, **1999**, *54*, 2947-2951.

[153] Utaka, T.; Okanishi, T.; Takeguchi, T.; Kikuchi, R.; Eguchi, K. Water gas shift reaction of reformed fuel over supported Ru catalysts. *Appl. Catal. A*, **2003**, *245*, 343-351.

[154] Wang, Y.; Tonkovich, A.L.Y. Catalysts, reactors and methods of producing hydrogen *via* water gas shift reaction. U.S. Patent 20020114762, August 22, 2002.

[155] Farrauto, R.J.; Ilinich, O.; Ruettinger, W. A new generation of water gas shift catalysts for fuel cell applications. *J. Power Sources*, **2003**, *118*(1-2), 61-65.

[156] Zhu, T.; Silver, R.G.; Emerson, S.C.; Bellows, R.J. Oxygen-assisted water gas shift reactor having a supported catalyst, and method of its use. U.S. Patent 20030026747, February 06, 2003.

[157] Zalc, J.M.; Sokolovskii, V.; Loffler, D.G. Are noble metal-based water-gas shift catalysts practical for automotive fuel processing? *J. Catal.*, **2002**, *206*, 169-171.

[158] Farrauto, R.; Liu, X.; Ruettinger, W.; Xu, X. Deactivation of Pt/CeO2 water-gas shift catalysts due to shutdown/startup modes for fuel cell applications. *Appl. Catal. B*, **2005**, *56*(1-2), 69-75.

[159] Deng, W.; Flytzani-Stephanopoulos, M.; Fu, Q.; Saltsburg, H. *Appl. Catal. B*, **2005**, *56*(1-2), 57-68.

[160] Kim, C.H.; Thompson, L.T. Deactivation of Au/CeOx water gas shift catalysts. *J. Catal.*, **2005**, *230*(1), 66-74.

[161] Wang, X.; Gorte, R.J.; Wagner, J.P. Deactivation mechanisms for Pd/ceria during the water-gas shift reaction. *J. Catal.*, **2002**, *212*, 225-230.

[162] Song, C. Fuel processing for low-temperature and high-temperature fuel cells. Challenges, and opportunities for sustainable development in the 21st century. *Catal. Today*, **2002**, *77*, 17-49.

[163] Nagai, M.; Matsuda, K. Low-temperature water-gas shift reaction over cobalt-molybdenum carbide catalyst. *J. Catal.*, **2006**, *238*, 489-496.

[164] Basile, A.; Paturzo, L.; Gallucci, F. Co-current and counter-current modes for water gas shift membrane reactor. *Catal. Today*, **2003**, *82*, 275-281.

[165] Diniz da Costa, J.; Giessler, S.; Jordan, L.; Lu, G.Q.M. Performance of hydrophobic and hydrophilic silica membrane reactors for the water gas shift reaction. *Sep. Purif. Technol.*, **2003**, *32*(1-3), 255-264.

[166] Wheeler, C.; Jhalani, A.; Klein, E.J.; Tummala, S.; Schmidt, L.D. The water-gas shift reaction at short contact times. *J. Catal.*, **2004**, *223*, 191-199.

[167] Ciora, R.J.; Fayyaz, B.; Paul, P.K.T.; Mallada, R.; Sahimi, M.; Suwanmethanond, V.; Tsotsis, T.T. Preparation and reactive applications of nanoporous silicon carbide membranes. *Chem. Eng. Sci.*, **2004**, *59*(22-23), 4957-4965.

[168] Choi, Y.; Stenger, H.G. Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen. *J. Power Sources*, **2005**, *142*(1-2), 81-91.

[169] Kim, G.-Y.; Mayor, J.R.; Ni, J. Parametric study of microreactor design for water gas shift reactor using an integrated reaction and heat exchange model. *Chem. Eng. J.*, **2005**, *110*(1-3), 1-10.

[170] Hatalis, M.K.; Kothare, M.V.; Mukherjee, S. Novel glass micro-reactor for water gas shift reaction characterization. *AIChE Spring Natl. Meet. Conf. Proc.*, Atlanta, GA, **2005**, 2941-2942.

[171] El-Azzami, L.; Ho, W.S.W.; Huang, J. Modeling of CO2-selective water gas shift membrane reactor for fuel cell. *J. Membr. Sci.*, **2005**, *261*(1-2), 67-75.

[172] Barbieri, G.; Bernardo, P.; Brunetti, A.; Drioli, E.; Granato, T. Engineering evaluations of a catalytic membrane reactor for the water gas shift reaction. *Ind. Eng. Chem. Res.*, **2005**, *44*(20), 7676-7683.

[173] Pex, P.P.A.C.; Van Delft, Y.C. Silica membranes for hydrogen fuel production by membrane water gas shift reaction and development of a mathematical model for a membrane reactor, Report ECN-RX-05-123, Energy Research Centre of the Netherlands ECN, Petten (Netherlands), **2005**.

[174] Koukou, M.K.; Markatos, N.C.; Papayannakos, N.; Vogiatzis, E. Membrane reactor modelling: a comparative study to evaluate the role of combined mass and heat dissipation in large-scale adiabatic membrane modules. *Chem. Eng. Res. Des.*, **2005**, *83*(10A), 1171-1178.

[175] Sohrabi, M.; Irandoukht, A. Synthesis and activity measurement of some water-gas shift reaction catalysts. *React. Kinet. Catal. Lett.*, **2003**, *80*(2), 303-309.

[176] Pex, P.P.A.C.; Van Delft, Y.C. In: *Carbon Dioxide Capture for Storage in Deep Geologic Fromations*., Volume 1, chapter 17 (Report Number ECN-RX—05-123, **2005**.

[177] Krumpelt, M.; Krause, T.R.; Carter, J.D.; Kopasz, J.P.; Ahmed, S. Fuel processing for fuel cell systems in transportation and portable power applications. *Catal. Today*, **2002**, *77*, 3-16.

[178] Gittleman, C.S.; Gupta, R. Combined water gas shift reactor/carbon dioxide absorber for use in a fuel cell system. U.S. Patent 20050204629, September 22, 2005.

[179] Choudhary, T.V.; Goodman, D.W. CO-free fuel processing for fuel cell applications. *Catal. Today*, **2002**, *77*, 65-78.

[180] Hatalis, M.K.; Kothare, M.V.; Mukherjee, S. *AIChE Spring Natl. Meet. Conf. Proc.*, Atlanta, GA, **2005**, 2941-2942.

[181] Hogarth, M.P.; Ralph, T.R. Catalysis for low temperature fuel cells. *Platinum Metals Rev.*, **2002**, *46*(4), 146-164.

[182] Schumacher, N.; Boisen, A.; Dahl, S.; Gokhale, A.A., Kandoi, S.; Grabow, L.C.; Dumesic, J.A.; Mavrikakis, M.; Chorkendorff, I. Trends in low-temperature water-gas shift reactivity on transition metals. *J. Catal.*, **2005**, *229*, 265-275.

[183] Deng, W.; De Jesus, J.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Low-content gold-ceria catalysts for the water-gas shift and preferential CO oxidation reactions. *Appl. Catal. A*, **2005**, *291*, 126-135.

[184] Andreeva, D.; Idakiev, V.; Tabakova, T.; Andreev, A. Low-temperature water-gas shift reaction over Au/Fe2O3. *J. Catal.*, **1996**, *158*, 354-355.

[185] Andreeva, D.; Idakiev, V.; Tabakova, T.; Andreev, A.; Giovanoli, R. Low-temperature water-gas shift reaction on Au/Fe2O3 catalyst. *Appl. Catal. A*, **1996**, *134*, 275-283.

[186] Andreeva, D.; Tabakova, T.; Idakiev, V.; Christov, P.; Giovanoli, R. Au/Fe2O3 catalyst for water-gas shift reaction prepared by deposition-.precipitation. *Appl. Catal. A*, **1998**, *169*, 9-14.

[187] Boccuzzi, F.; Chiorino, A.; Manzoli, M.; Andreeva, D.; Tabakova, T. FTIR study of the low temperature water-gas shift reaction on Au/Fe2O3 and Au/TiO2 catalysts. *J. Catal.*, **1999**, *188*, 176-185.

[188] Tabakova, T.; Idakiev, V.; Andreeva, D.; Mitov, I. Influence of the microscopic properties of the support on the catalytic activity of

Au/ZnO, Au/ZrO2, Au/Fe2O3, Au/Fe2O3-ZnO, Au/Fe2O3-ZrO2 catalysts for the WGS reaction. *Appl. Catal. A*, **2000**, *202*, 91-97.

[189] Sobczak, J.W.; Andreeva, D. XPS study of Au/TiO2 catalytic systems. *Stud. Surf. Sci. Catal.,* **2000**, *130*, 3303-3308.

[190] Andreeva, D. Low temperature water gas shift over gold catalysts. *Gold Bull.*, **2002**, *35*(3), 82-88.

[191] Mohamed, M.M.; Salama, T.M.; Ichikawa, M. Spectroscopic identification of adsorbed intermediates derived from the CO + H2O reaction on zeolite-encapsulated gold catalysts. *J. Colloid Interface Sci.*, **2000**, *224*, 366-371.

[192] Cameron, D.; Holliday, R.; Thompson, D. Gold´s future role in fuel cell systems. *J. Power Sources*, **2003**, *118*(1-2), 298-303.

[193] Sauvion, G.N.; Caillod, J. Conversion of carbon monoxide with water vapor using a sulfur-resistant catalyst. EP Patent 0,189,701, August 06, 1986.

[194] Li, Y.; Fu, Q.; Flytzani-Stephanopoulos, M. Low-temperature water-gas shift reaction over Cu- and Ni-loaded cerium oxide catalysts. *Appl. Catal. B*, **2000**, *27*, 179-191.

[195] Fu, Q.; Weber, A.; Flytzani-Stephanopoulos, M. Nanostructured Au-CeO2 catalysts for low-temperature water-gas shift. *Catal. Letters*, **2001**, *77*(1-3), 87-95.

[196] Deng, W.; Flytzani-Stephanopoulos, M. On the issue of the deactivation of Au-ceria and Pt-ceria water-gas shift catalysts in practical fuel-cell applications. *Angew. Chem. Int. Ed. Engl.*, **2006**, *45*, 2285-2289.

[197] Idakiev, V.; Su, B.-L.; Tabakova, T.; Yuan, Z.-Y. Titanium oxide nanotubes as supports of nano-sized gold catalysts for low temperature water-gas shift reaction. *Appl. Catal. A*, **2005**, *281*(1-2), 149-155.

[198] Daniells, S.T.; Makkee, M.; Moulijn, J.A. The effect of high-temperature pre-treatment and water on the low temperature CO oxidation with Au/Fe2O3 catalysts. *Catal. Lett.*, **2005**, *100*(1-2), 39-47.

[199] Akita, T.; Haruta, M.; Kiuchi, M.; Sakurai, H.; Tsubota, S. Low-temperature activity of Au/CeO2 for water gas shift reaction, and characterization by ADF-STEM, temperature-programmed reaction, and pulse reaction. *Appl. Catal. A*, **2005**, *291*(1-2), 179-187.

[200] Amieiro-Fonseca, A.; Fisher, J.M.; Thompsett, D. Water gas shift catalyst containing gold. WO Patent 05/087656, September 22, 2005.

[201] Deng, W.; Flytzani-Stephanopoulos, M.; Fu, Q.; Saltsburg, H. Activity and stability of low-content gold-cerium oxide catalysts for the water-gas shift reaction. *Appl. Catal. B*, **2005**, *56*(1-2), 57-68.

[202] Ricote, S.; Jacobs, G.; Milling, M.; Ji, Y.; Patterson, P.M.; Davis, B.H. Low temperature water-gas shift: characterization and testing of binary mixed oxides of ceria and zirconia promoted with Pt. *Appl. Catal. A*, **2006**, *303*, 35-47.

[203] Tabakova, T.; Boccuzzi, F.; Manzoli, M.; Sobczak, J.W.; Idakiev, V.; Andreeva, D. Effect of synthesis procedure on the low-temperature WGS activity of Au/ceria catalysts. *Appl. Catal. B*, **2004**, *49*, 73-81.

[204] Idakiev, V.; Tabakova, T.; Yuan, Z.-Y.; Su, B.-L. Gold catalysts supported on mesoporous titania for low-temperature water-gas shift reaction. *Appl. Catal. A*, **2004**, *270*,135-141.

[205] Venugopal, A.; Aluha, J.; Mogano, D.; Scurrell, M.S. The gold-ruthenium-iron oxide catalytic system for the low temperature water-gas-shift reaction: the examination of gold-ruthenium interactions. *Appl. Catal. A*, **2003**, *245*, 149-158.

[206] Scurrell, M.S.; Venugopal, A. Hydroxyapatite as a novel support for gold and ruthenium catalysts: behaviour in the water gas shift reaction. *Appl. Catal. A*, **2003**, *245*(1), 137-147.

[207] Haukka, M.; Venalainen, T.; Kallinen, M.; Pakkanen, T.A. Chemically activated ruthenium mono(bipyridine)/SiO2 catalysts in water-gas shift reaction. *J. Mol. Catal. A*, **1998**, *136*, 127-134.

[208] Luukkanen, S.; Homanen, P.; Haukka, M.; Pakkanen, T.A.; Deronzier, A.; Chardon-Noblat, S.; Zsoldos, D.; Ziessel, R. Chemically modified ruthenium mono(bipyridine) carbonyl complexes in water gas shift reaction. *Appl. Catal. A*, **1999**, *185*, 157-164.

[209] Luukkanen, S.; Haukka, M.; Kallinen, M.; Pakkanen, T.A. The low-temperature water-gas shift reaction catalyzed by sodium-bicarbonate-activated ruthenium mono(bipyridine)/SiO2 complexes. *Catal. Lett.*, **2000**, *70*, 123-125.

[210] Aguirre, P.; Moya, S.A.; Sariego, R.; Bozec, H.J.R.; Pardey, A.J. Water-gas shift reaction catalyzed by mononuclear ruthenium complexes containing bipyridine and phenanthroline derivatives. *Appl. Organomet. Chem*., **2002**, *16*(10), 597-600.

[211] Tanaka, Y.; Utaka, T.; Kikuchi, R.; Eguchi, K. Water gas shift reaction over Cu-based mixed oxides for CO removal from the reformed fuels. *Appl. Catal. A*, **2003**, *242*, 2.

[212] Ueda, A.; Yamada, Y.; Kobayashi, T. Catalyst for water gas shift reaction.WO Patent 03/099434, December 04, 2003.

[213] Basile, A.; Chiappetta, G.; Rizzello, C.; Tosti, S.; Violante, V. Pd-Ag membrane reactors for water gas shift reaction. *Chem. Eng. J*., **2003**, *93*(1), 23-30.

[214] Holzwarth, A.; Denton, P.; Zanthoff H., Mirodatos, C. Combinatorial approaches to heterogeneous catalysis: strategies and perspectives for academic research. *Catalysis Today*, **2001**, *67*(4), 309-318.

[215] Farrusseng, D.; Mirodatos, C. In High Throughput Screening in Chemical Catalysis; Hagemeyer, Strasser, Volpe, Eds.; Wiley-VCH: Weinheim, 2004.

[216] Jandeleit, B.; Schaefer, D.J.; Powers, T.S.; Turner, H.W.; Weinberg, W.H. Combinatorial Materials Science and Catalysis. *Angew. Chem. Int. Ed. Engl*., **1999**, *38*, 2495.

[217] Schuth, F.; Hoffmann, C.; Wolf, A.; Schunk, S.; Stichert, W.; Brenner, A. In Combinatorial Chemistry; Jung, Ed.; Wiley-VCH: Weinheim; **1999**, 463.

[218] Hagemeyer, A.; Jandeleit, B.; Liu, Y.; Poojary, D.M.; Turner, H.W.; Volpe Jr., A.F., Weinberg, W.H. Applications of combinatorial methods in catalysis. *Appl. Catal. A*, **2001**, *221*, 23.

[219] Senkan, S. Combinatorial heterogeneous catalysis-a new path in an old field. *Angew. Chem. Int. Ed*., **2001**, *40*(2), 312-329.

[220] Guliants V.V.; Ed., Special Issue on "Current Developments in Combinatorial Heterogeneous Catalysis". *Catal. Today*, **2001**, 67,

[221] Cawse, J. N. Experimental strategies for combinatorial and high throughput materials development. *Acc. Chem. Res*., **2001**, *34*(3), 213-221.

[222] Derouane, E.G.; Parmon, V.; Lemos, F.; Ramôa Ribeiro, F. NATO Science Series, II: Mathematics, Physics and Chemistry 69 (Principles and Methods for Accelerated Catalyst Design and Testing), **2002**, *3*, 101, 245, 449, 469.

[223] Schuth, F.; Busch, O.; Hoffmann, C.; Johann, T.; Kiener, C.; Demuth, D.; Klein, J.; Schunk, S.; Strehlau, W.; Zech, T. High throughput experimentation in oxidation catalysis. *Topics Catal*., **2002**, *21*(1-3), 55-66.

[224] Demuth, D.; Finger, K.-E.; Hill, J.-R.; Levine, S.M.; Lowenhauser, G.; Newsam, J.M.; Strehlau, W.; Tucker, J.; Vietze, U. Developing combinatorial support for high throughput experimentation applied to heterogeneous catalysis. *ACS Symposium Series*, **2002**, *814* (Combinatorial Materials Development), 147-164.

[225] Perego C.; Ed.; 81, Special Issue on "Combinatorial Catalysis" (Proceedings of the EuroCombiCat, Ischia, Italy, June 2-5, 2002), *Catal. Today*, **2003**.

[226] Maier W.F.; Ed.; Special Issue on "Combinatorial Catalysis". *Appl. Catal*., **2003**, 254.

[227] Jahnisch, K.; Hessel, V.; Lowe, H.; Baerns, M. Chemistry in microstructured reactors. *Angew. Chem. Int. Ed. Engl*., **2004**, *43*, 406-446.

[228] Hagemeyer, A.; Strasser, P.; Volpe A. High Throughput Screening in Chemical Catalysis, Wiley-VCH: Weinheim, **2004**.

[229] Willson, R.C. Catalyst testing process and apparatus. WO Patent 97/32208, September 04, 1997.

[230] Cong, P.; Doolen, R. D.; Fan, Q.; Giaquinta, D. M.; Guan, S.; McFarland, E. W.; Poojary, D. M.; Self, K.; Turner, H. W.; Weinberg, W. H. High throughput synthesis and screening of combinatorial heterogenous catalyst libraries. *Angew. Chem. Int. Ed. Engl*., **1999**, *38*, 484-488.

[231] Liu, Y.; Cong, P.; Doolen, R.D.; Turner, H.W.; Weinberg, W.H. High throughput synthesis and screening of V-Al-Nb and Cr-Al-Nb oxide libraries for ethane oxidative dehydrogenation to ethylene. *Catal. Today*, **2000**, *61*(1-4), 87-92.

[232] Bergh, S.; Cong, P.; Ehnebuske, B.; Guan, S.; Hagemeyer, A.; Lin, H.; Liu, Y.; Lugmair, C.G.; Turner, H.W.; Volpe Jr., A.F.; Weinberg, W.H.; Woo, L.; Zysk, J. Combinatorial heterogeneous catalysis: oxidative dehydrogenation of ethane to ethylene, selective oxidation of ethane to acetic acid, and selective ammoxidation of propane to acrylonitrile. *Topics Catal*., **2003**, *23*(1-4), 65.

[233] Yaccato, K.; Hagemeyer, A.; Lesik, A.; Volpe, A. F.; Turner, H. W.; Weinberg, W. H. High throughput screening of SCR and direct decomposition DeNOx catalysts in scanning mass spectrometer, 9th NICE Workshop on "High Temperature Catalysis", Durdent Court, UK, February 11-12, 2003.

[234] Yaccato, K.; Carhart, R.; Hagemeyer, A.; Lesik, A.; Turner, H. W.; Volpe, A. F.; Weinberg, W. H.; Grasselli, R. K. *CO and CO_2 methanation over supported noble metal catalysts in high throughput scanning mass spectrometer*, paper 166d, AIChE Spring Meeting, New Orleans, March 30-April 3, **2003**.

[235] Yaccato, K.; Hagemeyer, A.; Lesik, A.; Volpe, A. F.; Turner, H. W.; Weinberg, W. H. *High throughput screening of low temperature SCR and direct decomposition DeNOx catalysts in scanning mass spectrometer, preprints 6th international congress on catalysis and automotive pollution control (CAPoC 6)*, Brussels, Belgium, October 22-24, 2003; *Topics Catal.*, **2004**, *30/31*, 127-132.

[236] Yaccato, K.; Hagemeyer, A.; Liu, Y.; Volpe, A. F.; Weinberg, W. H. High Throughput Screening of Low Temperature CO Oxidation Catalysts for Cold-Start Automotive Emissions Control in Scanning Mass Spectrometer, paper 516a, AIChE Annual Meeting, San Francisco, November 16-21, **2003**.

[237] Guram, A.; Hagemeyer, A.; Lugmair, C. G.; Turner, H. W.; Volpe Jr, A. F.; Weinberg, W. H.; Yaccato, K. Application of high throughput screening to heterogeneous liquid and gas phase oxidation catalysis. *Adv. Synth. Catal.*, **2004**, *346*(2+3), 215-230.

[238] Yaccato, K.; Hagemeyer, A.; Volpe, A. F.; Weinberg, W. H. High throughput screening for the discovery of more efficient catalysts for emissions control, ACS national meeting, Anaheim, CA, March 28-April 1, **2004**.

[239] Yaccato, K.; Hagemeyer, A.; Lefort, L.; Turner, H. W.; Volpe, A. F.; Weinberg, W. H. High Throughput Screening of VOC Removal Catalysts in Scanning Mass Spectrometer, 13th International Catalysis Conference (ICC), Paris, France, July 11-16, **2004**.

[240] Hagemeyer, A.; Lesik, A.; Streukens, G.; Volpe Jr, A.F.; Turner, H.W.; Weinberg, W.H.; Yaccato, K. Discovery of Novel Catalytic Materials for Emissions Control using High Throughput Scanning Mass Spectrometry, 4th International Conference on Environmental Catalysis. Heidelberg, Germany, June 5-8, **2005**.

[241] Yaccato, K.; Carhart, R.; Hagemeyer, A.; Lesik, A.; Strasser, P.; Turner, H.; Volpe, A.; Weinberg, H. Competitive CO and CO2 methanation over supported noble metal catalysts in high throughput scanning mass spectrometer. *Appl. Catal. A*, **2005**, *296*(1), 30-48.

[242] Yaccato, K.; Carhart, R.; Hagemeyer, A.; Turner, H.; Volpe, A.; Weinberg, H. Fourier transform combinatorial catalysis applied to the discovery of novel Catalysts for the Water-Gas-Shift Reactions. AIChE Annual Meeting, Austin, TX, November 7-12, **2004**.

[243] Hagemeyer, A. Alkali-containing water gas shift catalysts for low and medium temperature hydrogen generation. U.S. Patent 20040175325, July 15, 2004.

[244] Brooks, C.; Hagemeyer, A.; Yaccato, K.; Carhart, R.; Herrmann, M.; Lesik, A.; Strasser, P.; Volpe, A.; Turner, H.; Weinberg, H. *Combinatorial methods for the discovery of novel catalysts for the WGS Reaction, ACS Spring Meeting*, San Diego, CA, March 13-17, **2005**.

[245] Brooks, C.; Hagemeyer, A.; Yaccato, K.; Carhart, R.; Herrmann, M.; Lesik, A.; Strasser, P.; Volpe, A.; Turner, H.; Weinberg, H. *Combinatorial methods for the discovery of novel catalysts for the WGS Reaction*. 19th NACS Meeting, Philadelphia, PA, May 22-27, **2005**.

[246] Yaccato, K.; Carhart, R.; Hagemeyer, A.; Herrmann, M.; Lesik, A.; Strasser, P.; Turner, H.; Volpe, A.; Weinberg, H. *High throughput discovery of families of high activity water-gas-shift catalysts. AIChE Spring Meeting, Orlando*, FL, April 23-27, **2006**.

[247] Cypes, S.; Grasselli, R.K.; Hagemeyer, A.; Hogan, Z.; Lesik, A.; Streukens, G.; Volpe, A.; Weinberg, H.; Yaccato, K.; Brooks, C. High throughput discovery of CO oxidation/VOC combustion and water-gas shift catalysts for industrial multi-component streams. *Topics Catal.*, **2006**, *38*(1-3), 195-209.

[248] Rust, W.C.; Nielson, R.B. Synthesizing combinatorial libraries of materials. EP Patent 1,175,645, January 30, 2002.

[249] Schultz, P.G.; Xiang, X.; Goldwasser, I. The combinatorial synthesis of novel materials. U.S. Patent 5,985,356, November 16, 1999.

[250] Hagemeyer, A.; Carhart, R.F.; Yaccato, K.; Lesik, A.; Brooks, C.J. Alkali-containing water gas shift catalysts for low and medium temperature hydrogen generation. WO Patent 2004058635, July 15, 2004.

[251] Hagemeyer, A.; Carhart, R.F.; Yaccato, K.; Strasser, P.; Herrmann, M.; Grasselli, R. K.; Brooks, C. J.; Phillips, C. B. Water gas shift catalysts for producing a hydrogen-rich fuel gas. WO Patent 2004058634, July 15, 2004.

[252] Hagemeyer, A.; Carhart, R.F.; Yaccato, K.; Herrmann, M.; Lesik, A.; Brooks, C.J.; Phillips, C. B.. Platinum-free ruthenium-cobalt water gas shift catalyst for hydrogen fuel generation. WO Patent 2004058633, July 15, 2004.

[253] Hagemeyer, A.; Carhart, R.F.; Yaccato, K.; Lesik, A.; Brooks, C.J.; Phillips, C.B. Platinum-alkali/alkaline-earth water gas shift catalysts for hydrogen fuel generation. WO Patent 2004058632, July 15, 2004.

[254] Hagemeyer, A.; Carhart, R. F.; Herrmann, M.; Yaccato, K.; Brooks, C. J. Noble metal-free nickel-containing water gas shift catalyst for hydrogen fuel generation. WO Patent 2004058631, July 15, 2004.

[255] Hagemeyer, A.; Carhart, R.F.; Yaccato, K.; Strasser, P.; Grasselli, R.K.; Brooks, C.J.; Phillips, C.B. Platinum and rhodium and/or iron containing catalyst formulations for hydrogen generation. WO Patent 2004058399, July 15, 2004.

[256] Hagemeyer, A.; Brooks, C. J.; Carhart, R. F.; Yaccato, K.; Lesik, A. Methods for the preparation of catalysts for hydrogen generation. WO Patent 2004058396, July 15, 2004.

[257] Hagemeyer, A.; Carhart, R.F.; Yaccato, K.; Strasser, P.; Grasselli, R.K.; Brooks, C.J.; Phillips, C.B. Platinum-ruthenium containing catalyst formulations for hydrogen generation. WO Patent 2004058395, July 15, 2004.

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