NEURAL NETWORKS ANALYSIS OF WATER GAS SHIFT REACTIONS OVER NOBLE METAL CATALYSTS USING PUBLISHED DATA IN LITERATURE

by

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to the world peace...

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ABSTRACT

NEURAL NETWORKS ANALYSIS OF WATER GAS SHIFT REACTIONS OVER NOBLE METAL CATALYSTS USING PUBLISHED DATA IN LITERATURE

The aim of this thesis is to apply the machine learning methodologies for knowledge extraction from experimental data for water gas shift reaction over noble metal catalysts from the papers published in the literature to understand the general trends and improve the catalyst design. First, the experimental data were extracted from 85 articles in the literature between 2002 and 2012 and a database containing 4372 data points with 87 variables was constructed. Then the methodology for knowledge extraction was selected; the neural networks and support vector machines, which are the two most effective machine learning tools, were compared using a dataset that was analyzed in our group before, and the neural network method showed better performance on prediction the unseen data. Hence the water gas shift reaction database was analyzed by using neural networks. An optimal network structure was determined by constructing various neural network topologies and comparing the testing RMSE, which is a measure of generalization ability of the model (prediction ability for the unseen data); two hidden layer network containing 21 nodes in each layer was found to be optimum to represent the database. Then, the experimental CO conversions in each article were predicted by the neural networks trained using the data from the remaining articles. The results in 29 articles out of 85 were predicted with a R^2 value of higher than 0.5, which can be considered as successful. The effects and relative significances of the catalyst design and operation variables were also analyzed and found to be generally in agreement with the literature.

ÖZET

SOY METAL KATALİZÖRLERİ ÜZERİNDE SU-GAZI GEÇİŞ REAKSİYONUNUN LİTERATÜRDE YAYINLANMIŞ VERİLER KULLANILARAK YAPAY SİNİR AĞLARIYLA İNCELENMESİ

Bu çalışmanın amacı, yapay öğrenme tekniklerini kullanarak soy metal katalizörleri üzerinde su-gazı geçiş reaksiyonu için literatürde yayınlanmış deneysel verilerden bilgi çıkarmak ve böylece literatürdeki eğilimleri anlayarak katalizör tasarımını iyileştirmektir. Bunun için ilk olarak, literatürde 2002 ve 2012 yılları arasında yayınlanan 85 makaleden deneysel veriler çıkarılmış ve 4372 veri noktası ve 87 değişken içeren bir veri tabanı oluşturulmuştur. Sonra, bilgi çıkarımı yapmak için kullanılacak yöntem seçilmiş, bunun için yapay öğrenmede en etkili yöntemler arasında yer alan destek yöney makinaları ve yapay sinir ağları yöntemleri daha önce laboratuvarımızda analiz edilmiş olan bir veri tabanı üzerinde test edilmiş, yapay sinir ağları daha başarılı bulunmuştur. Bu nedenle oluşturulan su gazı geçiş reaksiyonuna ait veritabanı sinir ağları yöntemiyle modellenmiştir. Optimum yapay sinir ağı yapısı, değişik ağ yapıları oluşturularak kıyaslanmış, bunun için bir modelin genelleme (modelin hiç görmediği veriyi tahmin edebilme) yeteneğinin ölçüsü olarak kabul edilen ortalama karekök hataların toplamı kullanılmıştır. Çalışma sonunda veri tabanına en uygun ağın her biri 21 nöron içeren iki saklı katmanlı ağ yapısının uygun olduğu görülmüştür. Daha sonra, her makaledeki veriler, diğer makalelerdeki veriler kullanılarak tekrar eğitilen modelle teker teker tahmin edilmeye çalışılmıştır. 85 makale içerisinden 29 makale, 0.5'in üzerinde bir R^2 değeri ile, başarılı sayılabilecek biçimde tahmin edilmiştir. Ayrıca, katalizör tasarım ve operasyonel değişkenlerin katalizör performansına etkileri ve göreceli önemleri sinir ağları yöntemiyle analiz edilmiş ve sonuçlar genel olarak literatüre uygun çıkmıştır.

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LIST OF SYMBOLS

b	Bias
C	Complexity parameter
F/W	Feed flowrate/ Catalyst weight
J	Hessian matrix
L	Epsilon parameter
L_P	Objective function in lagrange formulation
o_j	Actual output
t_j	Target output
x_i	Vector point
ω	Weight
α_i	Lagrange multiplier
γ	Gamma
ΔH	Enthalpy of the Reaction
η	Learning rate
ξ_i	Slack variable
ρ	Margin

LIST OF ACRONYMS/ABBREVIATIONS

HTS	High Temperature Stage
LTS	Low Temperature Stage
RMSE	Root mean squared error
SMO_{reg}	Sequential Minimal Optimization Regression
WGS	Water Gas Shift

1. INTRODUCTION

The global energy consumption continuously increases as a result of population growth and rapid industrial development. This results in a dramatic increase in industrial, transportation and residential CO_2 emissions due to the extensive use of fossil fuels (Song, 2002). In order to control greenhouse gas emissions in the world, the cleaner and more efficient energy conversion technologies should be developed.

The hydrogen based energy conversion technologies such as fuel cells seem to be among the promising alternatives for power generation in the future. The fuel cell can convert chemical energy directly into electrical energy with high efficiency and lower emission of pollutants. Hydrogen is the main source of fuel cells and it can be produced by using liquid fuels or natural gas in steam reforming, partial oxidation or auto thermal reforming in combination with the water gas shift reaction. (Cortes *et al.,* 2008)

The hydrogen production processes from a hydrocarbon also generates CO, which is harmful for the catalyst of the fuel cell. It is proposed that the CO in the feed can be reduced using the water gas shift (WGS) reaction, which also generates some additional hydrogen, followed by selective CO oxidation to remove the remaining CO (Song, 2002).

The water gas shift reaction is an old and established industrial process that can also be used in large scale operations such as ammonia production plants (Duarte de Farias *et al.,* 2008). The water in the form of steam is mixed with carbon monoxide in order to form hydrogen and carbon dioxide. The water gas shift reaction is exothermic; it is thermodynamically favorable at lower temperatures as obeying the Le Chatelier's principle. However the catalysts are not very active to maintain the equilibrium at low temperatures making the reaction kinetically limited. (Luengnaruemitchai *et al.,* 2003).

Although there are commercially available two stage (high and low temperature) WGS processes, they are not quite suitable for the low temperature small scale fuel cell

applications. Hence, an effective single-stage low temperature WGS processes over supported noble metal (Au, Rh, Pt and Pd) based catalysts have been investigated extensively in the recent years.(Song, 2002; Woods *et al*., 2010)

If the huge amount of experimental research about water gas shift reactions is considered, it can be said that a significant amount of knowledge has been accumulated in the literature over the years by spending time, money and effort. However, this accumulation cannot be utilized effectively by naked eyes because it was distributed over a very large number of publications. Instead some data mining tools can be used in order to extract knowledge from these data and feed the results to the experimental works to help to develop better catalysts.

One of the most popular machine learning techniques is the support vector machine (SVM). The support vector machine is a learning method that depends on the statistical learning theory. The basic idea of the support vector machine is mapping the input vectors to a high dimensional space non-linearly in order to reduce the effect of dimensionality. A linear decision area is constructed in this space and this area provides high generalization ability without errors (Vapnik, 1995).

Artificial neural network (ANN) is another method of machine learning that have superior ability on non-linear regression and data approximation. (Larose, 2005; Callan, 1999). It is based on the biological neurons. The artificial neural networks express the output as a function of input variables by creating very large number of correlations within the network. (Khajeh-Hosseini-Dalasm *et al*., 2011)

In this work, SVM and ANN methods were tested and compared to extract knowledge from an existing database involving selective CO oxidation, and ANN was selected for WGS reaction because it gave better performance. A detailed database of water gas shift reactions was constructed by using the experimental data published in various papers between the years 2002 and 2012. This dataset was analyzed using neural networks to extract some general trends from the experience in the literature and use them to predict the outcome of new (unstudied) set of experimental conditions.. The effects and significances of various catalyst design (noble metal type, promoter type, preparation

method, calcination conditions, support type) and reaction (such as temperature, feed composition and contact time) variables on the performance of the catalyst were also analyzed.

This thesis is composed of five chapters. The water gas shift reactions, support vector machines and neural networks were briefly reviewed in Literature Survey (Chapter 2). The computational details and the methodology of constructing the models are given in Materials and Methods (Chapter 3) while the results obtained for water gas shift reactions is discussed in Results and Discussion (Chapter 4). Finally, the conclusions drawn from this work and recommendations for future studies are presented in Conclusion Recommendation (Chapter 5).

2. LITERATURE SURVEY

2.1. Fuel Cells and Water Gas Shift Reactions

The global energy consumption continuously increases as a result of population growth and rapid industrial development. This results in a dramatic increase in industrial, transportation and residential CO_2 emissions due to the extensive use of fossil fuels.

In order to control greenhouse gas emissions in the world, the cleaner and more efficient energy conversion technologies should be developed. Hydrogen is an environmentally attractive fuel because it burns without producing carbon dioxide. The hydrogen based energy conversion technologies can be good alternatives for future (Royal Belgian Academy of Council of Applied Science Report, 2006). For example, fuel cells seem to be promising alternatives for combustion based technologies in primary power generation for stationary and mobile applications (Brown , 2001, Ruettinger *et al.,* 2003).

The working principle of fuel cells depends on converting chemical energy directly to electrical energy without any additional steps or cycles. Hydrogen is oxidized to hydrogen ions electrochemically at the anode part. These ions pass through a proton conductive membrane to the cathode part where they are combined with reduced O_2 (from air) to produce H_2O.The movement of the electrons in the external circuit provides power (Ruettinger *et al.,* 2003).

Hydrogen is not a primary energy source on earth; it is a storage medium and an energy carrier. Hence it must be produced from other sources. Hydrogen can be supplied to the fuel cell in two ways; as stored in pure form (compressed gas, etc.) or as on-site produced from hydrocarbons (i.e. natural gas) in a fuel processor. Today, fuel processors seem to be the most convenient method of providing hydrogen in the lack of a suitable infrastructure for hydrogen storage and distribution. They can generate hydrogen from hydrocarbons by either steam reforming or auto-thermal reforming. By generating hydrogen and CO_2, 8-12% CO is also generated in these reforming steps. Since CO is

adsorbed on the catalyst surface causing catalyst poisoning, it is important to reduce CO concentrations to a value less than 10 ppm for preventing irreversible damage and to facilitate the electrochemical reaction on the electrode (Brown, 2001). In order to achieve this, the water gas shift (WGS) reaction is used to convert CO to CO_2 to produce some additional hydrogen. The remaining 0.5-1 % CO is cleaned-up using some selective CO oxidation catalyst after WGS process.

The water gas shift reaction is widely used in the industry. It is generally applied to ammonium synthesis and hydrogen production processes from hydrocarbons. The main aim of the WGS reaction is to remove CO from the off-gas and increase the H_2/CO molar ratio. The WGS reaction is moderately exothermic and strongly controlled by thermodynamic equilibrium. The equilibrium conversion is said to be independent of pressure and favored under low temperatures because of its exothermic characteristic. Hence, the WGS reactor is a large and heavy process component and the equilibrium limitations determine the WGS reactor volume as the largest part of the hydrogen generation-purification system in fuel cell applications (Francesconi *et al.,* 2007).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298\,K} = -41.09\ \text{kJ/mol} \qquad (2.1)$$

The WGS reaction can be catalyzed by numerous materials, it is industrially performed in two adiabatic stages using two different catalysts with intermediate cooling: high temperature stage (HTS) and low temperature stage (LTS). The first stage, HTS, uses an iron-based catalyst (Fe/Cr) operating at 300–450 ◦C, and it converts the largest amount of CO. Typical CO levels in the outlet stream of a single reactor range between 2% and 4%. The second stage, LTS, operates at lower temperatures, between 180 ◦C and 230 ◦C, using a copper–zinc catalyst supported on alumina Cu/Zn/Al (Francesconi *et al.,* 2007).

In spite of the common use of two stage WGS processes, it is technically complex and inappropriate for mobile applications (Bartolomew *et al.,* 2006) Hence, a single-stage WGS process becomes more desirable. Supported noble metal (Au, Rh, Pt and Pd) based catalysts seem to be promising single stage WGS catalysts because of their robustness, suitability to operate at higher temperatures, being less sensitive to poisons and more active than Fe/Cr oxide-based HTS catalysts (Azzam *et al.,* 2007a).

A large number of articles about water gas shift reactions can be found in the literature because the activity of the catalyst depends on various parameters (i.e. metal and support type, preparation method and pretreatment conditions) that should be studied. A significant change in conversion can be observed in any variation in these factors as briefly explained below.

2.1.1. Noble-metal type

Supported noble metal-based catalysts are promising single-stage WGS catalysts because of their advantages such as being robust, suitability to operate at higher temperatures where the kinetics is more favorable, being less sensitive to poisons (Cl and S), being more active than HTS catalysts, and being stable during start up-shut down cycles.

A noble metal type is the main component of a catalyst that enhances the reaction. A great number of studies have been carried out on various types of noble metals such as Pt, Pd, Ru, Rh, Ir, and Au. For example Radhakrishnan *et al.* (2006) examined the WGS activity of various noble metals on ceria-zirconia supports, and they found that, Pt is the most active noble metal in water gas shift (WGS) reaction.

2.1.2.Support type

A catalyst support is a material that the catalyst is affixed. It is usually a solid with a high surface area and may or may not participate in catalytic reactions. Catalyst support materials have an effect directly on the cost, performance, and durability of polymer electrolyte membrane (PEM) fuel cells (Shao *et al.*, 2009).

The nature of oxide supports has a crucial effect on the performance of Pt-based catalysts in the water–gas shift reaction. Supports both determine the activity of the catalyst, and influence their stability. (Azzam *et al.*, 2007b).

In water gas shift catalysts, various supports such as YSZ, Al_2O_3, MgO, CeO_2, TiO_2, zeolite, ZnO, MnO, Y_2O_3, ZrO_2, hydroxyapatite, carbon, Tb_4O_7 and HfO_2 can be used, and

every support has different effect on conversion. As an example, Azzam *et al.* (2007a) investigated the roles of support on catalyst activity and stability. They found that among the catalysts studied, Pt/TiO_2 was the most active. Activity followed the following order: TiO_2 > $Ti_{0.5}Ce_{0.5}O_2$ > $Ce_{0.5}Zr_{0.5}O_2$ > CeO_2 > $Ti_{0.8}Ce_{0.2}O_2$ > $Ce_{0.8}Zr_{0.2}O_2$ > $Ti_{0.5}Zr_{0.5}O_2$ > ZrO_2. (Azzam *et al*., 2007a). Also, Vignatti *et al. (*2010) studied various support types with platinum and they observed the catalyst with SiO_2 support is more active than CeO_2 .They also found that the catalyst with mixed support gives a better conversion (Vignatti *et al*., 2011).

2.1.3. Preparation

Noble metal catalysts can be prepared using various methods. Besides the quality of the raw materials, every step of the preparation affects the catalytic properties of the heterogeneous catalysts. Some of the most common methods for water gas shift catalysts are incipient to wetness impregnation, wet impregnation, sol gel, precipitation and deposition-precipitation methods.

Incipient wetness impregnation (IW or IWI), also called capillary impregnation or dry impregnation is a commonly used technique for the synthesis of heterogeneous catalysts. Basically, the active metal precursor is dissolved in an aqueous or organic solution. Then the metal-containing solution is added to a catalyst support containing the same pore volume as the volume of the solution that was added. Wet impregnation is another type of impregnation. This time, an excess of solution is used and solid is separated from the solution and dried.

The sol gel method involves the transition of a solution system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Utilizing the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms.

The precipitation method can be also used to prepare single component on a supports or mixed catalysts. In this method, a solid is basically precipitated from a liquid solution; the aim is to form very small crystallites or mixed crystallites. Deposition-precipitation (DP) is a preferred method to obtain active gold catalysts (Bamwenda *et al.*, 1997).

Other methods such as urea gelation, surfactant templating, solution combustion technique are also used for preparing WGS catalyst.

Besides the preparation method of catalysts, the calcination also plays an important role in catalyst synthesis. The catalysts that have been calcined in different temperatures and time have different properties. For example the effect of calcination temperature on the catalytic activity of copper/alumina for water gas shift (WGS) reaction was investigated and it is found that the catalyst that calcined at 1073K, followed by the treatment in H2 at 523K, showed much higher activity for WGS reaction. (Yahiro *et al.*, 2006).

2.1.4. Promoter type

Promoters are the substances which are not catalysts but when a proper promoter is mixed with the catalysts in small quantities, it may increase the catalytic activity significantly while some may have none or negative impact on catalytic performance. For example, the effect of the promoter type was studied by Akpinar (2005) and it was found that Ce, Mn, Fe and Zr addition to Pt-Ce/Al_2O_3 catalyst improved the CO conversion while Ni, K and Co had negative impacts.

2.1.5. Feed Composition

The feed composition also has significant impact on the catalytic performance as expected. The effect of the steam/carbon ratio on CO conversion over various WGS catalysts was studied by various investigators. It was seen that the conversion of CO increased continuously with increasing steam/carbon ratio, until reaching a constant value. (Figueiredo *et al.*, 2005, Ladebeck and Wagner, 2003).

2.1.6. Operational Conditions

Water gas shift reactions are highly affected by operational conditions such as temperature, time of stream and F/W ratio. In order to get a high efficiency, these factors should be optimized. The temperature can both thermodynamically and kinetically affect the conversion. At lower temperatures, higher CO conversions are obtained because of the

exothermic nature of the water gas shift reaction. The WGS equilibrium constant is nearly 80 times greater at 200°C than 600°C (Ladebeck and Wagner, 2003).

The pressure effect can be considered as insignificant for the WGS reactions, which are equimolar. For example no significant change was observed in conversion between 3 and 30 atm indicating that there is no point to use higher pressures in WGS reactions (Ladebeck and Wagner, 2003).

2.2 Knowledge Extraction in Catalysis

2.2.1. Data Mining and Methodologies

According to Hand et al. (2002), "Data mining is the analysis of (often large) observational data sets to find unsuspected relationships and to summarize the data in novel ways that are both understandable and useful to the data owner." Another definition is, "Data mining is an interdisciplinary field bringing together techniques from machine learning, pattern recognition, statistics, databases and visualization to address the issue of information extraction from large data bases."(Cabena *et al.,* 1998). As the large amount of data is being generated in research and business area, data mining becomes an important field of research in order to have a better understanding of data by discovering patterns and make useful predictions. Some of the applications of data mining that is used for prediction are flooding, speech recognition, machine learning and pattern recognition. (Günay and Yıldırım, 2010)

Data mining is an application of machine learning to large databases; there are various methodologies to extract knowledge from the databases. These methods can be analyzed in three main categories: classification, clustering and regression.

Classification is used to separate data into predefined groups or classes. It can be referred as a supervised learning because the classes should be determined before examining the data.

Clustering is a machine learning technique used to place data elements into related groups without advance knowledge of the group definitions. It is an unsupervised learning technique because the groups are not predefined but rather defined by the data themselves. The grouping is accomplished by finding similarities between data points according to characteristics found in actual data (Günay and Yıldırım, 2010). The groups are called clusters and the similar data are grouped into the same clusters. Popular clustering techniques include k-means clustering and expectation maximization (EM) clustering.

Regression is a statistical tool for the investigation of relationships between variables. The aim is to fit the target data into some known type of function that is created from a known data. It deals with estimation of an output value based on input values.

Simple linear regression analysis is a statistical method that works by plotting a line through data points that minimizes the squared error. It quantifies the relationship between two continuous variables: dependent (the variable you want to predict) and independent/predictive variable. If the relationship between dependent and independent variables is not linear, regression can allow a better fit by changing linear plot to curvilinear relationship. Linear regression generally creates very robust models (Rud, 2001).

The logistic regression is similar to linear regression but the dependent variable is not continuous in this case. It may be discrete or categorical. In order to perform logistic regression, the dependent variable should be transformed into a continuous value that is function of the probability. This method can also create very robust models similar to linear regression (Rud, 2001).

Time series analysis is another methodology of data mining. In this method, the value of an attribute should be changing over time and data points should be evenly spaced in time such as daily, weekly, hourly, etc. An overall regime of a variable can be observed by plotting the time series, and, three basic functions can be performed in time series analysis: Distance measures are used to determine the similarity between different time series, the behavior of series can be determined from its structure of the line, and the historical time series plot can be used to predict future values (Dunham, 2003). The aim is

to be able to make a short term forecasting with some pattern in the values collected to the date.

Neural networks and support vector machines are the most popular data mining tools that are commonly used for estimation. Some successful implementations of these methods in the fields of chemistry, chemical engineering and catalysis were also reported through the years. For example, Burns and Whitesides reviewed the use of neural networks in chemistry as early as 1993 while Himmelblau's research in 2000 was about the early works of neural networks on chemical engineering. Numerous successful applications of neural networks in the field of catalysis are available in the literature since mid-1990s (Hattori and Kito, 1995; Kobayashi et al., 2010; Rodermerck *et al.,* 2004; Tompos *et al.,* 2005; Corma *et al.,* 2005; Kito and Hattori, 2007; Hattori and Kito, 2007; Song *et al.,* 2007; Günay and Yıldırım, 2010; Günay and Yıldırım, 2011). Baerns and Holena reviewed and discussed the use of neural networks for the study of catalytic materials in their book in 2009.

Support vector machines are also recently used in many applications related to pattern recognition such as isolated handwritten digit recognition (Cortes and Vapnik, 1995; Schölkopf *et al.,* 1995; Schölkopf *et al.,* 1996; Burges and Schölkopf, 1997) , object recognition (Blanz *et al.,* 1996), speaker identification (Schmidt, 1996), face detection in images (Osuna *et al.,* 1997) and text categorization (Joachims,1997) and regression estimation such as , time series prediction tests (Müller *et al.,* 1997; Mukherjee *et al.,* 1997), the Boston housing problem (Drucker *et al.,* 1997) and (on artificial data) on the PET operator inversion problem (Vapnik *et al.,* 1996).

In a field of heterogeneous catalysis, Baumes and Serra studied on support vector machines for predictive modeling in 2006 (Baumes *et al.,* 2006) while Chae and coworkers used this technique to predict catalytic activity of DeNOx catalyst over different supports. The reason of using support vector machine in this work was stated to be able to avoid over fitting of the data (Chae *et al.,* 2006). In another work, Balabin and Lomakina compared support vector machine and neural networks on the analysis of quantum chemistry data in 2011 (Balabin and Lomakina, 2011).

2.2.2. Support Vector Machines

One of the most popular machine learning techniques used in recent years is the support vector machines, which depends on the statistical learning theory (i.e. based on the theoretical analysis of the problem to gain knowledge from a collection of data). The support vector machines were first developed by Vapnik (1995) to solve classification problem, but later it has been extended to solve both classification and regression problems (Vapnik *et al.*, 1997).

The basic idea of the support vector machine is mapping the input vectors to a high dimensional space non-linearly in order to reduce the effect of dimensionality. A linear decision area is constructed in this space and this area provides high generalization ability without errors (Vapnik, 1995). The advantage of the method is to be able to overcome two problems. Firstly, it can deal with the complex functions at high dimensional space and has high generalization ability by using quadratic optimization formulation. Also it can perform numerical optimization in a high dimensional space by using the dual kernel representation of linear functions (Cherkassky and Mulier, 1998).

Support vector formulation uses the Structural Risk Minimization (SRM) principle rather than Empirical Risk Minimization (ERM). SRM has been shown superior to ERM (Gunn *et al*., 1997) because SRM minimizes an upper bound on the expected risk while ERM minimizes the error on the training data. Hence, support vector machines have better generalization ability than other traditional methods.

Support vector machine can be applied not only to classification problems but also to the case of regression. Support vector regression is used for function estimation. The approach is similar with the classification. The aim is to define a loss function that ignores errors situated in a certain distance of the true value. This function is called ε-sensitive loss function (Smola and Schölkopf, 2003). The linear model given for regression is

$$f(x) = x_i \cdot \omega + b \tag{2.2}$$

where x_i denotes a set of nonlinear transformations, and b is the "bias" term. The quality of estimation is measured by ε-sensitive loss function proposed by Vapnik (1995):

$$y_i - x_i \cdot w - b \leq \varepsilon \tag{2.3}$$

$$x_i \cdot w + b - y_i \leq \varepsilon \tag{2.4}$$

SVM regression performs linear regression in the high-dimension feature space using ε-insensitive loss and, at the same time, tries to reduce model complexity by minimizing $\|w\|^2$ (Figure 2).

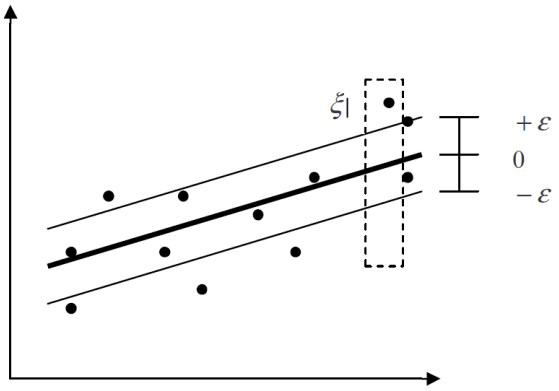

Figure 2.1. One-dimensional linear regression with epsilon intensive band (Basak *et al.*, 2007)

For non-linear data, the standard quadratic optimization method cannot be used because the complexity depends on the distance on a one dimensional hyperplane. Instead, another form of optimization called convex quadratic optimization can be used which depends on the number of training instances (Burges, 1998). Kernels non-linearly map the input data to a high dimensional space where it becomes linearly separable. Various Kernel functions (such as linear, polynomial and radial basis) can be used depending on the characteristics of the data. (Schölkopf *et al.*, 1998).

Traditional quadratic programming algorithms are not suitable for large size problems. Kernel matrix should be computed and stored in memory. This requires large

memory. Also, coding of these algorithms is difficult (Shevade *et al.,* 2000). One of the fastest iterative algorithms that are used in SVM is sequential minimal optimization algorithm. It divides the large quadratic problem (QP) into series of smallest QP problems so it is easier and faster to solve smaller problems. SMO can handle very large training sets (Platt, 1998**).** This method makes optimization at every step so fast that the overall QP problem can be solved quickly.

The accuracy of a model is highly dependent on its parameters, so selection of parameters plays a key role in the reliability of the model. Christianini *et al.* (1998) also declared that "One of the most important design choices for SVMs is the kernel-parameters, which implicitly defines the structure of the high dimensional feature space where a maximal margin hyperplane will be found. Too rich a feature space would cause the system to over fit the data, and conversely the system might not be capable of separating the data if the kernels are too poor."

As selecting the radial basis function kernel as a kernel type, two parameters needed to be adjusted. C is a complexity parameter that controls over fitting of the model. Gamma (γ) controls the degree of nonlinearity of the model. For SVM, the value of ε in the ε-insensitive loss function should also be adjusted. ε has an effect on the smoothness of the SVM's response and it affects the number of support vectors, so both the complexity and the generalization capability of the network depend on its value.

2.2.3. Neural Networks

The working principle of artificial neural network is similar to human brain that learns from each experience (Rud, 2001). Inspired from the behavior of learning in biological neurons, neural networks can be applied for modeling nonlinear complex problems in diverse areas (Günay and Yıldırım, 2010).

Neural networks are composed of a collection of units that are called neurons or nodes which are connected in some pattern to allow communication. The data set is split up into two groups; training and testing data sets. During the training process, after each iteration,

the predicted value is compared with the actual value and the model is constructed according to minimum error level.

The communication of neurons is regulated by a rule for combining input signals and an activation rule that takes the combined input to calculate an output signal. A signal may be sent to other units along connections which are known as weights. The weight can excite or inhibit the signal that is being communicated. A typical neural network is basically composed of some main features such as a set of simple processing units, a pattern of connectivity, a rule for propagating signals through the network, a rule for combining input signals, a rule for calculating an output signal and a learning rule to adapt the weights (Callan, 1999).

Neural networks can deal with nonlinear data that is difficult to model by using linear regression. On the other hand, over fitting may occur in the process. So it is important to validate the model carefully (Rud, 2001).

A neural network contains neurons in different layers such as an input layer, hidden layer and output layer. Input layer contains the input data, the results of the network are in the output layer. The hidden layer is located inside the network. The optimal number of hidden nodes should be searched for a good network. It depends on the structure of the network, types of activation functions, the training algorithm and the problem being solved (Callan, 1999). A large number of hidden nodes may cause over fitting while less number of hidden nodes makes the target function can not to be learned accurately (under fitting).

The decision function is created according to the given dataset. Firstly, the weights are obtained and the input variables are multiplied by their respective weighted connections. The bias value is added into the sum of the input variables to calculate the total input to the unit.

$$net_j = w_0 + \sum_{i=1}^{n} x_i w_{ij} \tag{2.5}$$

where net_{ij} is the net total input, w_0 is the bias and it is considered to be connected to a unit that always has an activation of 1, x_i is the activation for unit *i* and w_{ij} is the weight connecting from unit *i* to unit *j*.

In order to calculate the error, the equation used is described below.

$$E_P = \frac{1}{2}\sum_j (t_j - o_j)^2 \tag{2.6}$$

where t_j is the target or desired output from unit j and o_j is the actual output. The overall error is the sum of all the errors.

In order to adapt weights for an efficient network, the error should be minimized. Delta rule or Widrow-Hoff law is used for adapting weights. This rule is

$$\Delta w_{ij} = \eta \delta_j x_i \,, \quad \Delta w_{ij} = \eta \delta_j x_i \tag{2.7}$$

where t_j is the target or desired output from unit j, o_j is the actual output, x_i is the signal coming from unit *i*, η is the learning rate (how much to adapt the weight) and Δw_{ij} is the amount by which to change the weight connecting unit *i* with *j*.

Backpropagation is used as a weight adaptation rule in neural networks. The backpropagation algorithm follows two ways along the network: first way is to go forward from the input layer to the output layer and second way is to go backward from the output layer to the input layer. In the forward step, outputs at the output layers are determined by using input layer. In the backward step, the error values are propagated back through the network to determine how the weights should be changed during training. Values from the output layer pass through the reverse direction and the hidden layer which sends activation to every unit during forward step, receives error signals so the weights can be changed according to these error signals. Backpropagation occurs in a complete cycle and it stops until the error signals become in a tolerance. After repeating this algorithm with all the

samples (training data points) for many times, the sum of E gradually converges to a minimum value, so that the network becomes a fully trained one (Callan, 1999).

The Levenberg-Marquardt method of training contains both gradient descent and Gauss-Newton iteration. The equation is given in Equation (2.8) that compares the predicted and the actual values. The errors for all the patterns are shown in the Jacobian matrix in Equation 2.9 where w consists of all the weights. The weight update rule is presented in Equation 2.11, where, J is the Hessian matrix for the error vectors and η is the Levenberg-Marquardt learning parameter.

$$E = \frac{1}{2}\sum_{j}\left(t_j - y_j\right)^2 = \frac{1}{2}\sum_{j} e_j{}^2 \tag{2.8}$$

$$J = \begin{bmatrix} \frac{\partial e_1}{\partial w_1}, \frac{\partial e_1}{\partial w_2}, \ldots \frac{\partial e_1}{\partial w_N} \\ \frac{\partial e_2}{\partial w_1}, \frac{\partial e_2}{\partial w_2}, \ldots \frac{\partial e_2}{\partial w_N} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \frac{\partial e_n}{\partial w_1}, \frac{\partial e_n}{\partial w_2}, \ldots \frac{\partial e_n}{\partial w_N} \end{bmatrix} \tag{2.9}$$

$$w = \left[w_1, w_2, w_3 \ldots w_N\right]^T \tag{2.10}$$

$$w_{new} = w_{old} + \left(J^T \cdot J + \eta \cdot I\right)^{-1} \cdot J^T \cdot e \tag{2.11}$$

3. MATERIALS AND METHODS

3.1. Experimental Data

A detailed research has been made in literature between 2002 and 2012 on water gas shift reactions using the publications that can be reached online (mostly in the databases of Sciencedirect, Web of Science, Springer, Elsevier and American Chemical Society). Approximately 150 articles were reviewed, however 85 of them was used to construct the database because the remaining articles were not suitable to extract data that fit our purpose. In order to extract data from the graphs, "Digitizelt" software, which converts the plots into tables, was used. Totaly 4372 experimental data points were extracted to construct the database containing data about six noble metals, fourteen preparation methods, twenty two supports and thirty promoters as the design variables. Calcination and reaction temperature, pressure, H_2O, CO_2, CO, O_2, H_2, CH_4 concentrations in the feed stream time on stream and F/W (feed flow rate/catalyst weight) were the operating variables. Preparation methods were taken as a categorical attributes (0 or 1) while the other variables had continuous values within their ranges.. If two preparation methods (different for noble metal and promoter) were used together, the input variable "1" was used for both. The calcination temperature and time of the catalysts which are not calcined were taken as 25°C and 3.5 hours respectively. The time on stream was assumed to be 60 minutes for the articles in which no value was reported for this variable. The database was constructed using only the particulate catalysts excluding the other forms such as monoliths and nanotubes. The variables in the database are presented in Table 3.1 with their applicaple ranges.

3.2. Computational Details

First, the literature was analyzed by using simple descriptive statistics in order to understand the general trend of the research about water gas shift reactions. Then, the applicability of support vector machine for this type of database was tested using the database of CO oxidation over Cu-Ce catalyst because this database is not only smaller and simpler, but also well analyzed by our group in a previous work using artificial neural

networks (Günay and Yıldırım,2011). The results obtained by SVM and ANN were compared to decide the method (which was found to be ANN) to be used for WGS database.

Table 3.1. Input variables and their ranges

Input variable	**Range (for continuous variables) or Identity (for categorical variables)**
Base metal type and weight percentage	Pt, Au , Ru, Rh , Ir , Pd (0-100)
Preparation method	Incipient to wetness impregnation (IWI), Wet impregnation (WI), Homogenous deposition precipitation (DP), Sol-gel precipitation (SGP), Sequential impregnation (SI), Coprecipitation(CP), Flame spray pyrolysis reactor, Co-impregnation, Sequential precipitation, Urea Gelation(UGC), Surfactant templating, Solution combustion technique, Mechanochemical activation , Deposition-precipitation Citric acid method, Microemulsion(reverse addition)
Calcination Temperature (^{o}C)	25-700
Calcination Time (h)	0-10
Support Type	YSZ, AL_2O_3, MgO, CeO_2, TiO_2, Zeolite, ZnO, MnO, Yb_2O_3, Sm_2O_3, Gd_2O_3, Y_2O_3, ZrO_2, hydroxyapatite (HAP), Tb_4O_7, HfO_2, La_2O_3, Co_3O_4,ThO_2, SiO_2, Fe_2O_3
Promoter type	Li, Ce, Co, Mg, Fe, Mn, Zr, K, Ni, Na, La, V, Rb, Y, Sr, Ca, Cs, Tm, Sm, Er, Gd, Yb, Zn, Re, Ag, Ti, Cr, Ho, Nd,
Operating Temperature	5-810
H2O vol.%	0-93.1
CO2 vol.%	0-24.84
CO vol.%	0.2-99.5
O2 vol. %	0-1.358
H2 vol.%	0-60
CH4 vol. %	0-50.5
Operating Pressure (atm)	1-45
Time on Stream (min)	0-5920
F/W (mg.min/ml)	0-40.1

The successes of the models were determined by their ability to predict the unseen data during the testing process. The root mean squared error (RMSE), which is given in Equation 3.1, was used as the indicator of generalization accuracy. The models were tested using k-fold cross validation technique, which divides the whole database into k subsets

randomly and uses k-1 sets to train the network to predict the outcome of the remaining one set. Then, the errors between the predicted and experimental values were recorded; after k times repeating the procedure, the total RMSE was calculated through the entire database. The model that has the smallest total RMSE was considered as the best that represent the data base (Günay and Yıldırım, 2010).

$$RMSE = \sqrt{\frac{1}{n}\sum_{1}^{n}\left(p_i - t_i\right)^2} \tag{3.1}$$

here p_i is the predicted, t_i is the target value and n is the total number of experiments.

The coefficient of determination (R^2) was also used as the additional indicator for the fitness of the models. The value of R^2 can be between 0 and 1, and a value of 1 indicates a perfect fit . The mathematical formula used to calculate the coefficient of determination is shown in Equation 3.2.; where, y_i represents the experimental data, $\hat{y}_i$ is the estimated value of the corresponding experiment and $\bar{y}$ is the mean value of the experimental data.

$$R^2 = 1 - \frac{\sum\left(y_i - y_i\right)^2}{\sum\left(y_i - \bar{y}\right)^2} \tag{3.2}$$

The change of root mean square technique was used for the input significance analysis. The procedure begins with the removal of one of the input variables, then the network is trained with the remaining variables. After the training is complete, the RMSE value of the model calculated in the absence of this variable is compared with the value obtained in the presence of all inputs, and the difference is used as the indicator of the significance of this variable (Günay and Yıldırım, 2010; Günay and Yıldırım, 2011).

3.2.1. Support vector machines

Before using the WGS database, the support vector machine was tested using the dataset of selective CO oxidation over copper-based catalysts. This database contains less attributes and instances than the WGS database, and it was already analyzed using ANN in

a previous study (Günay, 2012). Then, the results of support vector machine model and neural network model were compared to decide the method for the WGS reaction.

Support vector machine was performed in WEKA 3.7.7. workbench and the sequential minimal optimization method for SVM regression (SMO_{reg}) was used. RBF kernel was employed because it fits the size and complexity of our database better than the other kernel function. Normalization was performed on the training data as a filter type. The parameters epsilon (L), complexity parameter (C) and gamma were selected in a way that the total RMSE was minimum.

3.2.2. Neural Networks

Artificial neural networks were created by using computer codes written in MATLAB environment by Günay (2012) and the networks were trained by backpropagation algorithm (with delta rule of error correction). In order to prevent any variable dominate the others, all the input variables were normalized in the range of 0-1.

The model was trained by the Levenberg-Marquardt method, which is a blend of gradient descent and Gauss-Newton iteration and the hyperbolic tangent function was used as the activation function in the hidden layers. The early-stopping technique was applied during the training of the neural networks to prevent over fitting.

The optimal network topology was determined by testing the performances of several networks according to their generalization accuracies (the ability to predict the data unseen during the training process) by comparing RMSE.

3.3. Testing SVM Model using Selective CO Oxidation over Noble Metal Catalysts Data

In order to construct the best model that represents the data set, the parameters C and gamma should be optimized and this was done in three ways:

- Automatic grid search using training data
- Manual grid search using training data

- Manual grid search using testing data

3.3.1. Automatic Grid Search using Training Data

First, the grid search option in Weka was used to select the best parameters. The optimum point for 2 fold cross validation was found to be as C=50 and gamma=10 leading to a RMSE value of 10.19; these parameters were C=20 and gamma=8 for 10 fold cross validation case corresponding to a RMSE value of 10.80. The L was kept constant at 0.01 during these tests. Then these values were used to test the ability of the model to predict the results of individual papers as follows: The data of each article were removed one by one and a new model was constructed each time with these optimum parameters. Then, each time, the removed article (i.e. the article that was not seen by the model) were tried to be predicted. The results of RMSE of prediction of all articles were compared with ANN results reported by Günay and Yıldırım (2011) in Table 3.2; both SVM models were unsuccessful compared to the ANN model.

Table 3.2. The RMSE of testing with the optimum points for 2 fold and 10 fold cross validation

Number of article	C=50, G=10	C=20, G=8	Neural Networks
1	44.50	45.58	21.5
2	49.38	50.96	12.4
3	6.67	6.71	15.3
4	39.13	38.77	7.3
6	41.05	40.24	25.4
7	46.48	46.48	9.5
8	44.01	44.64	16.2
11	10.78	10.75	9.6
12	49.80	52.08	15.2
13	38.65	40.51	25.3
14	43.74	44.98	17.6
16	12.38	10.33	5.1
17	41.08	41.24	9.7
20	29.09	28.43	26.0
∑RMSE	496.76	501.68	216.0

3.3.2. Manual Grid Search using Training Data

Next, the optimum points were searched manually by constructing a C versus gamma matrix for 2 fold, 4 fold and 10 fold cross validation at various epsilon (L) values. The procedure was as follows: C and gamma values were changed at a constant L. After an optimum pair was reached, the search was continued around this optimum using a smaller step sizes. This procedure was repeated for various L values for 2, 4 and 10 fold cross validation. Then the values of C and gamma giving the minimum RMSE were selected as optimum. The first step obtained at L=0.001 for 2 fold cross validations was given in Table 3.3 as example while the best values obtained in this section was summarized in Table 3.4.

Table 3.3. Grid search results for 2 fold cross validation, epsilon value L=0.001

	2 fold	C					
	L=0.001	0.1	1	5	10	30	50
Gamma	0.01	37.97	29.76	26.14	25.87	25.36	24.90
	1.00	24.85	19.58	18.02	17.85	17.76	17.54
	5.00	24.48	16.70	15.17	14.90	14.38	15.97
	10.00	24.24	15.02	13.06	13.14	14.69	15.53
	20.00	24.38	13.78	12.87	13.09	13.92	14.41
	30.00	24.89	14.29	13.67	13.82	14.28	14.69
	40.00	25.54	15.05	14.46	14.61	14.93	15.44

Table 3.4. The optimal parameters and RMSE values for different folds of cross validation

		C	**Gamma**	**RMSE**
L=0.001	10 fold	5	30	8.30
	4 fold	10	20	9.85
	2 fold	5	20	12.87
L=0.1	10 fold	20	10	10.51

When these values were used to predict the results of individual articles as discussed above, the results given in Table 3.5 were obtained. Again the values of total RMSE are well above the value of 216 obtained by ANN.

Table 3.5 The RMSE errors of testing articles

	L=0.001			L=0.1	
	2 fold	*4 fold*	*10 fold*	*10 fold*	*10 fold*
Number of article	C=5, G=20	C=10, G=20	C=5,G=30	C= 20, G=10	C=5, G=30
1	41.31	41.51	40.56	44.36	40.29
2	43.01	43.19	41.62	48.55	41.27
3	2.40	2.13	1.53	6.71	41.27
4	36.30	36.41	35.62	38.60	35.35
6	39.66	39.86	39.96	40.72	39.88
7	43.27	43.33	42.60	46.02	42.43
8	40.65	40.76	39.81	43.61	39.55
11	6.60	5.96	5.92	10.79	9.35
12	43.43	43.61	42.12	49.36	41.70
13	33.42	33.52	32.49	38.25	32.32
14	40.22	40.26	39.81	43.45	39.77
16	16.32	15.25	17.94	13.48	18.30
17	37.90	37.96	37.27	40.75	37.12
20	32.89	32.58	34.23	29.27	34.84
∑RMSE	457.38	456.35	451.47	493.91	493.43

3.3.3. Manual Grid Search using Testing Data

Lastly, the grid search was performed by testing the success of the model in predicting the results of each individual article at each value of C, gamma and L. The results of test performed at L=0.001 were presented in Table 3.6 as an example. As can be seen from the total RMSE values, this approach was also unsatisfactory compared to neural networks. The other values of L also produced similar results. Although this approach generated better results than the previous two approaches, the total RMSE could only be improved to the value of 357.2, which is still much higher than the value (216.0) in ANN. Then it was concluded that ANN fits the purpose of this work better, and only the ANN results were reported in Chapter 4 for WGS reaction.

Table 3.6. Performing grid search for predicting articles with L=0.001

	L=0.001													
	C (at G=1)					G (at C=1)								
# of article	0.01	0.9	1	5	10	0.001	0.01	0.05	0.1	10	30	50	100	1000
1	40.1	28.9	32.8	39.2	44.0	40.7	33.3	28.9	28.7	41.2	40.1	39.6	39.3	38.9
2	34.6	26.3	37.7	47.1	53.0	34.8	28.1	26.4	28.9	44.1	41.0	40.0	40.0	37.5
3	38.3	22.2	12.1	11.8	10.4	41.1	27.5	21.9	20.6	5.0	2.4	1.4	0.1	0.1
4	21.2	21.9	31.6	40.4	46.6	21.3	17.0	23.3	29.6	33.9	34.7	33.7	32.3	28.8
6	30.2	29.6	31.3	36.1	37.0	30.9	28.2	29.7	30.7	36.4	39.2	38.9	37.9	35.4
7	37.5	21.7	18.2	20.1	22.2	40.2	26.8	21.6	21.1	42.9	42.3	41.8	41.5	41.1
8	35.3	29.4	33.6	35.8	32.3	35.3	30.0	29.5	28.6	40.0	39.2	38.5	37.8	36.5
11	16.4	13.7	13.3	12.2	11.2	19.2	15.2	13.7	12.9	8.9	7.2	6.3	6.0	5.9
12	34.6	27.1	37.6	48.0	55.1	35.4	27.9	26.9	25.4	44.7	41.4	40.4	39.5	37.5
13	32.2	40.1	19.2	24.1	28.1	33.9	37.4	40.1	35.2	34.5	32.1	31.5	31.0	30.4
14	41.0	24.9	45.7	63.4	76.2	44.9	35.8	25.0	40.3	40.9	39.6	39.3	39.2	39.2
16	16.0	14.3	13.2	12.9	11.5	16.0	10.7	14.3	14.5	13.5	18.3	20.5	23.2	27.2
17	37.3	20.1	16.0	17.0	18.2	38.5	25.2	19.8	16.6	37.9	37.0	36.6	36.3	36.1
20	51.5	36.8	30.9	54.5	69.1	54.8	26.8	38.2	59.6	31.8	35.3	36.6	38.2	41.6
∑RMSE	466.4	357.0	373.1	462.6	514.8	487.1	370.0	359.5	392.8	456.2	449.8	445.3	442.2	436.1

4. RESULTS AND DISCUSSION

The results are discussed in three parts: First, a general review about the research on water gas shift reactions between 2002 and 2012 is presented. Then, the neural network analysis of water gas shift reaction is discussed. Lastly, the significances and effects of the input variables are analyzed.

4.1. A Review of the Publications of Water Gas Shift Reactions from 2002 to 2012

A comprehensive literature search was done on water gas shift reactions on noble metals from 2002 to present (August, 2012). Totally, 855 publications available online (provided by Springer, Elsevier, Wiley and American Chemical Society) were reviewed; 318 publications report the activity on noble metal catalysts. Figure 4.1 chronologically shows the number of publications on water gas shift reaction.

The number of publications on WGS reactions was steadily increased after 2002 reaching to a maximum in 2010; after that it tends to decrease even though 2012 is not fully covered. One possible reason for this may be the fact that the articles already published since 2002 covering most of the plausible noble metals, supports and conditions so it gets more difficult to find a unique design of the catalyst to study.

A significant portion of these works (318) were performed using noble metal catalysts such as gold and platinum. The number of publications over the noble metal catalyst showed the same tend as the total number of publications as seen in Figure 4.2.

Figure 4.3 show the number of studies performed by using various noble metals; Pt is the most common noble metal in water gas shift reactions and it also seems to be the most active one. The second common noble metal is Au followed by Pd and other noble metals although they are not studied as commonly as Pt and Au.

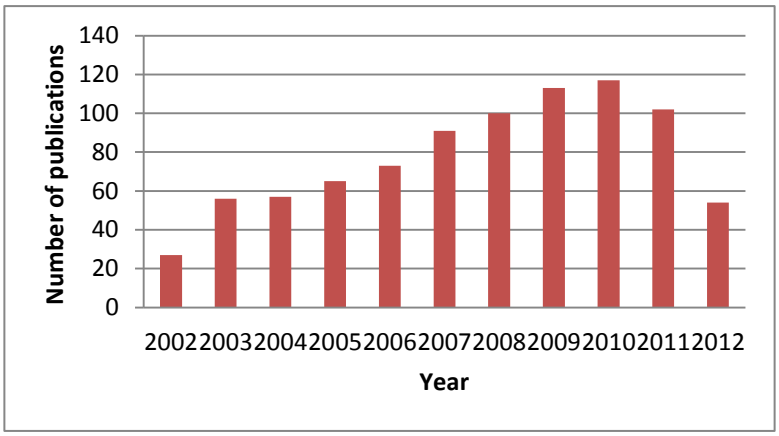

Figure 4.1. Number of publications on water gas shift reactions

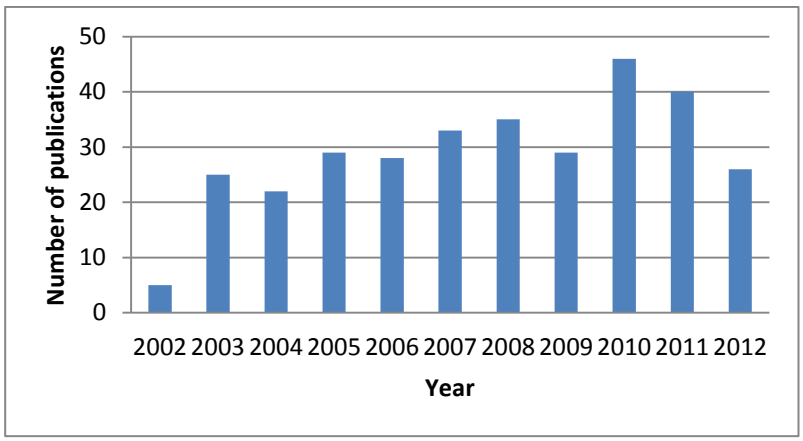

Figure 4.2. Number of publications on water gas shift reactions with noble metal catalysts

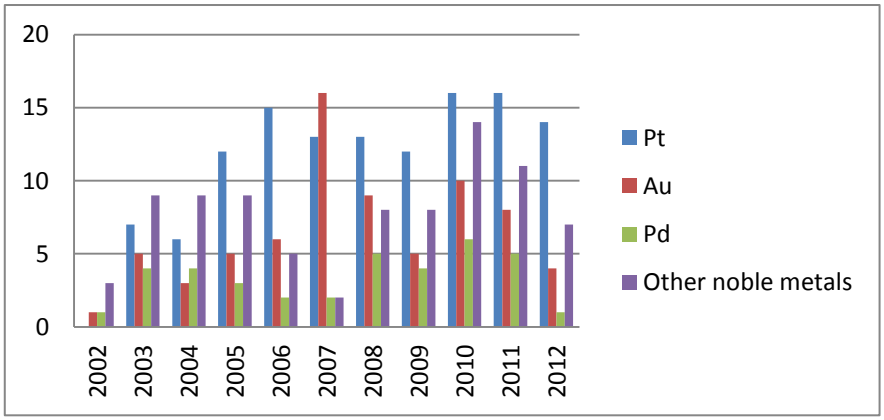

Figure 4.3. Number of publications on water gas shift reactions with different kinds of noble metal catalysts

4.2. Determining the Optimal Neural Network Topology

CO conversion which represents the effectiveness of the catalyst for WGS reaction was used as an output variable. As input neurons, 87 attributes that contains noble metal types, preparation methods, promoter types, support types and operational conditions were used. The details of the attributes are given in Section 3.1 and Table 3.1. First, the optimal neural network topology was determined and then it was used to analyze the significances of input variables and their effects on CO conversion.

The network topology contained an input layer, two hidden layers and an output layer. Fifteen neural networks with different number of neuron in the hidden layer were constructed and compared according to their RMSE. The RMSE of training was calculated by the error obtained between the experimental data points and the model predictions when all the data was used for training. The RMSE for testing was also calculated using 10 fold cross validation in order to test the generalization ability of the model (prediction ability for the unseen data). The results for training and testing for different networks are shown in Figure 4.4. The notation a-b, where the numbers below the bars, is used to label the networks represents the number of neurons in each hidden layer. The general trend is that the training error decreases with the increasing network size because of the use of more neurons (weights); the testing error, on the other hand, start to increases with the excessive use of neurons. In addition, the testing RMSE is always greater than training RMSE as expected because it is calculated from the prediction of the data unseen during training.

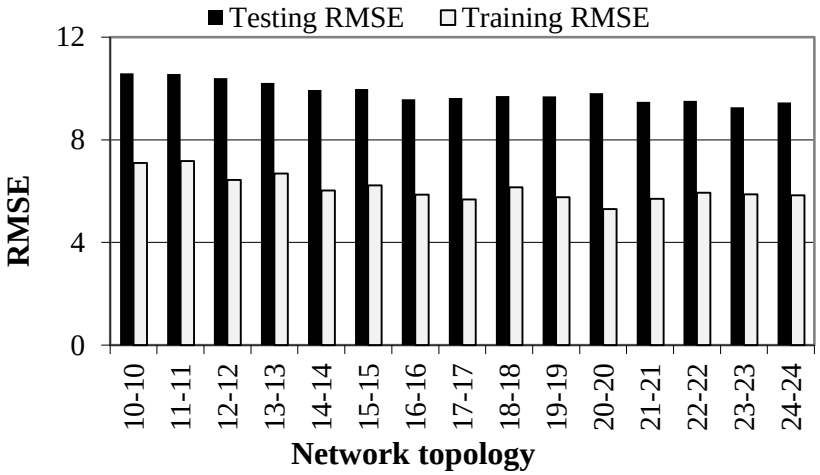

Figure 4.4. Training and testing errors of different neural networks

The optimum neural network should be decided by using testing RMSE because it shows the ability of network to predict the unseen data. Although the minimum RMSE for testing is observed at point 23-23 (9.26), 21-21 network, which has the second smallest RMSE (9.48), was selected because the difference in testing RMSE is minor and, the simpler model should be used if it is possible to avoid over fitting. The experimental vs. predicted CO conversions were plotted for both training and testing with 21-21 hidden layer and shown in Figure 4.5a,b. The RMSE and corresponding R^2 values are quite satisfactory.

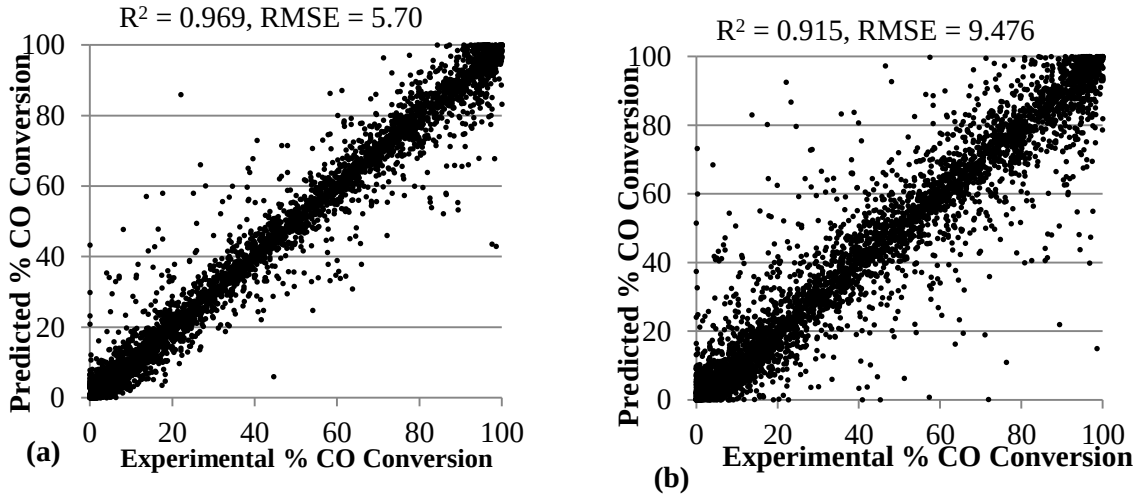

Figure 4.5. Experimental vs. predicted CO conversion values for the entire database: for (a) training, (b) testing.

4.3. Testing the Optimal Network to Predict the Results of Unseen Papers

The 21-21 network structure was used to predict the results of a paper that was not seen by ANN during testing. This was achieved by removing one paper from the database, training the network by remaining 84 papers and then predicting the results of one paper left during training**.** This procedure was repeated for 85 times and testing RMSE and corresponding R^2 values of all papers were calculated as the measure of success in predicting the outcome of a work that is not yet performed using the data published already.

29 articles among 85 had R^2_{test} values greater than 0.5 (Table 4.1); which can be considered quite successful considering that all these works were performed by different people under different set of conditions. Plots of the predicted versus experimental CO

conversions for the most successfully predicted six publications are presented in Figure 4.6. The other articles had R^2_{test} values smaller than 0.5 were shown in Table 4.2.

Table 4.1. Prediction errors of each publication for water gas shift reaction (R^2_{test}>0.5)

Author	**Testing RMSE**	$\mathbf{R_{test}^2}$
Olympiou *et al.* (2007)	16.89	0.788
Sandoval *et al.*(2007)	15.63	0.779
Fu *et al.* (2005)	7.69	0.759
Sungkwang *et al.*(2009)	13.31	0.726
Idakiev *et al*. (2007)	11.94	0.711
Hwang *et al.* (2011)	7.28	0.705
Panagiotopoulou *et al.* (2009)	19.96	0.704
Ribeiro *et al.* (2010)	18.75	0.694
Kam *et al.* (2010)	6.20	0.693
Akpınar (2005)	10.96	0.689
Panagiotopoulou and Kondarides (2011)	20.95	0.668
Çağlayan and Aksoylu (2005)	22.02	0.658
Venugopal and Scurrell (2003)	19.77	0.651
Gonzalez *et al.* (2010)	14.67	0.651
Vignatti *et al.* (2011)	14.03	0.645
Han *et al.* (2010)	20.28	0.643
Gonzales *et al*. (2008)	14.94	0.639
Panagiotopoulou and Kondarides (2004)	21.36	0.611
Radhakrishnan *et al.* (2006)	18.18	0.602
Zhu *et al.* (2009)	22.74	0.598
Idakiev *et al.* (2007)	10.51	0.593
Gayen *et al.* (2010)	19.49	0.592
Jacobs *et al.* (2003)	15.70	0.588
Andreeva *et al.(*2009)	20.68	0.587
Ribeiro *et al.* (2011)	18.16	0.575
Sakurai *et al.* (2005)	22.52	0.546
Kalamaras *et al.* (2011)	19.04	0.542
Hortado-Juan *et al.(*2008)	24.39	0.528
Yeung and Tsang (2010)	24.27	0.520

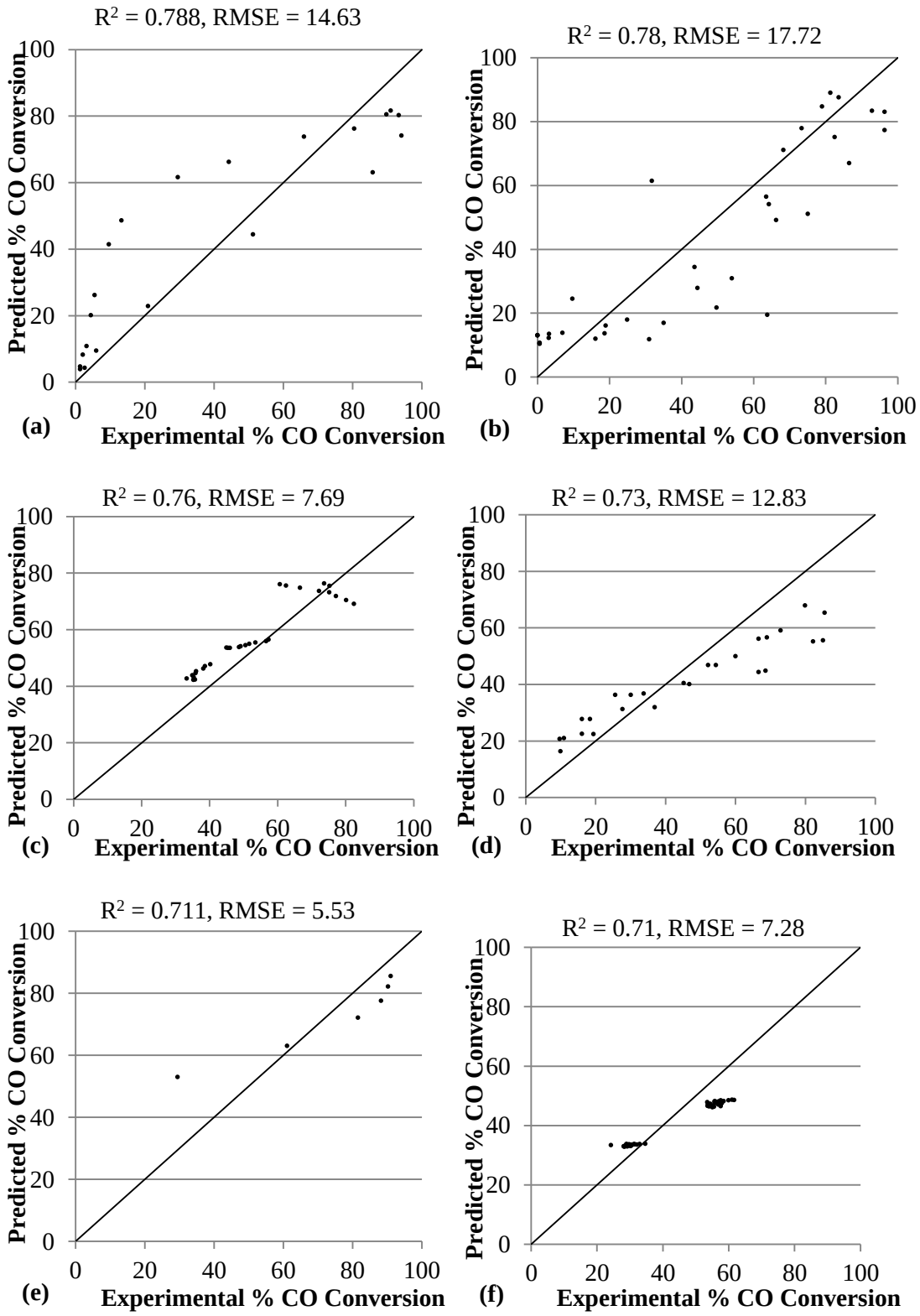

Figure 4.6. Experimental vs. predicted CO conversion for: (a) Olympiou *et al.* (2007), (b) Sandoval *et al.*(2007), (c) Fu *et al.* (2005), (d) Sungkwang *et al.*(2009), (e) Idakiev *et al.* (2007), (f) Hwang *et al.* (2011).

Table 4.2. Prediction errors of each publication for water gas shift reaction (R^2_{test}<0.5)

Author	**Testing RMSE**	**R_{test}^2**
Evin *et al.* (2008)	13.81	0.493
Liu *et al.* (2010)	21.44	0.484
Kim *et al.* (2009)	20.23	0.476
Panagiotopoulou *et al.* (2007)	27.22	0.470
Utaka *et al.* (2003)	19.53	0.461
Fu *et al.* (2003)	20.46	0.451
Jacobs *et al.* (2005)	18.09	0.416
Jeong *et al.* (2012)	24.29	0.400
Kim *et al.* (2012)	22.21	0.399
Linganiso *et al.* (2011)	17.07	0.392
Liang *et al.* (2009)	22.42	0.384
Andreeva *et al.* (2002)	20.49	0.371
Fonseca *et al.* (2007)	29.24	0.304
Jeong *et al.* (2011)	26.67	0.298
Piermartini *et al.* (2011)	17.42	0.288
Panagiotopoulou and Kondarines (2007)	30.60	0.281
Chenu *et al.* (2005)	17.22	0.262
Luengnaruemitchai (2003)	19.16	0.246
Duarte de Farias *et al.* (2008)	25.35	0.244
Galletti *et al.* (2009)	15.32	0.234
Zhang *et al.* (2007)	13.45	0.229
Güneş and Yıldırım (2010)	14.63	0.227
Zhai *et al.* (2010)	38.58	0.214
Deshpande (2010b)	21.15	0.210
Duarte de Farias *et al.* (2010)	13.50	0.194
Buitrago *et al.* (2012)	25.17	0.194
Germani and Schuurman (2006)	25.03	0.190
Jacobs et al. (2003)	31.01	0.177
Evin *et al.* (2008)	23.12	0.161

Table 4.2. Prediction errors of each publication for water gas shift reaction (R^2_{test}<0.5) (cont.)

Author	Testing RMSE	R_{test}^2
Thinon *et al.* (2008)	24.96	0.160
Bickford *et al.* (2005)	14.32	0.135
Gamboa-Rosales *et al.* (2012)	13.60	0.134
Idakiev *et al.* (2004)	18.72	0.101
Jacobs *et al.* (2005a)	28.36	0.062
Kugai *et al.* (2011a)	19.45	0.051
Kim and Thompson (2005)	6.11	0.020
Tabakova *et al.* (2006)	5.58	0.005
Yeung and Tsang (2009)	23.46	-0.001
Rosso *et al.* (2004)	37.43	-0.017
Wang *et al.* (2010)	33.07	-0.058
Kugai *et al.* (2011b)	8.69	-0.113
Deshpande *et al.* (2010)	36.56	-0.124
Tabakova *et al.* (2004)	34.42	-0.130
Gatica *et al.* (2012)	39.00	-0.155
Hatyanto *et al.* (2007)	24.99	-0.195
Vignatti *et al.* (2010)	26.31	-0.217
Bi *et al.* (2009)	4.67	-0.331
Watanabe *et al.* (2010)	17.42	-0.361
Kam *et al.* (2010)	8.07	-1.071
Fox *et al.* (2008)	26.08	-1.252
Mendes *et al.* (2009)	27.87	-1.443
Tang *et al.* (2012)	16.26	-1.802
Liu *et al.* (2011)	12.26	-2.159
Azzam *et al.* (2008)	24.46	-6.633
Duarte de Farias *et al.* (2007)	15.95	-9.950
Jacobs *et al.* (2005)	19.47	-5561.611

4.4 Significance Analysis for Input Variables

The significance of catalyst design and operational variables were also analyzed by using 21-21 neural network model described above. This is also as important as predicting the results of a set of conditions to understand water gas shift reactions and to be able to manipulate the variables to have the desired outcome.

The following procedure was performed to test the relative significance of input variables: Each time one variable removed from the list and 21-21 ANN network retrained using the remaining variables; the difference between the RMSE in the absence and presence of that variable was used as the indicator of its significance (larger the RMSE, higher the significance of variable). This procedure repeated for all the input variables and relative deviations from the RMSE of full model was used as the measure of relative significances. The results are shown in Table 4.2. It should be noted that the relative significances are valid within the limits of these variables in the database. Hence even a significant variable may be found as insignificant in this type analysis if it was not changed much though the database.

As a group, the reaction conditions were found to be the more influential (relative significance of 64.2%) than catalyst design variables. It is an understandable result because the reaction conditions are usually changed in a wider range than the catalyst preparation variables. Especially the temperature is found to be the most significant variable as expected because the temperature affects both equilibrium and reaction rates significantly; hence a wide range of temperature was studied in the literature. The equilibrium constant increases as the temperature decreases because the WGS reaction moderately exothermic. The lower temperatures enhance the production of H_2 while the higher temperatures may be needed to obtain necessary reaction rates.

H_2O/CO ratio was also reported to be an important variable in the literature For example, Andreeva *et al.* (2002) reported that the catalytic activity over Au/CeO_2 catalyst slightly increased as a function of the H_2O/CO ratio at various temperatures (220, 230, 260^oC). Çağlayan *et al.* (2006) also found the similar results that CO conversion levels

were found to increase with increasing H_2O/CO ratio in the feed over bimetallic Pt-Ni/Al_2O_3 catalyst. However, neither H_2O nor CO was found to be significant in our analysis as it is evident from Table 4.2. Apparently H_2O/CO ratio was significantly optimized through years and it was changed only in a narrow margins.

Base metal, promoter and support types were the significant design variables as expected and again, their apparent significances are well below than the temperature because these variables were also changed in a much narrower ranges. As a matter of fact the majority of the articles in our database contain the experiments with Pt and Au. Similarly the support is an important variable because of the interaction with the base metals. For example a comparative study of gold nanoparticles supported on reducible (TiO_2 and CeO_2) and non-reducible oxides (Al_2O_3 and SiO_2) as catalysts in the WGS reaction were studied at different temperatures by Sadoval *et al.* (2007). This and similar conclusions are already used during the works in the database were performed; hence the variations in support selection does not be seen as highly significant.

Table 4.3. Relative Input Significance Analysis of WGS data

	RMSE without the variable	RMSE Difference*	Relative Significance (%)	Group Significance (%)
Base Metal Type	9.46	3.77	10.1	Catalyst design variables 35.5
Preparation Method	6.51	0.81	2.2	
Calcination Conditions	6.31	0.61	1.6	
Support Type	10.16	4.46	12.0	
Promoter Type	9.27	3.57	9.6	
H_2O%	6.03	0.33	0.9	Operation variables 64.6
CO_2%	6.34	0.64	1.7	
TOS	5.99	0.30	0.8	
CO %	5.83	0.13	0.4	
O_2%	5.99	0.29	0.8	
H_2%	6.87	1.17	3.1	
CH_4 %	5.81	0.11	0.3	
F/W	6.84	1.14	3.1	
Temperature	25.64	19.94	53.5	

*the difference between RMSE obtained without the variable and RMSE of the original model

4.5. Predicting the Effects of Catalyst Variables

Besides the ability to predict an unknown data, the knowledge extraction should also aim to give information about the effects caused by changing the level of catalyst preparation and operating variables in order to understand the catalytic processes better. In this section, 21-21 ANN model was also tested if it could predict the change in conversion with changing a variable as reported in the literature. The three articles predicted best in Table 4.1 were selected and analyzed.

Olympiou *et al.* (2007) studied three different noble metals (Pt, Rh and Pd) at different temperatures. The weight percentages of the metals (%5) and other conditions were the same. The experimental and predicted values of temperature effects on CO conversions are shown in Figure 4.7. As the temperature increases, the conversion also increases in all three catalysts and the trend is successfully predicted by the ANN model.

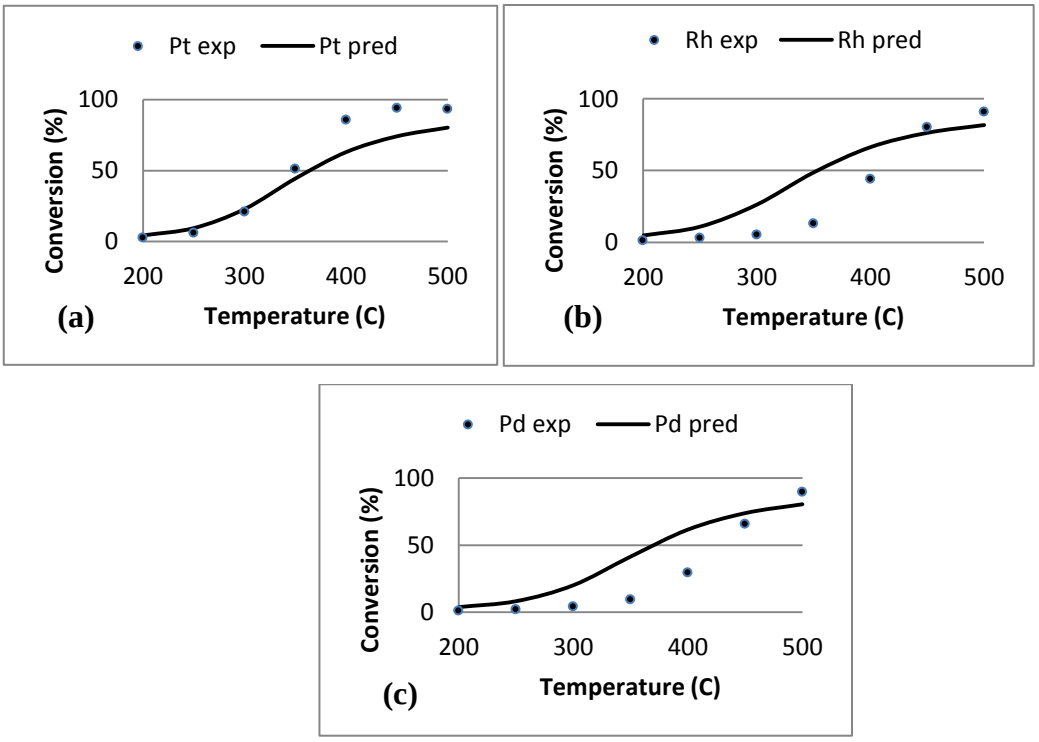

Figure 4.7. CO conversion at different temperatures with (a) Pt, (b) Rh and (c) Pd. (Olympiou *et al.*, 2007)

The effect of support type was studied by Sandoval *et al*. (2007). Au was used as a noble metal type with a fixed weight percentage (%8). Two different supports were used (TiO_2 and CeO_2) and the change of CO conversion was observed with changing temperature. The predictions for these effects are presented in Figure 4.8; they are again quite satisfactory.

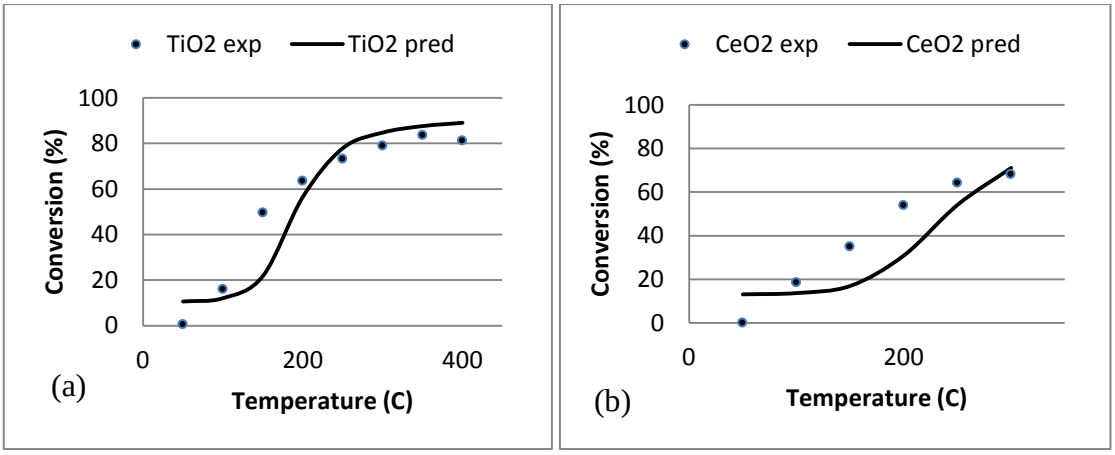

Figure 4.8. CO conversion at different temperatures with different supports (a) TiO_2, (b) CeO_2.(Sandoval *et al*., 2007).

Finally, the effect of the weight percentage of noble metal type (Au) was studied by Fu *et al.* (2007); Au was used with the weight percentages of 8% , 4.7% and 0.44% on lanthana doped ceria support. The conversion was observed in different time of stream (TOS) values at 250 ^{o}C. The results of the article and the neural network predictions, which are quite good, are shown in Figure 4.9.

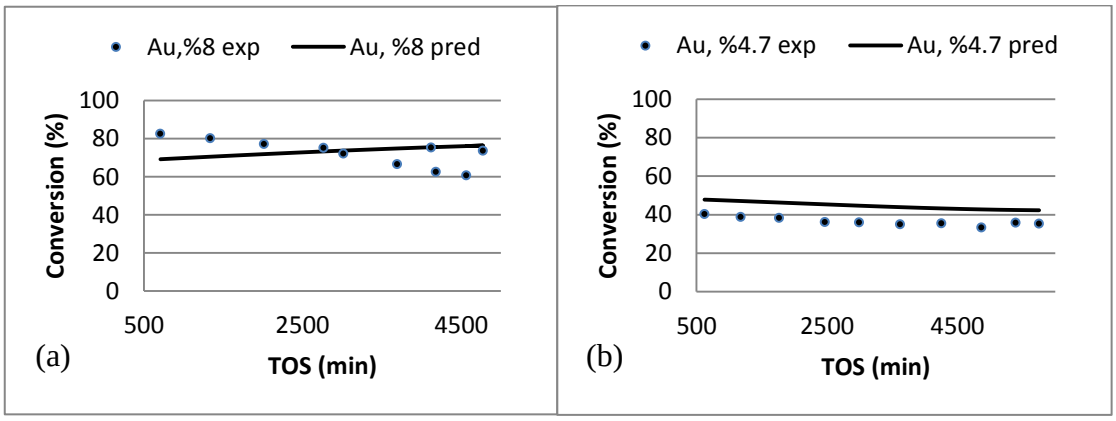

Figure 4.9. CO conversion at different TOS values with (a) Au, %8, (b) Au, %4.7

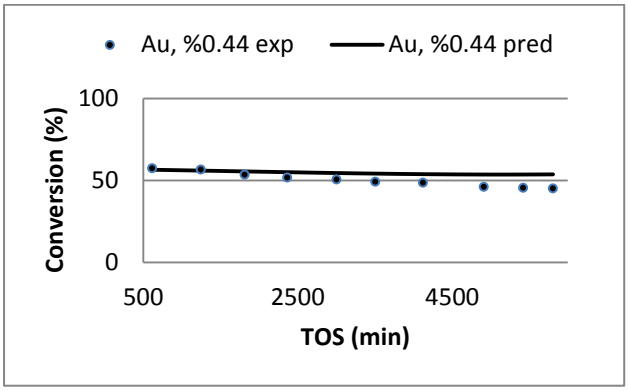

Figure 4.10. CO conversion at different TOS values with Au, %0.44. (Fu *et al*., 2007)

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The aim of this study was to extract knowledge from experimental data using data mining tools to get a better knowledge about the catalysis. Two different methods, namely support vector machines and artificial neural networks were applied to a simpler dataset (CO oxidation over Cu-Ce catalysts) to compare their abilities in such an analysis. ANN found to be much more successful and used for the analysis of WGS database, which contained 4372 data points with 87 variables retrieved from 85 papers published in the literature between 2002-2012.

In ANN analysis, the hyperbolic tangent function was used as an activation function. The delta rule was used as the error correcting rule and the backpropagation algorithm was performed as the learning algorithm to adapt the weights. The network topology was composed of an input layer, two hidden layers and an output layer. The optimum network topology was selected by testing the entire database and found to be 21-21 nodes in two hidden layers network structure.

The predictions were performed for each article and it was found that 29 articles among 85 had the R^2_{test} values greater than 0.5, which can be considered as successful.

The input significance analysis revealed that the temperature is the most significant variable (with the relative significance of 53.5%) followed by the support (12%), base metal (10.1%) and promoter type (9.6%). The operational variables have higher group significance (64.6%) than the catalyst design variables (35.5 %) within the range of database. The ANN models could also predict the effects of input variables in a considerable success.

To conclude, the artificial neural network can be successfully used to model and extract knowledge from the WGS publications in the literature, and it helps to understand this catalytic system and perform the future works better.

5.2. Recommendations

Based on the results obtained in this work, the recommendations for the future studies can be stated as follows;

- Analysis may be carried out using other data mining tools (like clustering and classification) to extract more knowledge from the same data set.
- The database can be extended o cover wider time (earlier than 2002) and resources (including patents and research reports)
- Data mining tools can also be applied for other important catalytic reactions and other fields such as to model the reaction rate from the operating variables to acquire the reaction mechanisms and the kinetic parameters.

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