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Knowledge extraction for water gas shift reaction over noble metal catalysts from publications in the literature between 2002 and 2012

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ABSTRACT

In this work, a database (containing 4360 experimental data points) on water gas shift reaction (WGS) over Pt and Au based catalysts was constructed using the data obtained from the published papers between the years 2002 and 2012. Then, the database was analyzed using three data mining tools to extract knowledge in three areas: Decision trees to determine the empirical rules and conditions that lead to high catalytic performance (high CO conversion); artificial neural networks (ANNs) to determine the relative importance of various catalyst preparation and operational variables and their effects on CO conversion; support vector machines (SVMs) to predict the outcome of unstudied experimental conditions. It was concluded that, all three models were quite successful and they complement each other to extract knowledge from the past published works and to deduce useful trends, rules and correlations, which are not easily comprehensible by the naked eyes.

1. Introduction

Researches for more efficient and environmentally friendly energy technologies have increased in recent years as a result of continuous increase in world energy demand and growing concerns for environment. The fuel cell technology, which electrochemically converts hydrogen and oxygen to electricity and water, seems to be one of the most promising energy conversion systems for the future. Due to the technical difficulties in hydrogen storage, on-site production of hydrogen from a hydrocarbon using a fuel processor is considered to be the most feasible solution for small size proton exchange membrane (PEM) fuel cell applications in the near future. However, the hydrogen stream produced by the reforming process contains CO, CO_2 and H_2O. Especially, CO is known to be harmful to the anode catalyst of the PEM fuel cell even in trace amounts; hence, it must be totally eliminated [1]. It was suggested that water–gas shift (WGS) reaction can remove most of the CO coming from reformer (also producing some additional hydrogen), followed by the preferential CO oxidation (PROX) for the complete elimination of the remaining about 1% CO [2].

WGS is a commercially well-established two-step process: high temperature shift (573–723 K) over Fe–Cr based catalysts and low temperature shift (473–523 K) over Cu–Zn catalysts to

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reduce the amount of CO further. However, these catalysts are not suitable for fuel cell applications due to their low activity and stability as well as their special pretreatment and regeneration requirements [2]. Instead, noble metal catalysts (such us Pt, Rh, Pd, Ru and Au) over various supports (such as CeO_2, Al_2O_3, ZnO and MgO) have been investigated extensively for fuel cell applications in recent years.

WGS activity of noble metal catalysts seems to depend on very large number of variables and the complex interactions among them. The catalyst preparation variables such as the type and the amount of noble metal, type of the support, type and the amount of promoter (if it is used) and the choice of the catalyst preparation method have significant influence on the catalytic activity. The same is true for the operational variables such as the reaction temperature, the space time and the feed composition. For example, the reaction temperature plays a crucial role on the CO conversion since WGS reaction is equilibrium limited and mildly exothermic; at low temperatures, the reaction is kinetically controlled whereas it is limited by thermodynamic equilibrium at high temperatures [3]. Similarly, the feed composition (especially CO/H_2O ratio) has a substantial impact on the catalytic performance.

It is quite clear that the most suitable catalyst preparation and operational conditions cannot be determined in a single experimental work considering the presence of large number of variables in wide experimental ranges; that is why researchers usually survey the literature first and focus their efforts on the experimental region that has not been explored yet and seemingly promising for the good catalytic performance. However, simple manual review of literature may not be sufficient anymore to find the right answers because the publications are too large in number (i.e. hundreds for WGS reactions), scattered over various sources, and containing significant amount of non-uniformities, gaps, mismatches and even conflicts. Hence, we need more systematic and effective approaches and tools to extract knowledge from the published literature. If we can do that, this massive accumulation of experience will become an invaluable source; the databases created from these works can be easily used to develop models and deduce patterns and rules. This may be considered as analogous to interpret the results of a statistical experimental design. Although the data points in the literature are not created statistically and not performed under the same conditions as a statistical experimental design, the existence of large number of data points in the entire experimental spectra may still allow us to capture some useful information by using some effective data mining tools, which are readily available thanks to the fast developments in computational resources in the recent years.

Data mining is a field of computer science to extract knowledge in a database. It helps to spot the patterns that are too hard to detect with the naked eyes, and use these patterns to derive conclusions or make predictions using classification (like decision trees and support vector machines (SVM)), clustering (such as k-means clustering and Kohonen networks) and estimation (such as artificial neural networks (ANN) and SVM) techniques [4]. These techniques have become quite widespread in many fields in the last two decades.

ANNs are one of the most common tools used for approximation [4,5]; various successful applications of ANN in chemistry and chemical engineering as well as in the field of catalysis were discussed in details elsewhere [6]. Decision trees, on the other hand, can help to derive simple but valuable rules, such as finding the variables leading to high or low catalytic performance levels. Although there are various applications of this tool in diverse areas, their use is quite new in the field of catalysis [7–9]. Similarly, the SVMs, which can be used both for classification and estimation, had some limited application on catalysis such as the work of Baumes et al. [10] and Chae et al. [11] although it is widely used in other fields.

In all the works referenced above, the data mining tools are employed to analyze the data produced in single set of experimental results generated by the same group. To the best of our knowledge, there are only four works (three of them are ours) that involve the analysis of the entire literature in the field of catalysis [12–14].

Table 1 – Input variables and their ranges.

Input variable	Range (for continuous variables) or identity (for categorical variables)
Base metal type and weight %	Pt (0–27), Au (0–8), Ru (0–3), Rh (0–3), Ir (0–3), Cu (0–40), Pd (0–3)[a]
Preparation method	incipient to wetness impregnation (IWI), wet impregnation (WI), co-impregnation (CI), sequential impregnation (SI), sol–gel precipitation (SGP), co-precipitation (CP), homogenous deposition precipitation (HDP), Urea Gelation co-precipitation (UGC), solution combustion technique (SCT), flame spray pyrolysis (FSP), micro emulsion (ME), deposition precipitation (DP)
Calcination temperature (°C)	200–700
Calcination time (h)	1–10
Support type	Al_2O_3, MgO, CeO_2, TiO_2, MnO, Y_2O_3, ZrO_2,Tb_4O_7, HfO_2, La_2O_3, Co_3O_4, ThO_2, SiO_2, Fe_2O_3, Sm_2O_3, Gd_2O_3, Yb_2O_3,CaO, zeolite, hydroxyapatite, activated carbon
Promoter type and weight %	Li (0–1), Ce (0–79), Co (0–20), Mg (0–10), Fe (0–10), Mn (0–10), Zr (0–1), K (0–4), Ni (0–15), Ca (0–10), Cs (0–9), V (0–6), Rb (0–14), Y (0–10), Na (0–10), La (0–12), Gd (0–10), Yb (0–10), Zn (0–10), Re (0–1), Ti (0–10), Cr (0–10), Ho (0–10), Nd (0–10), Tm (0–10), Sm (0–10), Er (0–10),Sr (0–2), YSZ (0–1)[a]
Reaction temperature (°C)	5–810
H_2 vol.% in the feed	0–60
O_2 vol.% in the feed	0–1.4
CO vol.% in the feed	0.2–99.5
H_2O vol.% in the feed	0–93
CO_2 vol.% in the feed	0–25
CH_4 vol.% in the feed	0–51
time on stream (min)	0–5900
W/F ($cm^3\ min^{-1}\ g^{-1}$)	0.006–40

[a] Weight percent of the metals in the catalyst.

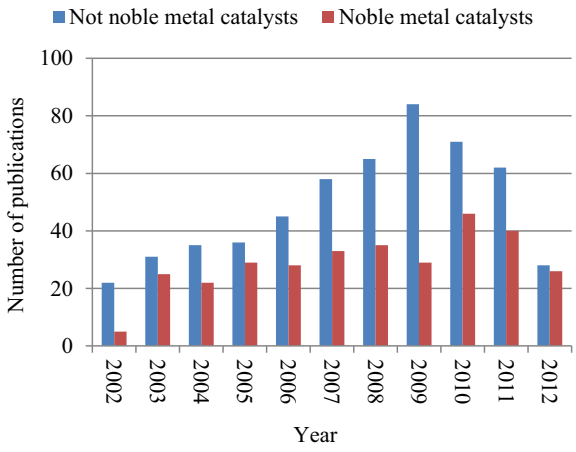

Fig. 1 – Number of publications on water gas shift reactions over years.

In this work, a database containing the past published works for water gas shift reaction over noble metal catalysts was generated and analyzed using a combination of data mining tools (decision trees, artificial neural networks and support vector machines) to deduce useful trends, rules, guidelines and correlations, which are not easily comprehensible by the naked eyes.

2. Materials and methods

2.1. *Experimental data used*

A detailed research has been performed on the published works on WGS reaction dated from 2002 to 2012, which can be reached online (mostly in the databases of Web of Science, Springer, Elsevier and American Chemical Society). Exactly 855 articles on WGS were inspected and 318 of them were found to be about the activity of noble metal catalysts. Then, we prepared a database containing 4360 experimental data points using 84 of the publications, in which the data related to the effects of various conditions on CO conversion were reported (the remaining articles were not suitable to extract data that fit our purpose). The dataset is given in Supplementary Material-1. The data correlating catalyst preparation and operational variables with CO conversion were extracted from the tables or figures reported in these publications. Base metal type and weight % (7 different metals), preparation method (12 different techniques), support type (21 different materials), promoter type and weight % (29 different materials) and the calcination temperature and time were considered as the catalyst preparation variables while H_2, O_2, CO, H_2O, CO_2, CH_4 concentrations in the feed stream together with the reaction temperature, time on stream and W/F (catalyst weight/feed flow rate) were the operating variables. 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 1 with their applicable ranges.

2.2. *Computational details*

First, we analyzed the database using some simple descriptive statistics to understand the variables, their mostly studied ranges preferred by the researchers and trends in catalytic WGS reaction literature sated from 2002 to 2012. Then, we systematically employed three data mining techniques (decision trees, ANNs and SVMs) to extract more detailed knowledge in the following three areas, which are quite essential for catalytic research:

- **Determining conditions and rules for high catalytic performance:** As we all know, the ultimate goal in the catalyst design is to achieve an active, selective, stable and cheap catalyst. Most of the published works on catalytic reactions in the literature focus on the activity (indicated by CO conversion for this catalyst system), which is explicitly reported in almost all publications. Although there are also data and comments on selectivity and stability in some publications, these variables are not as complete as the CO conversion throughout the entire database. Hence, only the CO conversion was used as the dependent variable in our analysis. In this part of the work, decision tree classification was used to reveal the conditions and rules leading high CO conversion. CO conversion levels were described in three classes as ***high*** (more than 75%), ***average*** (between 50 and 75%) and ***low*** (less than 50%). It should be noted that this division is completely arbitrary; both the number of classes and CO conversion levels describing them can be changed if it is needed.
- **Determining the importance and effects of specific input variables:** This kind of knowledge is also valuable for catalytic research. First of all, it helps us to understand the catalytic phenomena (especially the effects of operational conditions such as temperature and feed composition) and aid us to design better catalysts by pointing out the variables that should be manipulated. For this purpose, we constructed ANN models, which were proven to be effective to represent such databases in the previous works

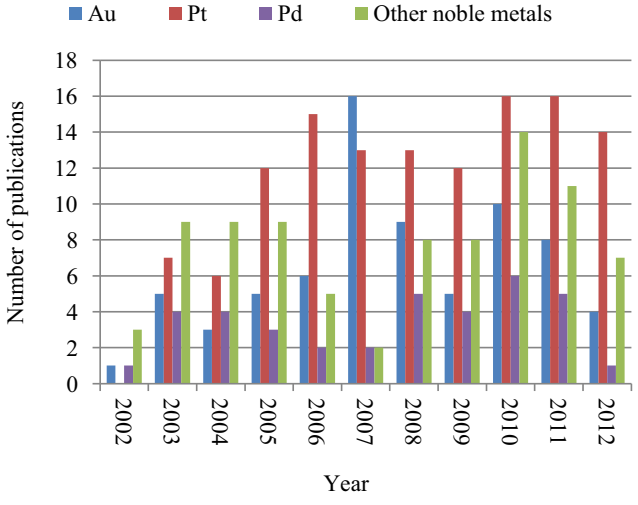

Fig. 2 – Number of publications on water gas shift reactions with various noble metals.

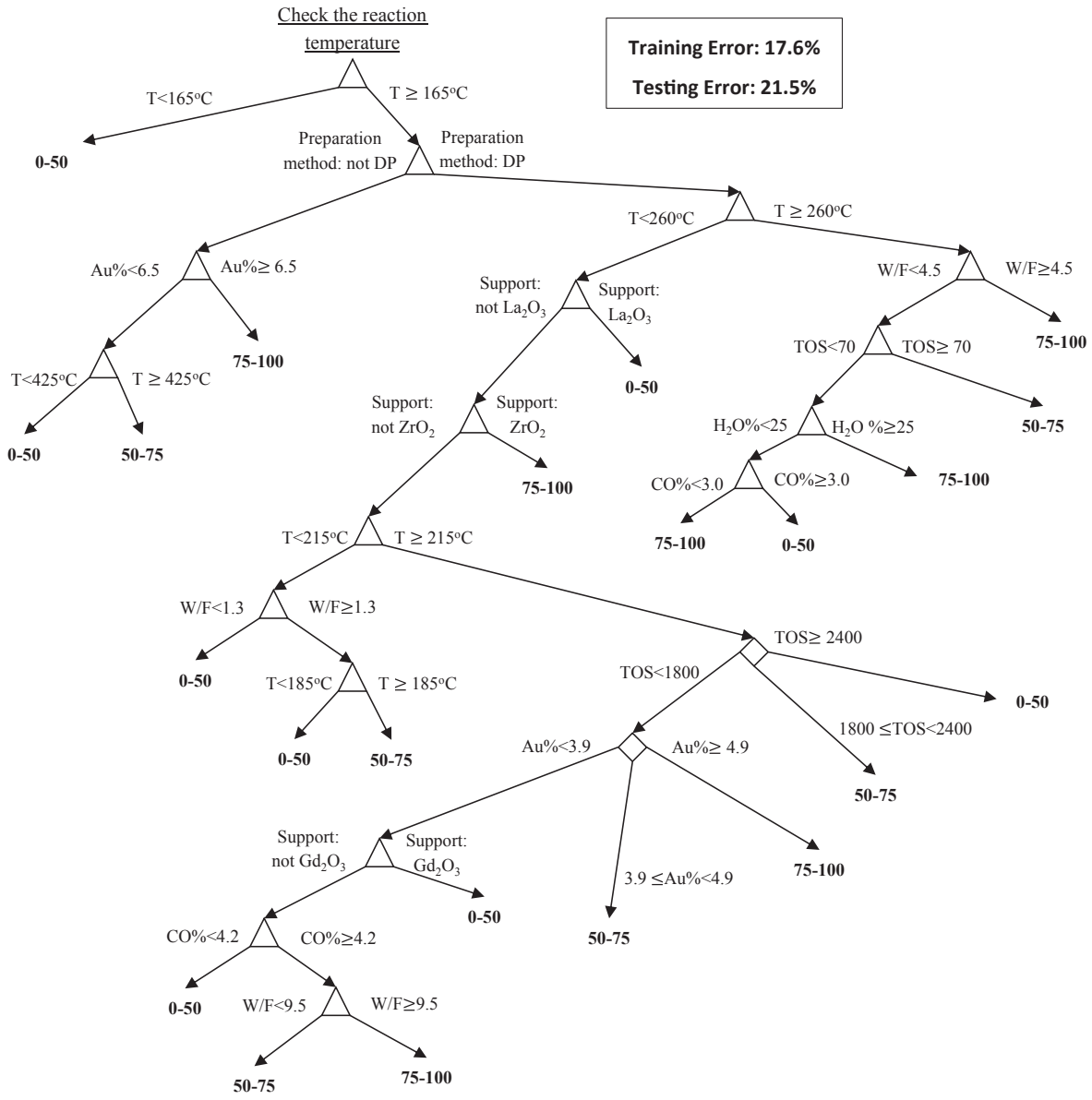

Fig. 3 – Decision tree classification of Au catalysts based on CO conversion.

[6,13]. The relative significances of catalyst preparation variables (mostly categorical variables) were determined using the change of mean square error technique (applied on the training data) while the operational variables (continuous variables) were determined by the method of partial differentiation of the neural network. Both techniques are explained in the Supplementary Material-2.

- **Predicting the outcome of unstudied conditions.** As in the case of statistical experimental design procedures, one of the common goals of model development is to predict the outcome of a certain set of conditions without doing a real experiment, which was also one of the objectives of this work. To have any practical value, the model should be able to predict the outcome of the conditions that have not been encountered before; hence, the data to develop the model (training) and the data to test it should be completely separated. For this purpose, we divided the experimental data of each publication one by one and constructed models with the data in the remaining publications, and tried to predict the CO conversions reported in the article whose data had been excluded for testing. Although both ANN and SVM models are usually successful in such kind of prediction, none of them gave highly satisfactory results. However, SVM method in the classification mode was very successful in this step. Six CO conversion classes (90–100%, 80–90%, 70–80%, 60–70%, 50–60% and 0–50% CO) were redefined this time and SVM classification was used to predict the conversion interval (class) of a new set of experimental conditions. Since the prediction accuracy should be high for any practical use,

Table 2 – Rules for 75–100% CO conversion over Au catalysts, shaded region describes the conditions for high conversion.

catalyst variables											conversion
T<165°C											<75%
T≥165°C	prep. methodIWP, CP, HDP or UGC	Au%<6.5									<75%
		Au%≥6.5									≥75%
	prep. method DP	T<260°C	support CeO_2, TiO_2, La_2O_3 or Gd_2O_3	T<215°C							<75%
				T≥215°C	TOS<1800	Au%<3.9	support CeO_2 or TiO_2	CO%<4.2			<75%
								CO%≥4.2	W/F<9.5		<75%
									W/F≥9.5		≥75%
							support Gd_2O_3				<75%
						3.9≤Au%<4.9					<75%
						Au%≥4.9					≥75%
					TOS≥1800						<75%
			support ZrO_2								≥75%
		T≥260°C	W/F<4.5								≥75%
			W/F≥4.5	TOS<70	H_2O%<25	CO%<3.0					≥75%
						CO%≥3.0					<75%
					H_2O%≥25						≥75%
				TOS≥70							<75%

DP: deposition precipitation, IWP: Incipient to Wetness, CP: co-precipitation, HDP: homogeneous deposition precipitation, UGC: Urea gelation)

the data were divided into larger number of classes (with smaller ranges) compared to three classes used in decision tree although they are still arbitrary.

Decision trees and ANNs were constructed by writing computer codes in MATLAB 7.13 (R2011b) environment while WEKA 3.7.7 software was used for SVM [15]. The computational details are explained further in the Supplementary Material-2.

3. Results and discussion

In this section, some simple descriptive statistics for WGS research between the years 2002 and 2012 will be presented first. Then, the analysis for rule deduction for best conditions (by decision tree), significance and effects of input variables (by ANNs) and predicting the results of the unstudied conditions (by SVMs) will be discussed.

3.1. *Review of literature*

A comprehensive literature search was performed on water gas shift reactions on noble metals from 2002 to August, 2012. 855 WGS publications available online (provided by Web of Science, Springer, Elsevier and American Chemical Society) were reviewed, 318 of them found to be about the activity on noble metal catalysts. Fig. 1 shows the change of total and noble metal WGS publications through years. It seems that the number of publications on WGS reactions steadily increased

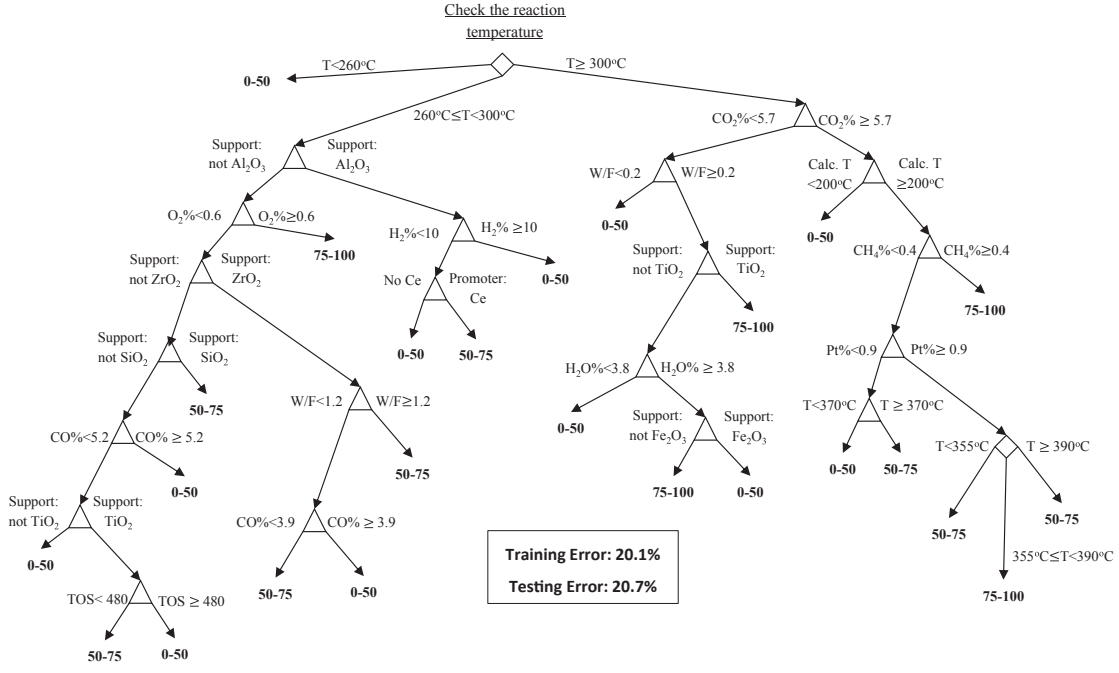

Fig. 4 – Decision tree classification of Pt catalysts based on CO conversion.

Table 3 – Rules for 75–100% CO conversion over Pt catalysts, shaded region describes the conditions for high conversion.

catalyst variables						conversion
T<260°C						<75%
260°C ≤T<300°C	support CeO_2, TiO_2, ZrO_2 or SiO_2	O_2%<0.6				<75%
		O_2%≥0.6				≥75%
	support Al_2O_3					<75%
T≥ 300°C	CO_2%<5.7	W/F<0.2				<75%
		W/F≥0.2	support Al_2O_3, MgO, CeO_2, ZrO_2, La_2O_3, SiO_2, Sm_2O_3 or Fe_2O_3	H_2O%<3.8		<75%
				H_2O%≥3.8	support Al_2O_3, MgO, CeO_2, ZrO_2, La_2O_3, SiO_2, Sm_2O_3	≥75%
					support Fe_2O_3	<75%
			support TiO_2			≥75%
	CO_2%≥5.7	Calc. T<200°C				<75%
		Calc. T≥200°C	CH_4%<0.4	Pt%<0.9		<75%
				Pt%≥0.9	T<355°C	<75%
					355°C ≤T<390°C	≥75%
					T≥390°C	<75%
			CH_4%≥0.4			≥75%

in the first years of 2000s, reaching to a maximum in 2009; after that it tended to decrease (even though 2012 is not fully covered).

Fig. 2 shows the number of studies performed by using various noble metals; Pt was the most common noble metal for WGS as it was also reported to be the most active noble metal for this reaction [16]. The second common noble metal was Au followed by Pd and the others although they were not studied as frequently as Pt and Au.

The most commonly studied support in the literature was CeO_2; although there were also extensive works on Pt over TiO_2 and ZrO_2. Ceria was the most common promoter for Pt, if it was not used as the support. The metal like Co, Na, La, and Ni were also used time to time.

The choice of catalyst preparation method seemed to completely depend on the noble metal. The impregnation (either as incipient to wetness or wet impregnation) was the most common method for Pt followed by the techniques such as precipitation and sol–gel. For the Au catalysts on the other hand, the deposition precipitation (or homogenous deposition precipitation) technique dominated the others.

3.2. *Determining conditions and rules for high catalytic performance*

First a decision tree was constructed for the entire database; however it was too large and too complicated to have any practical value. Besides, the type of the noble metal is the most important characteristic of the WGS catalysts determining the range of all the other variables. Hence, we decided to divide the database into smaller database containing only one noble metal and perform the decision tree analysis for each noble metal separately; only Au and Pt catalysts had sufficient data for this purpose.

The CO conversion values in the database were divided into three levels (0–50%, 50–75%, and 75–100%); then, a decision tree was constructed for each dataset to determine the conditions and rules leading to high catalytic performance. As mentioned in the computational details, the CO conversion levels in this section were arbitrarily created and they can be changed depending on the objective of analysis (by considering that narrower ranges give more detailed information but higher errors).

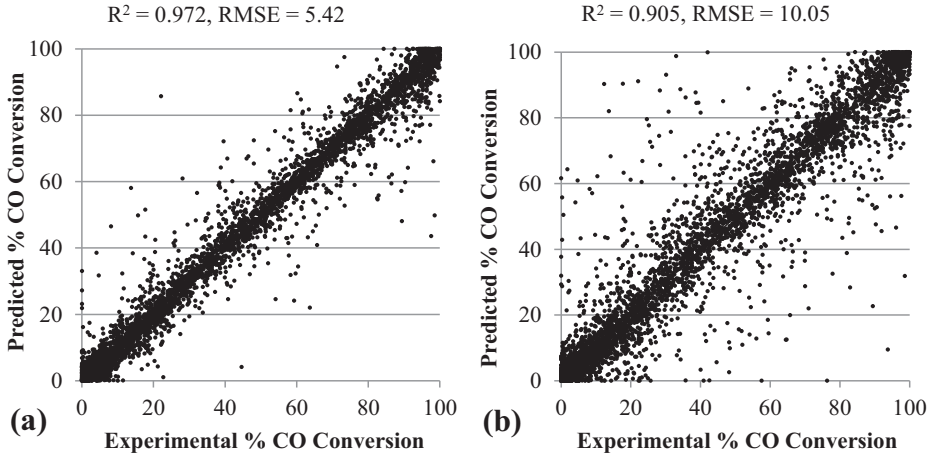

Fig. 5 – Experimental versus ANN predicted CO conversion values for (a) training, (b) testing.

Table 4 – Relative significances of preparation and operational variables.

Type of variable	Catalyst variable	% Relative significance		% Group significance (change of RMSE)
		Change of RMSE	Partial differentiation	
Preparation variables	Support type	32.6		35.0
	Base metal type and amount	29.6		
	Promoter type and amount	26.1		
	Preparation method	6.0		
	Calcination conditions	5.6		
Operating variables	Reaction temperature		20.7	65.0
	CO vol.%		16.1	
	W/F		15.7	
	H_2O vol.%		13.3	
	O_2 vol.%		8.0	
	H_2 vol.%		7.7	
	CH_4 vol.%		7.4	
	CO_2 vol.%		6.7	

The decision tree analysis for Au based catalyst is given in Fig. 3. The training error was found to be 17.5% (i.e. tree wrongly classified 17.5% of the training data) while the testing error was 21.5% (i.e. tree wrongly classified 21.5% of the testing data). 21.5% testing error should be considered as acceptable since it indicates the error made by the tree during the classification of the data not seen before.

The tree made the first division according to the reaction temperature establishing that the temperatures less than 165 °C were not suitable for WGS reaction; this was an expected result since high conversions usually require higher temperatures depending also on the other conditions. This result was in harmony with the results achieved by Venugopal and Scurrell who investigated WGS activity at various reaction temperatures and found that CO conversion was too low at 100 °C; in addition, they observed an increase in activity at higher temperatures [17]. It should be noted here that 165 °C was the split value calculated by the learning algorithm of the decision tree; it is not an exact physical limit. The same is true for the values of all the other parameters; hence, they should be treated as some empirical approximations.

The second decision point was the choice of the catalyst preparation method as ***deposition precipitation (DP)*** and the ***others***. It is well known that nano-sized Au particles are more active than larger particles and the deposition precipitation method is a very efficient method to prepare nano-sized Au particles well dispersed over the support [18]. High CO conversion was only possible with high Au contents if a method other than DP was used. This was also observed by Fu et al., who reported that the catalysts prepared by co-precipitation and urea gelation with 8 wt% Au resulted high CO conversion [19,20]. They concluded that gelation or co-precipitation techniques could be used to prepare a catalyst with large concentration of active sites strengthening the interaction of Au with ceria and resulting a high catalytic activity.

For the catalysts that were prepared by deposition–precipitation technique, another division was done according to the operation temperature (below or above 260 °C). If the temperature was below 260 °C, the desired efficiency was possible only if W/F is equal or higher than 4.5 $cm^3\ min^{-1}\ g^{-1}$ [21], otherwise time on stream, H_2O and CO concentrations in the stream became significant for achieving high efficiency. The ZrO_2 support increased the efficiency of the catalysts prepared by deposition–precipitation method for the mid-level temperatures (165–260 °C), which was also reported by Fonseca et al. [22] and Sakurai et al. [22,23].

The rules for high CO conversion (more than 75%) are summarized in Table 2. The shaded regions in the table show the conditions required for more than 75% conversion; the statements on the foremost left present the most general conditions while they become more specific with each step to the right. Although the tree can generate rules for any of the

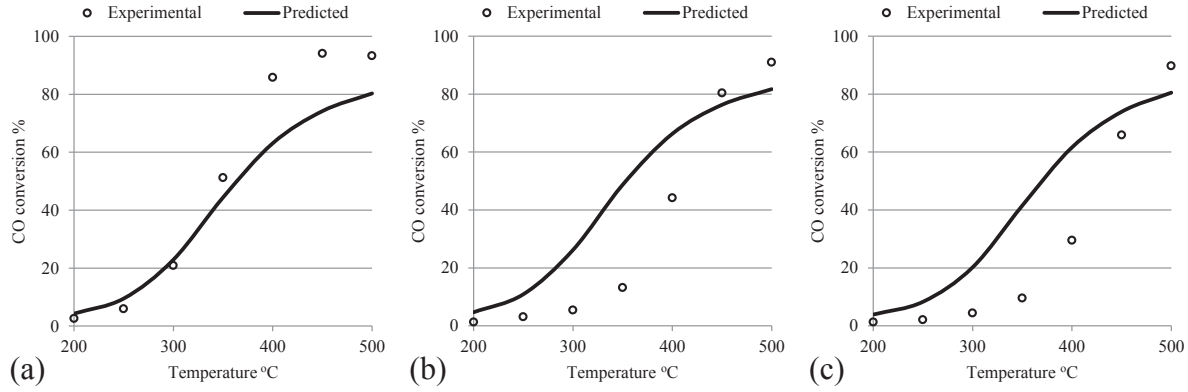

Fig. 6 – Experimental and ANN predicted CO conversion values at various temperatures over (a) Pt, (b) Rh and (c) Pd [30].

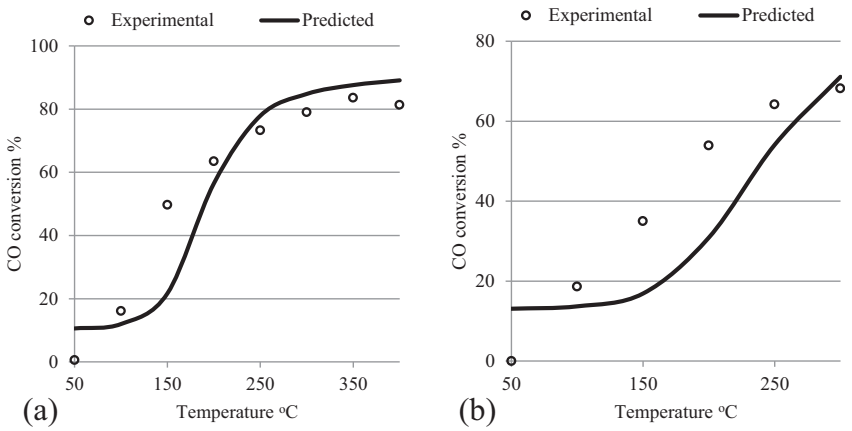

Fig. 7 – Experimental and ANN predicted CO conversion values at various temperatures over Au on various supports (a) TiO_2, (b) CeO_2 [21].

three classes, the rules leading to a CO conversion between 75 and 100%, which can be considered to be the desired outcome of the catalyst efficiency, are underlined here. It should be noted here again that the word ***rule*** does not imply any theoretical rule; instead, it describes the ***statement*** that explains the empirical patterns derived from the database.

The decision tree classifying the Pt based catalysts is given in Fig. 4 with the training and testing errors of 20.1% and 20.7%, respectively. The testing error was found to be slightly higher than the training error because of the same reason discussed for Au based catalysts; however, both error values can be considered as acceptable. Similar to Au catalysts, the first division was based on the reaction temperature leading to three temperature ranges. According to the tree, high CO conversion was not possible below 260 °C; for the mid-level temperatures (260–300 °C), only the presence of some oxygen (more than 0.6%) resulted high CO conversion as reported by Rosso et al., who achieved such CO conversions with inlet O_2 levels of 1 and 0.75% [24].

The decision tree analysis showed also that the CO conversion was more likely to occur at 300 °C or higher temperatures depending on W/F, Pt amount in the catalyst and CO_2 and CH_4 contents of the feed. For example, ifCO_2 concentration was lower than 5.7%, W/F ratio was higher than 0.2 $cm^3\ min^{-1}\ g^{-1}$ and TiO_2 was used as the support, then high CO conversion was achieved as reported by Panagiotopoulou and Kondarines [25–27] and Kalamaras et al. [28]. The same result could be obtained over the other supports (except Fe_2O_3) if H_2O in the feed stream was higher than 3.8%. For higher CO_2 concentrations, on the other hand, more specific conditions seem to be required such as the presence of CH_4, having or higher temperatures higher Pt contents. All these results are summarized in Table 3.

3.3. *Determining the importance and effects of input variables*

Various two hidden layer neural network topologies with 15 input variables introduced through 80 input neurons (as explained in Section 2.1) and 1 output variable (CO conversion) were created, and their accuracies of prediction were compared with each other by using their root mean square error (RMSE) of training and testing. The optimal neural network topology was found as 80-20-20-1 (containing 80 input neurons, 20 neurons in the first and 20 neurons in the second hidden layer, and 1 output variable). The plots of the experimental versus predicted CO conversions of training and testing for this network is shown in Fig. 5, which indicates considerable success with the training and testing R^2 values of 0.972 and 0.905 respectively.

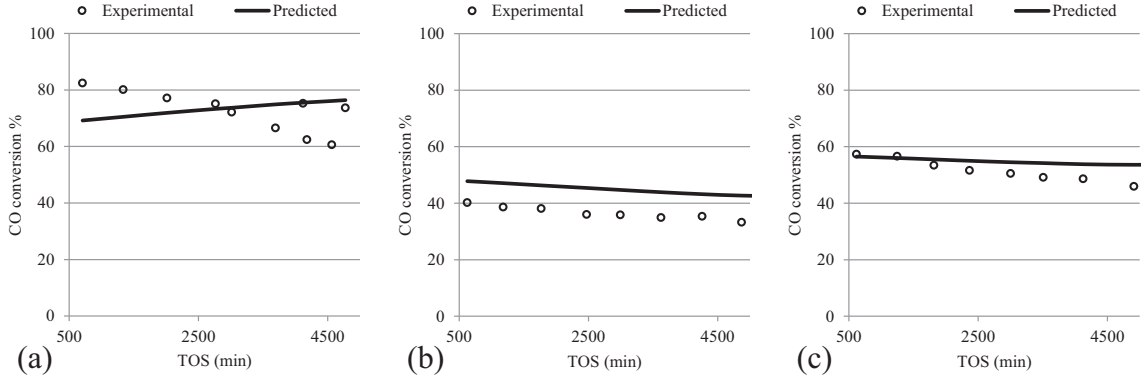

Fig. 8 – Experimental versus CO conversion values at various TOS values over (a) Au, %8, (b) Au, %4.7, (c) Au, %0.44 [20].

Table 5 – SVM classification of Au catalysts.

	RMSE	Correct %		RMSE	Correct %
Günes and Yildirim [31]	0.3132	94	Sandoval et al. [21]	0.3349	58
Luengnaruemitchai et al. [32]	0.3103	100	Thinon et al. [43]	0.3152	95
Kim and Thompson [33]	0.3282	60	Gamboa-Rosales et al. [44]	0.3148	86
Tabakova et al. [34]	0.3159	89	Wang et al. [45]	0.327	67
Andreeva et al. [35]	0.3141	89	Fu et al. [19]	0.353	45
Hurtado-Juan et al. [36]	0.3133	92	Venugopal and Scurrell [17]	0.3235	67
Zhang et al. [37]	0.3323	47	Jacobs et al. [46]	0.3136	91
Andreeva et al. [38]	0.3261	59	Idakiev et al. [47]	0.3103	100
Jacobs et al. [39]	0.322	67	Yuan et al. [48]	0.3333	33
Fu et al. [20]	0.3502	37	Yeung and Tsang [49]	0.3162	83
Tabakova et al. [40]	0.3236	80	Fonseca et al. [22]	0.3194	75
Jacobs et al. [41]	0.3103	100	Sakurai et al. [23]	0.3179	87
Idakiev et al. [42]	0.319	82			

Next, the relative importance of input variables were determined starting with the relative group significances of ***catalyst preparation*** and ***operational*** variables against each other by the "change of root mean square error", which is suitable for both categorical and continuous variables [29]. Then, the relative importance of each individual variable relative to the other variables in the same group was calculated using ***change of root mean square error*** for the catalyst preparation variables and ***partial differentiation of the trained network*** for the operational variables. Although the second method is more sensitive in general, it cannot be applied to the categorical variables such as most of the catalyst preparation variables; hence, the change of mean square error technique was applied for this group [29]. The details of both techniques are explained in Supplementary Material-2 while the results are summarized in Table 4. It should be noted that the relative significance values here indicate how the CO conversion is affected when that variable changes within its range in the database; hence, the results are rather empirical. For example, if a variable (say noble metal loading) is well optimized through years and not changed significantly through the database, the effect of this change, and therefore its relative significance will be small. Therefore, results in this section should be interpreted accordingly and used as some general guidelines pointing the variables that should be manipulated.

The results indicated that the overall relative significance of operational variables (65.0%) were much higher than that of preparation variables (35.0%); this makes sense considering that the reaction temperature, which was also the most influential operating variable, as well as the concentration of CO and H_2O ratio (and their ratio) were the most important factors affecting the CO conversion. The noble metal, promoter and the support were found to be the most influential catalyst preparation variables as expected.

The same ANN model was also tested if it could predict the change in conversion with changing a variable as reported in the literature. For this purpose, the results of three articles were selected as examples and their reported experimental CO conversions were tried to be predicted without actually doing those experiments; then, the accuracy of these predictions were analyzed. It should be noted here that the estimation of an experimental result of a publication was done by using only the data of the other articles (i.e. the data belonging these three papers were removed from the database during training).

Olympiou et al. (2007) [30] 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 Fig. 6, which indicates that as the temperature increases conversion also increases in all three catalysts. This trend was successfully predicted by the ANN model.

The effect of support type was studied by Sandoval et al. (2007) [21] who used Au catalyst with a fixed weight percentage (8%). Two different supports were employed (TiO_2 and CeO_2) and the change of CO conversion was observed with changing temperature. The predictions for these effects are presented in Fig. 7; they were again found to be quite satisfactory.

Finally, the effect of the weight percentage of noble metal type (Au) was studied by Fu et al. [20]; Au was used with the weight percentages of 8, 4.7 and 0.44 over ceria support. The

Table 6 – Confusion matrix for Au catalysts indicating predicted and experimental number of data points in each CO conversion level (bold numbers in the diagonal represent correct predictions).

		Predicted classes					
		0–50	50–60	60–70	70–80	80–90	90–100
Experimental classes	0–50	**312**	10	2	0	0	0
	50–60	11	**32**	14	0	0	0
	60–70	2	31	**20**	4	0	0
	70–80	0	4	22	**24**	12	0
	80–90	1	0	7	13	**56**	13
	90–100	0	0	1	2	46	**58**

Table 7 – SVM classification of Pt catalysts.

	RMSE	Correct %		RMSE	Correct %
Linganiso et al. [96]	0.3132	92	Jacobs et al. [41]	0.3199	73
Panagiotopoulou et al. [50]	0.3219	83	Radhakrishnan et al. [16]	0.314	90
Kam et al. [51]	0.3103	100	Caglayan and Aksoylu [73]	0.3153	88
Duarte de Farias et al. [52]	0.3179	78	Bi et al. [74]	0.3389	23
Zhu et al. [53]	0.314	89	Panagiotopoulou and Kondarines [75]	0.3113	97
Mendes et al. [54]	0.3191	75	Deshpande et al. [76]	0.3195	77
Kalamaras et al. [28]	0.3162	83	Vignatti et al. [77]	0.3221	70
Luengnaruemitchai et al. [32]	0.3113	97	Kim et al. [78]	0.3188	77
Jacobs et al. [46]	0.3103	100	Buitrago et al. [79]	0.3125	94
Azzam et al. [55]	0.314	90	Liu et al. [80]	0.3154	86
Duarte de Farias et al. [56]	0.3229	64	Liu et al. [81]	0.3118	96
Lim et al. [57]	0.3171	88			
Thinon et al. [43]	0.3151	87	Gallettiet al. [82]	0.3103	100
Gunay et al. [58]	0.3125	94	Gonzales et al. [83]	0.3139	90
Jeong et al. [59]	0.3103	100	Evin et al. [84]	0.3137	89
Jeong et al. [60]	0.3148	88	Fonseca et al. [22]	0.3103	100
Ribeiro et al. [61]	0.3132	92	Germani and Schuurman [85]	0.3189	75
Piermartini et al. [62]	0.3695	50	Sakurai et al. [23]	0.3162	83
Hwang et al. [63]	0.3183	78	Utaka et al. [86]	0.3103	100
Panagiotopoulou and Kondarides [27]	0.3122	95	Jacobs et al. [87]	0.3103	100
Zhai et al. [64]	0.3103	100	Jacobs et al. [88]	0.3103	100
Watanabe et al. [65]	0.3139	90	Panagiotopoulou and Kondarines [25]	0.3143	89
Deshpande et al. [66]	0.3156	85	Haryanto et al. [89]	0.318	75
Gonzalez et al. [67]	0.3139	90	Olympiou et al. [12]	0.3103	100
Yeung and Tsang [68]	0.3217	81	Panagiotopoulou and Kondarines [26]	0.3233	81
Hurtado-Juan et al. [35]	0.3103	100	Liang et al. [90]	0.3129	93
Evin et al. [69]	0.3216	86	Kim et al. [91]	0.3137	90
Duarte de Farias et al. [70]	0.3176	79	Gayen et al. [92]	0.3103	100
Chenu et al. [71]	0.3133	92	Tang et al. [93]	0.3103	100
Jacobs et al. [38]	0.3154	86	Vignatti et al. [94]	0.3103	100
Rosso et al. [23]	0.3219	67	Yeung and Tsang [48]	0.3103	100
Kugai et al. [72]	0.3103	100	Kugai et al. [95]	0.3103	100

conversion was observed in different time of stream values at 250 °C. The results of the article and the neural network predictions were found to be in good agreement as shown in Fig. 8.

3.4. *Predicting the outcome of unstudied conditions*

In this part, the possibility of using the optimal neural network topology proposed above for predicting the outcome of unstudied conditions was tested first. For this purpose, we separated the experimental data of one publication and retrained the network with the data from 83 out of the 84 publications, and then tried to predict the CO conversions reported in the article whose data had been excluded for testing. The procedure was repeated 84 times, and the predicted CO conversion values were compared with the experimental results reported in each publication.

First of all, 19 out of 84 publications contained unique variables; hence, these publications were left out of testing since it was impossible to estimate the results due of an unusual catalyst material. Then, it was found that the experimental results of 20 articles among the rest of 65 were predicted with R^2 values greater than 0.5 by using the data of the other publications as presented in Supplementary Material-2. Although this result has some statistical significance considering that all these works were performed by different people under different set of conditions (with lots of different variables and less frequently studied variable ranges) [13], it is not sufficient for practical purposes. Hence, we also tested the use of SVM technique to predict the results of the conditions that are not

Table 8 – Confusion matrix for Pt catalysts indicating predicted and experimental number of data points in each CO conversion level (bold numbers in the diagonal represent correct predictions).

		Predicted classes					
		0–50	50–60	60–70	70–80	80–90	90–100
Experimental classes	0–50	**1824**	31	45	0	0	0
	50–60	29	**165**	25	0	0	0
	60–70	1	80	**158**	14	0	0
	70–80	1	1	37	**178**	24	0
	80–90	0	0	8	39	**100**	16
	90–100	4	0	26	20	20	**259**

seen by the model. We started with the prediction option of WEKA software [15] using a procedure similar to ANN analysis; we constructed a SVM model (i.e. determining SVM parameters) using the data of 84 publications and tested the model with the experimental results of the remaining article. Unfortunately, the results were not satisfactory as well. Thus, we tried the classification option of SVM in the following manner: we defined more narrower ranges of classes in the higher CO conversion regions (six classes with conversion levels of 0–50, 50–60, 60–70, 70–80, 80–90 and 90–100%); this is equivalent to accept an about ±10–20% error in the higher conversion region. We also divided the dataset into three subsets in a way that the data from one publication can only be in one subset as we did in the decision tree analysis. Then, we used two subsets to train the SVM (i.e. to determine the SVM parameters) and used the remaining subset (not seen during training) for testing. This way, the classes of the experimental results of all the publications were predicted by using the data reported in the other articles. In other words, the SVM model was forced to classify the data not seen by the model before.

The SVM classification results of Au based catalysts are given in Table 5, where it is indicated that the experimental data of 15 out of 25 publications have correct classification rates higher than 75%, and only the data of 4 publications have correct classification rates below 50%. Besides, most of the time, the incorrectly classified data points were placed just to a neighboring class. For example, if a data point between 70 and 80% range is wrongly predicted, it is either predicted as it belongs to one of 60–70% or 80–90% classes; in other words, even the error in the incorrect predictions are mostly acceptable.

The confusion matrix, which gives the details of SVM prediction accuracy, is presented in Table 6 for all the data points over Au catalysts. For example, 58 of 107 data points in the range of 90–100% were predicted correctly while 46 of them were predicted as if they were in the 80–90% range. Only 3 data points were predicted less accurately.

The SVM prediction accuracy for the Pt based catalysts were more noteworthy (Table 7); the experimental data for a significant number of the publications were classified with 100% accuracy while the errors in most of the remaining articles were also insignificant; this is also evident from the confusion matrix indicated in Table 8. Higher accuracy in the case of Pt is probably due to the fact that this noble metal was studied more extensively; not only resulting more experimental data points but also accumulating more experience in selecting the experimental conditions and refining the range in the database.

It should be noted that the remarkable classification accuracies of both Au and Pt catalysts were obtained without feeding any piece of information from the publication to be tested to the SVM model; instead, the experimental data of the other articles were used to predict the outcome of the tested publication. These results indicate that SVM can indeed be used to predict the results of some specific conditions to at least some degree, and help to improve the efficiency of the experimental works.

4. Conclusions

In this communication, the experimental data for WGS over noble metal catalysts were collected from the publications in the literature dated from 2002 to 2012, and the data were analyzed using various data mining tools in order to demonstrate that valuable knowledge can be extracted from the past data. The analysis performed and the conclusions drawn can be summarized in three major areas:

(1) Most of the works in WGS (as any other catalytic system) aim to find the catalyst preparation and operational conditions for higher catalytic performance (CO conversion in this case), and any guidelines or rules to ease this will help the researchers significantly. Analysis of the past data using decision tree classification seems to be quite suitable for this purpose, giving empirical rules that lead to high catalytic performance.
(2) Again most of the WGS research involves changing the values of catalyst design and operational variables systematically to see their effects on performance; this does not only result in the best conditions but also helps to understand the catalytic phenomena better. ANN analysis was quite successful to determine the relative significance of input variables and their effects on CO conversion.
(3) The experimental domain is quite large for WGS reaction in noble metals due to the large number of variables; and any model to predict the unstudied conditions to some degree has a great value. Although artificial neural networks are quite suitable for this purpose, it did not produce satisfactory results for WGS reactions. SVM in classification mode, however, was quite successful to predicting the outcome of most of the articles within ±10% conversion range.

Then, it can be concluded that data mining tools can be indeed very beneficial to analyze the past data for WGS over noble metal catalysts as well as other similar systems with large number of publications in the literature.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2014.01.160.

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