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Keywords

Water-gas shift, Pd, Pt, Rh, Fe, FePd alloys, ceria

Comments

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The Activity of Fe-Pd Alloys for the Water-Gas Shift Reaction

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Abstract

The role of Fe promoters has been investigated on Pd/ceria, Pt/ceria and Rh/ceria catalysts for the water-gas shift (WGS) reaction in 25 Torr of CO and H₂O, under differential reaction conditions. While no enhancement was observed with Pt and Rh, the activity of Pd/ceria increased by as much as an order of magnitude upon the addition of an optimal amount of Fe. Similarly, the addition of 1 wt% Pd to an Fe₂O₃ catalyst increased the WGS rate at 453 K by a factor of 10 over that measured on Fe₂O₃ alone, while the addition of Pt or Rh to Fe₂O₃ had no effect on rates. The amount of Fe that was necessary to optimize the rates increased with Pd loading but was independent of the order in which Fe and Pd were added to the ceria. Increased WGS activity was also observed upon the addition of Fe to Pd supported on Ce_{0.5}Zr_{0.5}O₂. XRD measurements, performed after running the catalyst under WGS conditions, show the formation of a Fe-Pd alloy, even though similar measurements on an Fe/ceria catalyst showed that Fe₃O₄ was the stable phase for Fe in the absence of Pd. Possible implications of these results on the development of new WGS catalysts are discussed.

Keywords: Water-gas shift, Pd, Pt, Rh, Fe, FePd alloys, ceria.

Short Title: Fe-Pd Alloys for Water-Gas Shift

Introduction

There is a need for better water-gas shift (WGS) catalysts for the development of efficient fuel processors for fuel-cell applications [1,2]. Getting higher WGS activities is crucial because it would allow the reaction to be carried out at lower temperatures where the equilibrium concentration of CO, a serious poison for low-temperature fuel cells, is decreased. Materials that are typically used for the WGS reaction in large-scale operations, such as Cu/ZnO, are not applicable for many fuel-cell applications due to the fact that they are sensitive to start-up/shut-down cycles and may be pyrophoric [1,2]. Ceria-supported, precious-metal catalysts are one class of materials that have been identified as exhibiting very interesting properties for the WGS reaction with fuel cells [1-6]. The properties of ceria-supported precious metals are well known because of their application to automotive, emissions-control catalysis; however, the application of these materials to low-temperature WGS will require optimization in a very different manner.

While ceria-supported precious metals can exhibit higher rates than that obtained on commercially available Cu/ZnO catalysts under some conditions of interest for fuel-cell applications [1,4], even higher activities would be desirable to offset the cost of the precious metals. In recent work from our laboratory [7], the effect of a large number of promoters was investigated on Pd/ceria catalysts. The majority of these "promoters" (Tb, Gd, Y, Sn, Sm, Pr, Eu, Bi, and Cr) had minimal effect on the catalytic activity. A few others (V, Pb, and Mo) decreased WGS rates over Pd/ceria. However, rates on the Fe-promoted samples were found to be as much as 8 times higher than on unpromoted Pd/ceria at 473 K. Furthermore, there was an optimum Fe content that gave rise to the highest rates.

In the present study, we set out to investigate the reason for the enhancement in the WGS activity found on Pd/ceria. What we will show is that the enhanced activity associated with adding Fe₂O₃ to Pd/ceria is due to formation of a Fe-Pd alloy. The addition of Fe₂O₃ did not enhance rates on Pt/ceria or Rh/ceria, suggesting that there may be something unique about the Fe-Pd system. Interestingly, the stable form of Fe under WGS conditions in the absence of Pd is Fe₃O₄, suggesting that formation of the alloy provides a driving force for the reduction of Fe.

Experimental

The ceria used for all of the measurements in this study was synthesized by decomposition of Ce(NO₃)₃·6H₂O (Alfa Aesar, 99.5%) in air at 873 K. A ceria-zirconia, mixed oxide (Ce_{0.5}Zr_{0.5}O₂) was also prepared by mixing aqueous solutions of ZrO(NO₃)₂·xH₂O

(Aldrich) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, then drying the mixed solution at 383 K overnight, and finally calcining the dried powder in air at 873 K for 4 h. The Fe_2O_3 sample that was used as a support was prepared by decomposing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich, 99.99+%) in air at 873 K. For most experiments, Fe was added to the ceria or ceria-zirconia supports by aqueous impregnation with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After impregnation with the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, the samples were again dried at 383 K overnight and calcined in air at 873 K for 4 h. The BET surface areas for the supports used in this study are shown in Table 1, with the Fe loadings calculated as weight percent Fe_2O_3 .

The precious metals were also added to the oxide supports by wet impregnation using aqueous solutions of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ (Aldrich, 99.99%), $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Alfa Aesar, 99.99%), or $\text{Rh}(\text{NO}_3)_3$ (Alfa Aesar, 99.9%). Following impregnation of the precious metal salts, the catalysts were dried at 383 K and calcined at 873 K. To determine whether the order in which Pd and Fe were added to ceria was important, we prepared a sample with 1 wt% Pd and 2.2 wt% Fe_2O_3 in which $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ was added first, dried overnight, and, finally calcined in air at 873 K for 4 h before adding $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Still other catalysts was prepared by co-impregnation of Fe and Pd onto the ceria support, again using aqueous solutions of $\text{Fe}(\text{NO}_3)_3$ and $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ and similar drying and calcination procedures.

The WGS reaction rates were measured in a 1/4-inch, Pyrex, tubular reactor using 0.10 g of catalyst. Water was introduced by saturation of a He carrier gas flowing through a bubbler with de-ionized water. While the reactor pressure was always atmospheric, the partial pressures of CO, H_2O and He were controlled by adjusting the relative flow rates of each component. All of the reaction measurements in this study were collected with partial pressures for CO and H_2O of 25 torr. All the reaction rates were measured under differential conditions, with the conversions of CO and H_2O kept below 10%. To avoid potential transients associated with catalyst oxidation and reduction, we always allowed the reaction to run for at least 30 min before analyzing the products. To ensure that the results were reproducible, the rates at each point were measured at least three times. The concentration of the effluent from the reactor was determined using an on-line gas chromatograph, SRI8610C, equipped with a Hayesep Q column and a TCD detector.

Phase identification in the samples was performed via x-ray diffraction with a Rigaku X-ray diffractometer, using Ni-filtered, $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The diffraction measurements were performed in the range of $2\theta = 30^\circ - 50^\circ$ with a scanning speed of $2^\circ 2\theta/\text{min}$.

Results and Discussion

The first evidence that the addition of Fe to the ceria support must do more than simply modify the properties of the ceria support came from WGS rate measurements with various Fe:Pd ratios, with representative data for the Fe-impregnated ceria catalysts reported in Fig. 1 and Table 2. Fig. 1 shows Arrhenius plots for the WGS reaction, in 25 torr of both CO and H₂O, with results for catalysts with 1 wt% Pd shown in Fig. 1a) and results for catalysts with 2 wt% Pd shown in Fig. 1b). In order to maintain differential conversions, it was necessary to use a higher temperature range for the less active catalysts, so that the most active catalysts are those for which the data is on upper right of the plots. In agreement with the earlier study of Pd on Fe-doped ceria [7], the activities of the Pd catalysts prepared with Fe-doped ceria were higher than that with undoped ceria; and there is an optimal Fe content for maximizing the rates. However, the optimum Fe content was different for the two Pd loadings. For 1 wt% Pd, the maximum rates occur with 2.2 wt% Fe₂O₃; with 2-wt% Pd, the maximum rates occur at 4.3 wt% Fe₂O₃. In both of these catalyst, the Fe:Pd molar ratio is the same, approximately 3:1.

Table 2 summarizes the data in Fig. 1 by giving the rates and activation energies at 453 K for each of the catalysts. As might be expected, rates with 2-wt% Pd on pure ceria were approximately twice that of the rates on the 1 wt% catalysts. Pd/Fe₂O₃ showed rates that were comparable to Pd/ceria, but both of these catalysts were much less active than the catalysts containing all three components. In agreement with an earlier study [7], the activation energy of the Fe-containing catalysts was somewhat higher than that found on Pd/ceria. Finally, it should be noted that the activity of 2.2 wt% Fe₂O₃ on ceria, extrapolated to 453 K, is expected to be only 0.0012×10^{18} molecules/s·g, much lower than any of the Pd-containing catalysts.

The fact that there is a specific Fe-Pd stoichiometry associated with maximum WGS activity suggests that Fe-Pd compounds could be responsible for the increased activity. In this case, it would be expected that the order in which Pd and Fe are added to the catalyst should not matter. To explore this possibility, we prepared ceria-supported catalysts with 2.2 wt% Fe₂O₃ and 1 wt% Pd by co-impregnation of the Pd and Fe precursor salts and by impregnating Pd before Fe. The rate data for these three samples are listed in Table 3 and demonstrate that there is no significant difference between the three samples.

To determine whether Fe could also promote Pt and Rh catalysts, we investigated 1 wt% Pt and Rh catalysts on some of the same supports listed in Table 1, with the rates reported in

Table 4. At 453 K, the rates on Pt/ceria and Rh/ceria are essentially identical to that which we observed on undoped Pd/ceria, although the activation energies on the Pt and Rh catalysts were slightly higher. What is more striking about the rates in Table 4 is the fact that the addition of Fe had no measurable effect on the rates with Pt- and Rh-based catalysts. Table 5, which gives the WGS rates for each of the precious metals when supported on pure Fe_2O_3 , also demonstrates that enhanced rates only occur with Pd. The Fe_2O_3 -supported Pt and Rh catalysts showed rates that were indistinguishable from that over the Fe_2O_3 catalyst itself.

Since ceria-zirconia mixed oxides are usually found to be more active and stable than pure ceria, we measured reaction rates for 1 wt% Pd, Pt, and Rh on the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ support, both with and without the addition of Fe, with the results shown in Table 6. First, the rates for each of the precious metals on the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ support are very similar to the rates on pure ceria. Again, the addition of 2.9 wt% Fe_2O_3 led to a significant enhancement with the Pd catalyst, but there was essentially no change in rates upon the addition of Fe to the Pt and Rh catalysts.

To identify the phases responsible for the high activity in the Pd-Fe/ceria catalyst, we prepared the following catalysts: 6 wt% Pd on ceria; 13 wt% Fe_2O_3 on ceria; and 6 wt% Pd, 13 wt% Fe_2O_3 on ceria. Each sample was then exposed to the same WGS reaction conditions at 473 K for 2 h, then cooled in He to room temperature. Because initial experiments showed that the samples were re-oxidized when exposed to air at room temperature, we first passed 1-butene over the catalysts for 30 min at room temperature, before taking the samples out of the reactor, since the carbon-covered catalysts are not as susceptible to re-oxidation. Fig. 2 shows a comparison of XRD patterns on the three catalysts in the range of 30 to 50 degrees 2θ . The metallic Pd peak at 40.12 degrees 2θ was clearly observed for 6 wt% Pd/ceria. Based on the Scherrer analysis of the peak width at half height, we estimate the average Pd particle size to be approximately 7 nm, in reasonable agreement with a previous report showing the Pd particle size after the WGS reaction [8]. On the Fe_2O_3 /ceria sample, the peak at 36.85 degrees 2θ shows that Fe remains in an oxidized form, but as Fe_3O_4 . The 6 wt% Pd, 13 wt% Fe_2O_3 sample still shows the peak that we associate with Fe_3O_4 , but now the peak associated with Pd has shifted upward to near 41.22 degrees 2θ , which would be associated with the (111) plane of the alloy, FePd. The diffraction lines remain broad due to the small metal particle sizes, but there may also be particles with a range of compositions. Finally, it is noteworthy that others have also reported that Fe-Pd alloys can form when Pd is deposited onto supports containing Fe_2O_3 [9].

Our finding that Fe exists as Fe₃O₄ under WGS conditions agrees with previous work on Fe-based catalysts and with thermodynamic calculations of the expected phase for Fe under these conditions [10]. For the Fe-Pd alloy to form under the same conditions implies that formation of the alloy must provide an energetic driving force for reduction of Fe. The phase diagram for the Pd-Fe system shows two alloy phases, a FePd phase and a FePd₃ phase [11]. Since the maximum rates seem to occur in catalysts for which the Fe:Pd ratio is ~3, a large excess over the 1:1 ratio in FePd, and since Fe₃O₄ is observed together with the FePd phase under WGS conditions, there may be an equilibrium between Fe₃O₄ and FePd. This may explain why Pt and Rh catalysts are not affected in the same way as Pd catalysts. If alloys had formed with Pt and Rh, one should expect that the reaction rates on those catalysts would have been affected, either positively or negatively. While alloys of these metals with Fe do exist, there is evidence that they do not form as readily as FePd [12]. Finally, it is interesting to observe that Pd-Zn alloys also exhibit unique properties for steam reforming of methanol [13].

A thermodynamic driving force for reducing Fe₃O₄ could explain the enhanced WGS activity that is observed for these catalysts. In previous work from our laboratory [5], it has been proposed that the WGS reaction over ceria-supported precious metals proceeds through a redox mechanism, as shown below:



According to this picture, CO adsorbs on the precious-metal sites (σ) and the adsorbed CO is then oxidized with oxygen from the ceria; the reduced ceria is then re-oxidized by H₂O. If Fe, by its intimate contact with Pd, can enhance either the oxidation by water or reduction by CO, one should expect increased reaction rates for the alloy catalyst.

Independent of what mechanism is responsible for the rate enhancement upon formation of the Fe-Pd alloy, the results are intriguing in that they suggest that this and other alloys could prove to be interesting WGS catalysts. In addition to increasing reaction rates, alloy catalysts could exhibit increased stabilities and possibly allow decreased loadings of the precious metal. Certainly, the observation that Fe-Pd alloys show significantly higher reaction rates suggests that the combination of precious and base metals is an avenue worth exploring.

Conclusion

We have demonstrated that the enhanced WGS activity observed upon the addition of Fe to Pd/ceria catalysts is probably due to the formation of a Fe-Pd alloy. Under WGS conditions, Fe would normally exist as Fe_3O_4 , suggesting that formation of the alloy could provide a thermodynamic driving force for Fe reduction. Enhanced WGS activity was not observed upon the addition of Fe to either Pt or Rh catalysts, providing further evidence that specific interactions between Fe and Pd must be responsible for the higher rates observed in materials containing both elements.

Acknowledgement

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Table 1. BET surface areas of supports used in this study, after outgassing at 623 K.

Support	BET surface area m ² /g
CeO ₂	61
Ce _{0.5} Zr _{0.5} O ₂	84
Fe-ceria, 0.7 wt% Fe ₂ O ₃	64
Fe-ceria, 1.4 wt% Fe ₂ O ₃	64
Fe-ceria, 2.2 wt% Fe ₂ O ₃	60
Fe-ceria, 2.9 wt% Fe ₂ O ₃	54
Fe-ceria, 5.7 wt% Fe ₂ O ₃	43
Fe-ceria, 11.4 wt% Fe ₂ O ₃	41
Fe ₂ O ₃	12

Table 2. Differential Rates and Activation Energies for the Water-Gas-Shift Reaction on Fe Promoted, Pd/Ceria Catalysts

Catalyst		Rate at 453 K (x 10 ¹⁸ molecules/s g cat)	Activation Energy (kJ/mol)
1 wt% Pd	Pd/ceria	0.27	49
	Pd/Fe-ceria, 0.7 wt% Fe ₂ O ₃	0.84	52
	Pd/Fe-ceria, 1.4 wt% Fe ₂ O ₃	1.58	60
	Pd/Fe-ceria, 2.2 wt% Fe ₂ O ₃	2.42	67
	Pd/Fe-ceria, 2.9 wt% Fe ₂ O ₃	1.91	61
	Pd/Fe-ceria, 5.7 wt% Fe ₂ O ₃	1.21	57
	Pd/Fe ₂ O ₃	0.47	55
2 wt% Pd	Pd/ceria	0.61	43
	Pd/Fe-ceria, 0.7 wt% Fe ₂ O ₃	0.98	61
	Pd/Fe-ceria, 2.2 wt% Fe ₂ O ₃	2.52	60
	Pd/Fe-ceria, 4.3 wt% Fe ₂ O ₃	3.15	61
	Pd/Fe-ceria, 5.7 wt% Fe ₂ O ₃	1.95	60
	Pd/Fe-ceria, 11.4 wt% Fe ₂ O ₃	1.63	62
	Pd/Fe ₂ O ₃	0.29	47
Fe/ceria (Fe ₂ O ₃ : 2.2 wt%)		0.0012 ^a	80

a. The reaction rate was extrapolated from higher temperature data.

Table 3. The Effect of Preparation Conditions for Pd/Fe-Ceria

Catalyst	Rate at 453 K ($\times 10^{18}$ molecules/s·g cat)	Activation Energy (kJ/mol)
1wt%Pd/ceria	0.27	49
1wt%Pd/Fe-ceria ^a (2.2 wt% Fe ₂ O ₃)	2.42	67
Fe/1wt%Pd-ceria ^b (2.2 wt% Fe ₂ O ₃)	2.21	52
1wt%Pd-Fe/ceria ^c (2.2 wt% Fe ₂ O ₃)	2.89	59

- a. Fe₂O₃ was loaded onto ceria first, then Pd was loaded.
- b. Pd was loaded onto ceria first, then Fe₂O₃ was loaded.
- c. Pd and Fe₂O₃ were loaded onto ceria by co-impregnation.

Table 4. Differential Rates and Activation Energies for the Water-Gas-Shift Reaction on Fe-Modified Pt/ceria and Rh/ceria Catalysts

Catalyst		Rate at 453 K (x 10 ¹⁸ molecules/s·g cat)	Activation Energy (kJ/mol)
1 wt% Pt	Pt/ceria	0.24	61
	Pt/Fe-ceria, 0.7 wt% Fe ₂ O ₃	0.24	69
	Pt/Fe-ceria, 1.4 wt% Fe ₂ O ₃	0.28	73
	Pt/Fe-ceria, 2.2 wt% Fe ₂ O ₃	0.29	73
	Pt/Fe-ceria, 2.9 wt% Fe ₂ O ₃	0.25	66
	Pt/Fe-ceria, 5.7wt% Fe ₂ O ₃	0.27	71
1 wt% Rh	Rh/ceria	0.23	55
	Rh/Fe-ceria, 2.2 wt% Fe ₂ O ₃	0.23	57
	Rh/Fe-ceria, 2.9 wt% Fe ₂ O ₃	0.25	58
	Rh/Fe-ceria, 5.7 wt% Fe ₂ O ₃	0.23	58

Table 5. Differential Rates and Activation Energies for the Water-Gas-Shift Reaction for Pd, Pt, and Rh Supported on Fe₂O₃.

Catalyst ^a	Rate at 453 K (x 10 ¹⁸ molecules/s·g cat)	Activation Energy (kJ/mol)
Fe ₂ O ₃	0.04 ^b	58
Pd/ Fe ₂ O ₃	0.84	55
Pt/ Fe ₂ O ₃	0.09	70
Rh/ Fe ₂ O ₃	0.06	69

a. Pd, Pt and Rh loading were 1 wt%.

b. Rate was extrapolated from higher temperature data.

Table 6. Differential Rates and Activation Energies for the Water-Gas-Shift Reaction on Ce_{0.5}Zr_{0.5}O₂-Supported Pt, Pd, and Rh Catalysts

Catalyst ^a	Rate at 453 K (x 10 ¹⁸ molecules/s·g cat)	Activation Energy (kJ/mol)
Pd/Ce _{0.5} Zr _{0.5} O ₂	0.34	49
Pd/Fe-Ce _{0.5} Zr _{0.5} O ₂ (Fe ₂ O ₃ : 2.9 wt%)	1.97	58
Pt/Ce _{0.5} Zr _{0.5} O ₂	0.30	50
Pt/Fe-Ce _{0.5} Zr _{0.5} O ₂ (Fe ₂ O ₃ : 2.9 wt%)	0.26	47
Rh/Ce _{0.5} Zr _{0.5} O ₂	0.21	47
Rh/Fe-Ce _{0.5} Zr _{0.5} O ₂ (Fe ₂ O ₃ : 2.9 wt%)	0.19	55

a. Pd, Pt and Rh loading were 1 wt%.

Captions:

Fig.1 a) Differential rates for the WGS reaction on 1%Pd/ceria (■), 1%Pd/Fe/ceria (0.7 wt% Fe₂O₃)(▲), 1%Pd/Fe/ceria (1.4 wt% Fe₂O₃)(◆), 1%Pd/Fe/ceria (2.2 wt% Fe₂O₃) (●), 1%Pd/Fe/ceria (2.9 wt% Fe₂O₃) (○), 1%Pd/Fe/ceria (5.7 wt% Fe₂O₃)(□).

b) Differential rates for the WGS reaction on 2%Pd/ceria (■), 2%Pd/Fe/ceria (0.7 wt% Fe₂O₃) (▲), 2%Pd/Fe/ceria (2.2 wt% Fe₂O₃) (○), 2%Pd/Fe/ceria (4.3 wt% Fe₂O₃) (●), 2%Pd/Fe/ceria (5.7 wt% Fe₂O₃) (◆), 2%Pd/Fe/ceria (11.4 wt% Fe₂O₃) (□).

Fig. 2 XRD data for (a) 6%Pd/ceria, (b) Fe/ceria (13 wt% Fe₂O₃) and (c) 6%Pd-Fe/ceria (13 wt% Fe₂O₃). Samples were pretreated in the WGS condition at 473 K for 2 h. For Fe/ceria (13 wt% Fe₂O₃) and 6%Pd-Fe/ceria (13 wt% Fe₂O₃), after treatment under WGS conditions, cooling to room temperature, and then exposure to 1-butene to prevent sample reoxidation.

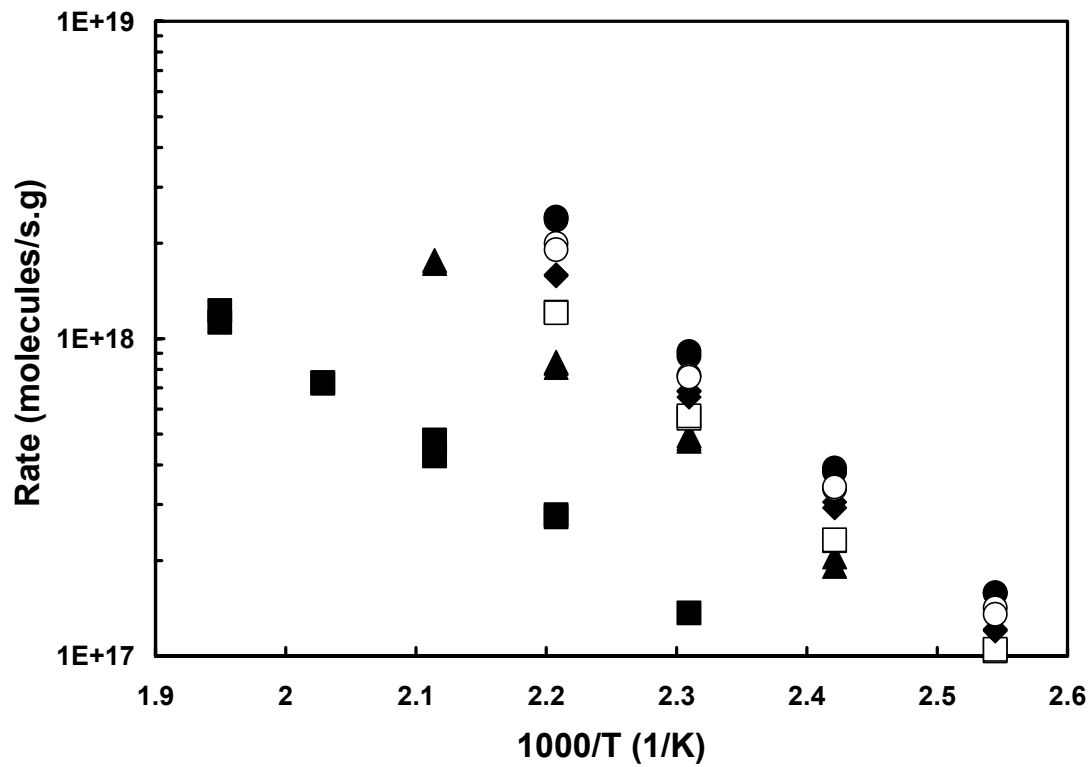


Fig.1a

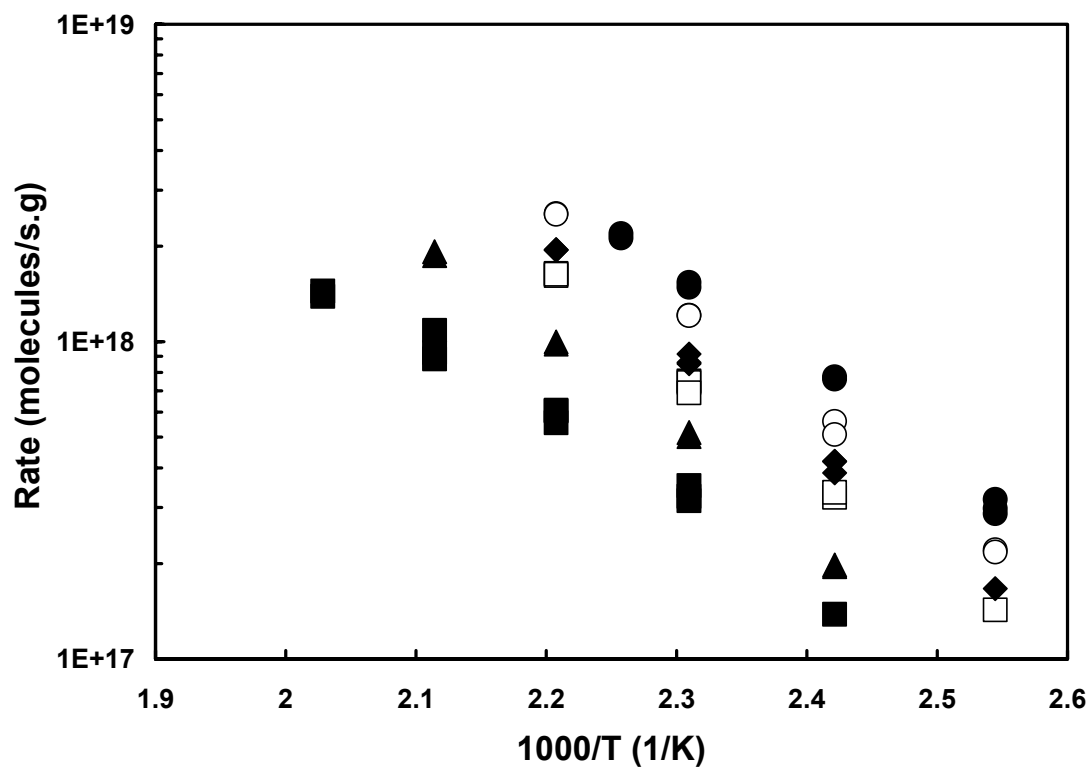


Fig.1b

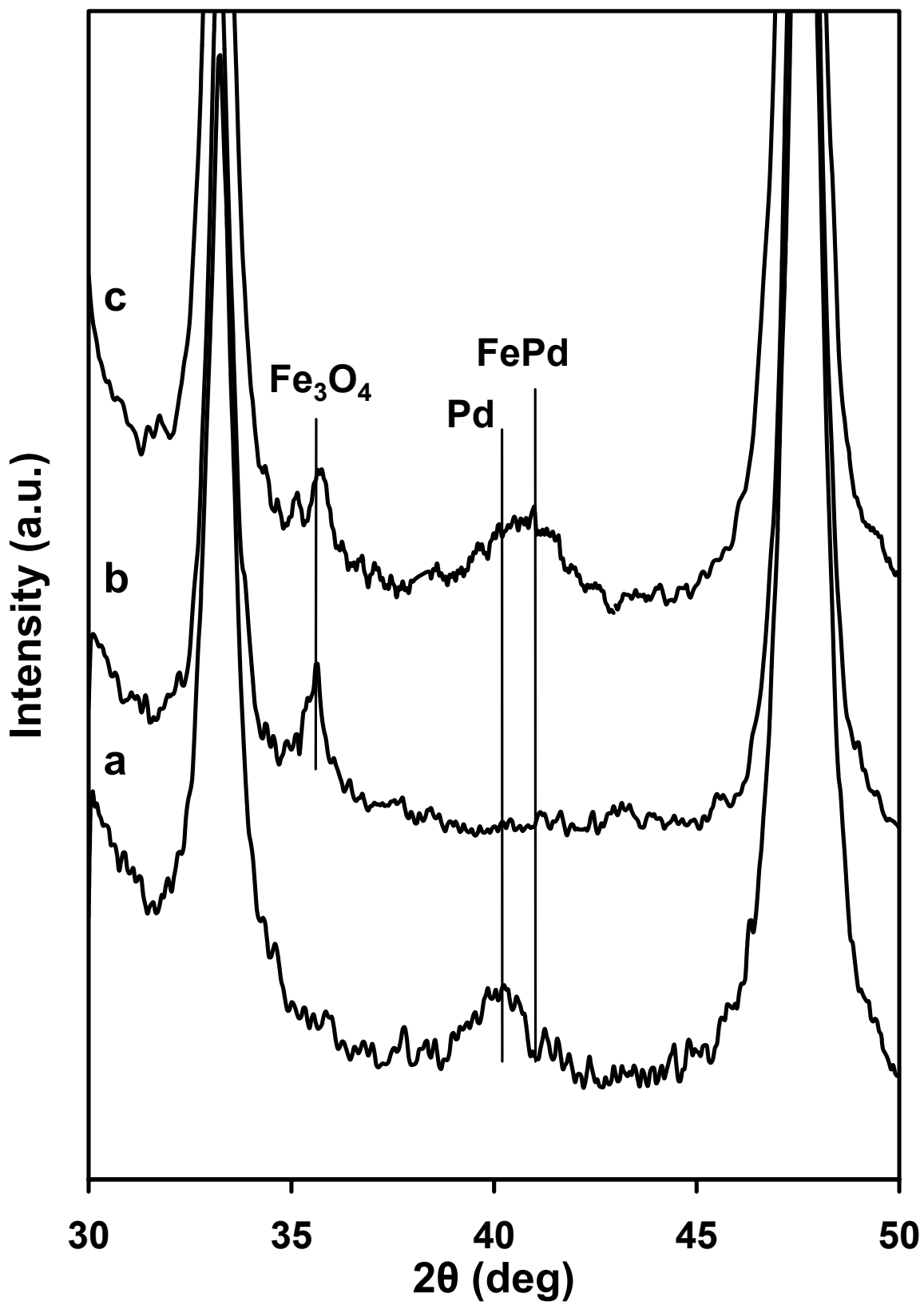


Fig.2