Thiophene hydrodesulfurization over noble metal modified Co-clay catalysts

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Abstract

This paper presents the effects of noble metal modification of Co-HPS (high porous saponite) on thiophene hydrodesulfurization. The modification was done by two different ways: (I) single noble metal and (II) bi-noble metal. The noble metal loading was varied from 0.1 to 2 wt.% of the catalyst. In catalyst preparation direct impregnation technique was used for the loading of noble metal and an ion-exchange was followed for Co loading on HPS. The catalysts were characterized by elemental analysis and temperature programmed reduction (TPR). Elemental analysis shows that the Co loading was slightly affected by noble metal modification. TPR study displayed that the reducibility of the catalysts was enhanced in presence of noble metal(s). Thiophene hydrodesulfurization activities were measured in a pulse micro reactor. The noble metal modified catalysts exhibited significantly higher activity as compared to the Co-HPS. Rh shows the highest activity among the three noble metals used for Co-HPS modification. The thiophene hydrodesulfurization activity was further enhanced by a bi-noble metal modification. The Pt-Rh combination shows better performance as compared to the Pd-Rh combination.
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1. Introduction

Hydrodesulfurization probably is the most important hydrotreating process in petroleum refining industry to produce the clean fuels. Recent trend of environmental regulation is becoming increasingly stringent with regards to sulfur content in fuels. Therefore, the demand for efficient hydrotreating process/catalysts becomes more evident. Due to the fact, the hydrotreating catalyst development research has been significantly increased for the last decade to obtain more effective and stable catalysts towards the production of sulfur-free fuels. Many of such recent works are devoted to develop new hydrodesulfurization catalysts to obtain more efficient sulfur removal than the conventional $CoMo/Al_2O_3$ catalysts [1].

The key objective in developing a successful catalyst is to achieve the targeted sulfur level under milder reaction conditions [2]. In conventional catalysts suitable transition metals from Group VIB (Mo or W) and/or VIII (Co or Ni) have been used as the active species supported on Al_2O_3 or zeolites [3], but the demand for more efficient catalyst is ahead to meet the further reduction (possibly to zero) of sulfur level in the coming years. Along with the conventional supports and active metals a number of different support materials and active metals are being explored to achieve the goal. Titina is one of the interesting support materials that has shown some unique performances in residual oil hydrotreating [4]. Silica is also found to be an alternative support, when Ni was deposited on it, the catalysts showed excellent activity and stability in thiophene hydrodesulfurization [5]. The clay minerals also are found to be interesting as a support for hydrotreating catalysts. Comparable (to commercial catalysts) hydrodesulfurization activity was found when Co and Ni pillared high surface area saponite clays were exposed to vacuum gas oil feed stock into a batch reactor [6]. Mesoporous smectite clays have been reported to be very promising for hydrodesulfurization catalysts [7]. Co containing smectite clay displayed high activity in hydrodesulfurization of thio-

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phene [8]. Recently, high porous saponite supported (HPS) Co catalyst reported to be very promising for both hydrocracking and hydrodesulfurization of vacuum gas oil [3].

In the present work, we also have explored the possibility of Co-clay catalysts modified with noble metals for the purpose of hydrodesulfurization. It has been reported that noble metal promoted Co-HPS demonstrated a significant increased activity in treatment of vacuum gas oil in a flow reactor [9]. The present authors also tested the noble metal modified Co-HPS catalysts in a batch autoclave reactor using vacuum gas oil (VGO) as feedstock. Both hydorcracking and hydrodesulfurizarion activities of Co-HPS were significantly increased when the catalysts were modified with a trace amount of Pt-Rh [10]. In this communication we will report the effects of modification of Co-HPS on thiophene hydrodesulfurization performances by single noble metals like Pt, Pd and Rh and their combinations such as Pt-Rh and Pd-Rh.

2. Experimental methods

2.1. Catalyst preparation

Before catalyst preparation the high porous saponite clay (received from Kunimine Kogyo Co. Ltd., Japan) was calcined at 600 °C for 4 h. For catalyst preparation, at first the support was modified by noble metal(s) by direct impregnation method using noble metal chloride aqueous solutions. Then it was dried at 120 °C followed by calcinations at 600 °C over night. The Co loading was done by ion-exchange technique, as described below.

$Co(NO_3)_2 \cdot 6H_2O$ solution was prepared and aged at 80 °C for 2 h. The modified HPS was added to the solution and the mixture was stirred at 80 °C for another 2 h. After cooling down to the room temperature the solution was filtered and washed with distilled water, followed by ethanol and then dried at 120 °C. Finally, the dried powder was calcined at 600 °C for 4 h and was pelletized for characterization and evaluation.

2.2. Catalyst characterization

2.2.1. Elemental analysis

The compositions of different metals loaded were measured by elemental analysis using a CHNS analyzer. The catalyst samples were dissolved into a suitable organic solvent (usually chloroform) in order to measure the metal content in the CHNS analyzer.

2.2.2. Temperature programmed reduction (TPR)

The TPR measurements were carried out in a system supplied by Ohkura Riken Co. Ltd, Japan (model TP-2000). During the TPR, the hydrogen concentration was measured by a thermal conductivity detector (TCD). A catalyst sample of 150 mg was used for all the measurements. Before start-

ing the TPR measurement the catalyst sample was degassed by flowing air at 400 °C for 2 h. The temperature was programmed to increase at a rate of 10 °C/min from room temperature to 1030 °C, and the H_2 consumption was recorded.

2.3. Thiophene hydrodesulfurization (HDS) activity measurements

The catalyst evaluation was c onducted in a pulse micro fixed bed reactor supplied by Ohkura Riken Co. Ltd., Japan. Prior to activity test, the catalyst (sample weight: 5 mg) was sulfided in situ with a mixed gas flow (60 ml/min) of 5% hydrogen sulfide in 95% hydrogen at 400 °C for 2 h. After sulfiding, the gas was switched to the reaction conditions, i.e. H_2 at 60 ml/min and specified temperature. Thiophene was injected (0.3 ml) after the reactor reached at steady state condition. The products confirmed by the GC peak were more than 99%. Finally, the HDS activity was determined using the area under the peak of the chromatogram.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Elemental analysis

For bifunction catalysts like HDS and hydorcracking catalysts it is very important to balance the acidity of the support and the amount of metal loading on the catalyst in order to obtain the optimum performance. The element analysis was carried out to have a clear knowledge about the composition of different metals in the fresh catalysts; in particular, the effects of the noble metal on the loading of Co, which is the main active component of the catalyst. Table 1 lists the elemental analysis of unpromoted and noble metal promoted Co-HPS catalysts. It is noticed that the Co loading was slightly varied in presence of the noble metal and the maximum loading (18. 5 wt.%) was occurred on unpromoted

Table 1
Elemental analysis of fresh catalysts

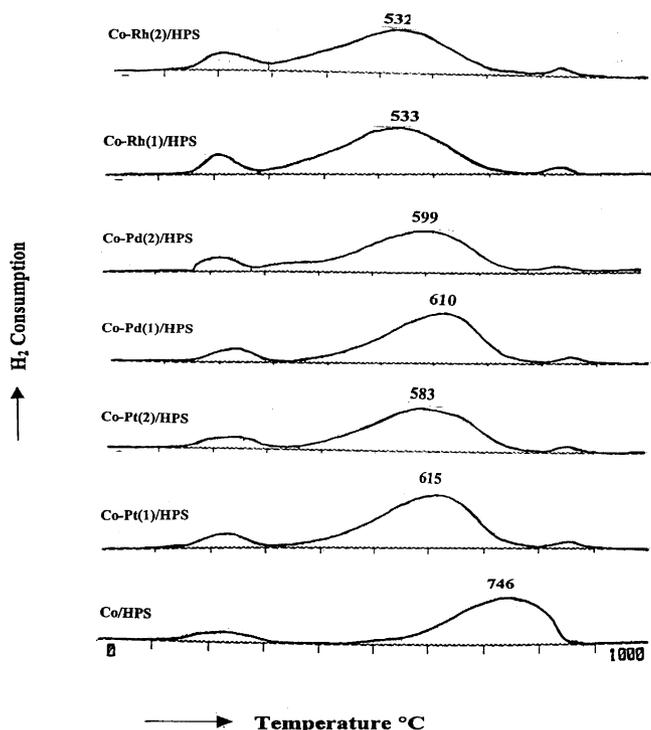| Catalyst description	Metal loaded (wt.%)			
	Co	Pt	Rh	Pd
Co/HPS	18.5	–	–	–
Co-Pt(2)/HPS	15.0	2.0	–	–
Co-Pt(1)/HPS	17.5	1.0	–	–
Co-Rh(2)/HPS	16.2	–	2.0	–
Co-Rh(1)/HPS	18.3	–	1.0	–
Co-Pd(2)/HPS	17.1	–	–	2.0
Co-Pd(1)/HPS	18.3	–	–	1.0
Co-Pt(1)-Rh(0.1)/HPS	18.4	1.0	0.1	–
Co-Pt(1)-Rh(0.2)/HPS	16.4	1.0	0.2	–
Co-Pt(1)-Rh(0.8)/HPS	16.2	1.0	0.8	–
Co-Pd(1)-Rh(0.2)/HPS	18.4	–	0.2	1.0
Co-Pd(1)-Rh(0.5)/HPS	16.6	–	0.5	1.0
Co-Pd(1)-Rh(0.8)/HPS	16.5	–	0.8	1.0

Fig. 1. TPR spectra of unpromoted and noble metal promoted Co/HPS.

Co-HPS. This variation is probably due to the occupation of ion-exchange sites (mainly Na and Mg) on HPS by the noble metals. However, no further attempt was taken to find a relation between the degrees of variation of Co loading on noble metal variation since it was out of scope of the present work.

3.1.2. Temperature programmed reduction

It is well known that the metals are present on the catalysts in their oxide forms and they need to be reduced to their metallic/sulfide state before putting into the reaction since they are more active in metallic/sulfide form. A TPR measurement can provide information about the reducibility of the metal species in the catalysts. Fig. 1 shows the TPR profile of Co-HPS and single noble metal promoted Co-HPS catalysts. For Co-HPS two major peaks were observed at 226 and 746 °C, respectively. The first peak at 226 °C was assumed to be the easily reducible large particles of cobalt oxide (species I), and the second peak at 746 °C was highly dispersed cobalt oxide phase (species II) [11]. Upon noble metal modification the TPR profiles remained almost unchanged; only a significant amount of shift of the second peak was observed. A very tiny third peak also noticed was possibly the remaining portion of the second peak of Co-HPS. The shift of the second peak was in the range of 103–215 °C, which was attributed to the noble metal effects on cobalt oxide reduction. This promotional effect has been reported in three possible ways [12]: (I) lowering the activation energy of the rate-determining step of the Co oxide reduction, (II) direct increasing of the number of nucleation sites for reduction and (III) the so-called hydrogen

spillover effects, which provided enough reactive hydrogen to reduce the Co oxide species at lower temperature. It has been claimed that the shifting of the reduction temperature can also happen in the following way: the noble metal aids the initiation of the reduction of Co oxides. The noble metals can dissociate molecular hydrogen to reactive hydrogen at comparatively lower temperature and such reactive hydrogen can easily attack the cobalt oxides and reduce them at lower temperature [10].

In the case of Pt and Pd promoted Co-HPS the peak temperatures were quite similar and they were found to be around 600 °C, which was shifted by 150 °C from unpromoted catalyst. On the other hand Rh shows more pronounced effects by shifting the peak by 220 °C. This reveals that Rh has higher strength to reduce the Co-HPS catalysts than Pt/Pd. Another important observation was the incremental effects of noble metal loading. With increasing Rh loading from 1 to 2 wt.% the peak did not shift further towards the left, while in the case of Pt and Pd it was slightly shifted. Therefore, it might be concluded that the catalysts already reached the optimum promotional effects by 1 wt.% noble metal loading.

Based on the results of single noble metal effects, the next attempt was to employ the bi-noble metal on Co-HPS. As it was observed earlier that Rh has shown best promotional effects, but its price is almost two times higher than that of Pt/Pd. Therefore, the goal was set in such a way to achieve the similar effects as with Rh by Pt-Rh and Pd-Rh combinations using a very small amount of Rh. In this context the Pt/Pd loading was kept constant at 1 wt.%, while Rh was varied from 0.1 to 0.8 wt.%. TPR profiles of such catalysts are presented in Figs. 2 and 3. Here, less amount of Rh (∼0.1 wt.%) with 1 wt.% Pt/Pd caused almost the similar shifting of the second peak to lower the temperature at 1 wt.% Rh did individually. With increasing the Rh loading the peak temperature was further shifted towards lower, however, after 0.2 wt.% Rh loading the peak was not shifted significantly. So, it seems that this is possibly the maximum promotional effect by Rh that can be achieved with the present preparation method of the catalysts. The bi-noble metal effects can be explained reasonably as follows: Pt/Pd reduces more easily in presence of Rh and the reduced Pt/Pd thus plays in more dissociation of hydrogen towards the cobalt oxides and consequently reduces them at lower temperature [13].

The amount of hydrogen uptake by each peak of different catalyst was also measured and has been described elsewhere in detail [10]. From those measurements, it was revealed that the amount of cobalt oxide species reduction was not significantly influenced by the noble metals. Their presence only caused a shift in shifting the reduction temperature.

3.2. Catalyst evaluation

Table 2 shows the thiophene hydrodesulfurization activity of plain and noble metal promoted Co/HPS catalysts at
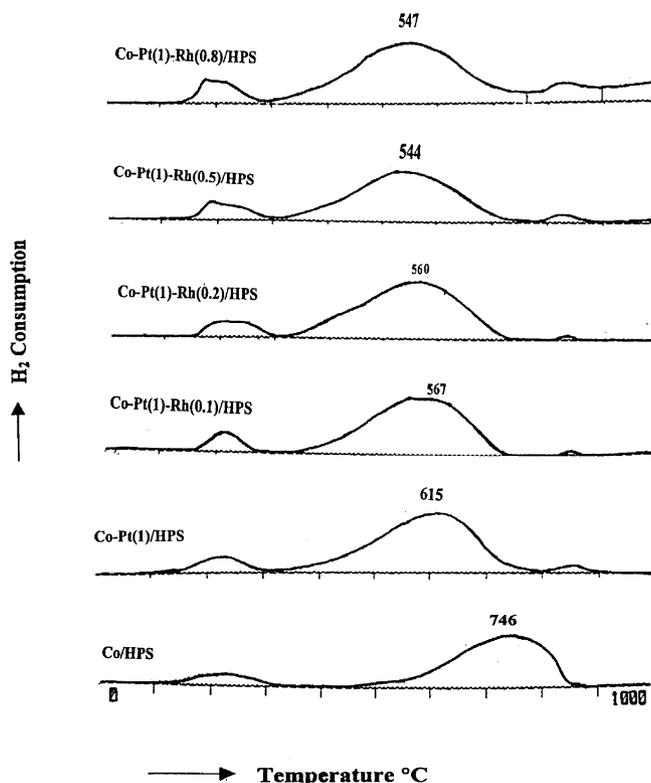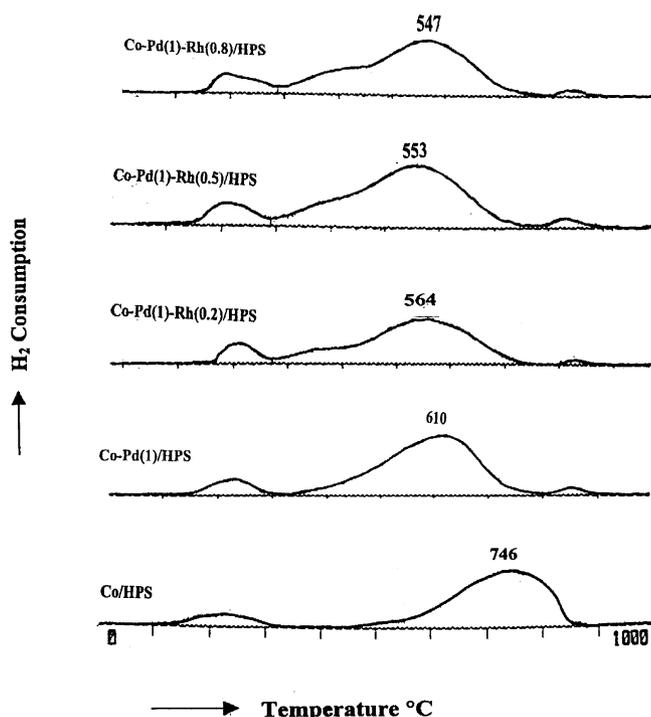
Fig. 2. TPR profile of Pt-Rh modified Co/HPS.

Table 2
HDS activity of commercial Co-Mo/Al$_2$O$_3$, plain and noble metal modified Co/HPS catalysts

Catalyst description	Thiophene conversion (wt.%)		
	250 °C	275 °C	300 °C
Co-Mo/Al$_2$O$_3$	59.1	68	80.5
Co/HPS	58	70	85
Co-Pt(2)/HPS	59.7	71	78.7
Co-Pt(1)/HPS	63	72	84
Co-Rh(2)/HPS	61	81	83
Co-Rh(1)/HPS	74.3	80.9	89.1
Co-Pd(2)/HPS	49.2	61.75	71.7
Co-Pd(1)/HPS	61	69	80.1
Co-Pt(1)-Rh(0.1)/HPS	68.8	75.8	84.4
Co-Pt(1)-Rh(0.2)/HPS	68.5	74.5	85.5
Co-Pt(1)-Rh(0.8)/HPS	75.1	78.3	82.7
Co-Pd(1)-Rh(0.2)/HPS	61.2	70.8	84.5
Co-Pd(1)-Rh(0.5)/HPS	61.8	73	86
Co-Pd(1)-Rh(0.8)/HPS	60.8	72.7	85.8

port was to discuss the effect of noble metal(s) on thiophene HDS activity of Co-HPS catalysts, the commercial catalyst was not included in the subsequent discussion.

From elemental analysis, it was observed that the cobalt (the main active species) loading was slightly varied in presence of noble metals. Therefore, to eliminate the effects of this variation on HDS activity, the "activity index" as defined below, was used in place of activity.

$$\text{Activity index} = \frac{\text{conversion}}{\text{atom Co}}\%$$

and this term will be used in discussion of the following sections.

Figs. 4 and 5 display the HDS activity indexes of plain and noble metal promoted Co/HPS catalysts. The HDS activity indexes of noble metal modified catalysts were shown to be significantly higher than that of unpromoted Co-HPS. The higher activities of those catalysts are attributed to the noble metal effects, which was expected and is consistent with

three levels of reaction temperatures (250, 275 and 300 °C). For comparison, activity data of a commercial CoMo/Al$_2$O$_3$ catalyst evaluated under same reaction conditions also included in the same table. Since the main purpose of this re-

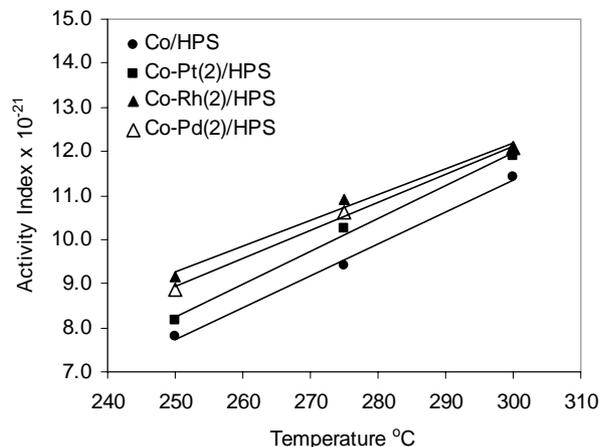Fig. 3. TPR profile of Pd-Rh modified Co/HPS.

Fig. 4. HDS activity of Pt/Rh/Pd modified (by 2 wt.%) and unmodified Co/HPS.
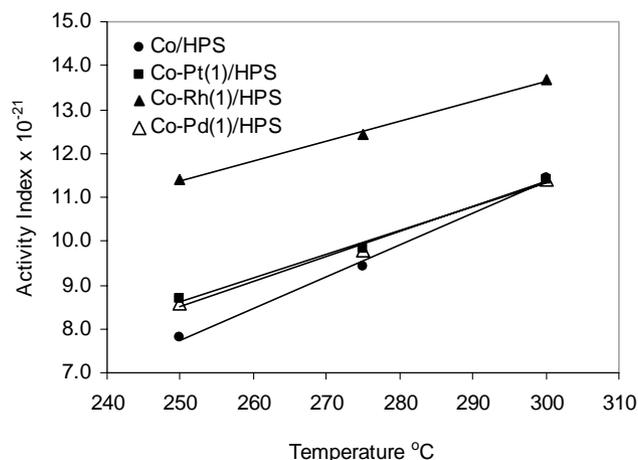
Fig. 5. HDS activity of Pt/Rh/Pd modified (by 1 wt.%) and unmodified Co/HPS.

Fig. 6. HDS activity of Pt-Rh promoted and unprompted Co/HPS at 1 wt.% Pt loading.

the TPR results of those catalysts [14,15]. Here, the noble metals play the role of sources of supplying reactive hydrogen to the Co sites where the hydrogenation reaction takes place [10,16]. It is noticed (Figs. 4 and 5) that the activity indexes of both Pt and Pd promoted catalysts were almost similar and it did not change with increasing (2 wt.%) the loading of both metals. This was also expected from the TPR studies of those catalysts where the reduction peak was not further shifted towards the lower temperature by addition of more noble metals. Contrary to Pt/Pd, the Rh modified catalysts have shown less activity in 2 wt.% Rh loaded catalyst than 1 wt.% Rh loaded one. This was an unexpected observation according to the TPR measurement because in TPR both catalysts have given the peak about 530 °C. This result indicates that the excess amount of noble metal might also affect the HPS support where the acidic sites are located, which are responsible for the initiation reaction by opening the ring to remove S atom from thiophene. However, this result was not confirmed by other measurements.

After observing the higher activity with comparatively less amount of Rh, the next two series of catalysts were prepared and evaluated by using Pt-Rh and Pd-Rh combinations. The activity indexes of those catalysts are presented in Figs. 6 and 7. In both series, the activity indexes of bi-noble metal promoted catalysts are significantly higher than that of the unpromoted Co-HPS. Figs. 8 and 9 plot the effects of Rh loading on HDS activity index at constant (1 wt.%) Pt and Pd loading, respectively. It is interesting to notice that a trace amount of Rh (0.1–0.2 wt.%) increased the HDS activity significantly but after that no considerable increments were observed with further addition of the Rh. This observation matched with the TPR data of the same catalysts where cobalt oxide reduction peak was not further decreased to the lower temperature with addition of more Rh. Another interesting observation was the higher promotional activity of Pt-Rh catalysts than Pd-Rh combination. For all combinations Pt-Rh showed superior activity than its Pd-Rh counterpart. This result is similar to that reported by Sugioka et al.
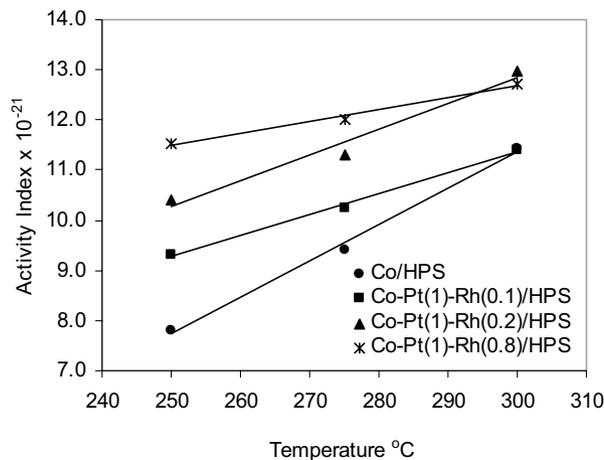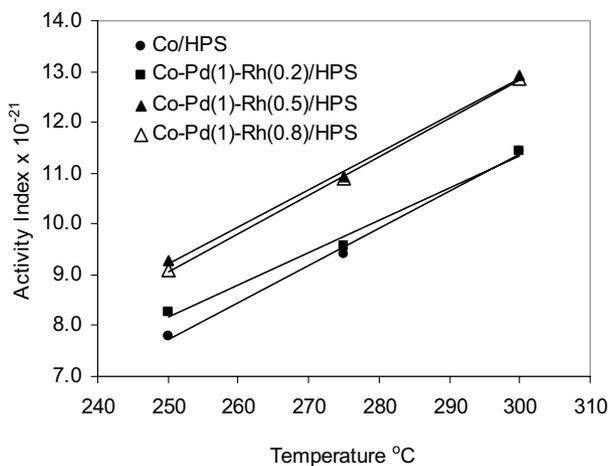

Fig. 7. HDS activity of Pd-Rh promoted and unprompted Co/HPS at 1 wt.% Pd loading.
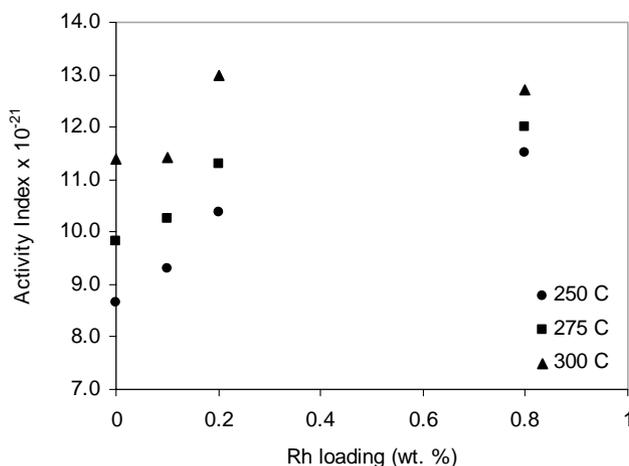

Fig. 8. Effects of Rh loading on HDS activity of Pt-Rh promoted Co/HPS at 1 wt.% Pt loading.
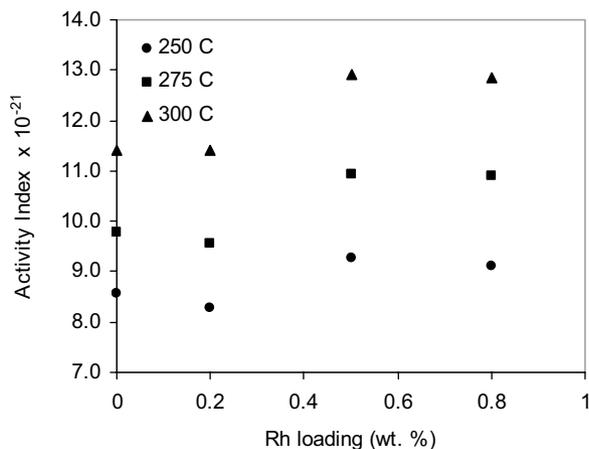
Fig. 9. Effects of Rh loading on HDS activity of Pd-Rh promoted Co/HPS at 1 wt.% Pd loading.
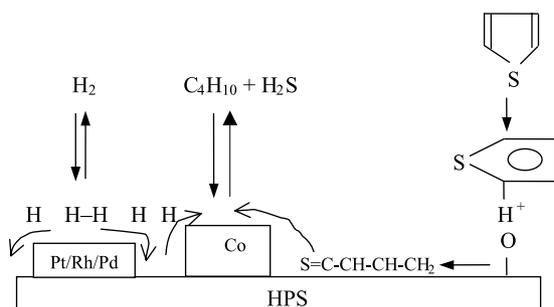

Fig. 10. The possible mechanism of thiophene hydrodesulfurization on noble metal modified Co/HPS.

[14,15] for thiophene HDS on USY zeolite supported Pt and Pd catalysts. By XRD analysis they confirmed that the dispersion of Pt on the support was comparatively higher than that in the case of Pd and which might be the reason of the less activity of Pd catalysts.

Hydrogen sulfide and *n*-butane were the products observed during the thiophene hydrodesulfurization under the given reaction conditions. This is a significant observation from the practical point of view that the saturated C_4 (*n*-butane) was the only product in all catalysts regardless of the noble metal promoted and unpromoted Co-HPS, which indicates a superior hydrogenation activity of the catalysts [8]. Also, the catalyst did not produce the deep cracked lighter hydrocarbon products.

On the basis of the above results and discussion, a possible mechanism of hydrodesulfurization of thiopnene on noble metal modified Co-HPS catalysts is shown in Fig. 10. In this mechanism, thiophene is adsorbed and cracked on acidic HPS and gas phase hydrogen adsorbed and dissociated on the noble metal sites. Finally, the cracked hydrocarbon intermediate and sulfur react with the reactive hydrogen specie on Co sites. Hence the catalyst displayed more efficient HDS activity.

4. Conclusion

The addition of noble metal(s) affects the Co loading on high porous saponite. The reducibility of Co-HPS was significantly enhanced with modification of catalysts by noble metals. Pulse reactor evaluation revealed that all the Pt, Pd and Rh modified catalysts showed higher thiophene hydrodesulfurization and Rh showed the best activity among them. The bi-noble metal promoted catalysts also have shown some interesting results, a trace amount of Rh is sufficient to modify activity of Co-HPS HDS activity. Among the Pt-Rh and Pd-Rh catalysts the first combination displayed its superiority as compared to the second combination. Therefore, this study revealed the possibility that noble metal modified Co-HPS is very promising for selective thiophene hydrodesulfurization purposes.

Acknowledgements

References

[1] R. Prins, V.H.J. de Beer, G.A. Somorjai, Catal. Rev. Sci. Eng. 31 (1989) 1.
[2] E. Lecrenay, K. Sakanishi, T. Nagamatsu, I. Mochida, T. Suzuka, Appl. Catal. B. 18 (1998) 325.
[3] T. Kimura, K. Al-Nawad, S.A. Ali, Y. Suzuki, H. Hamid, T. Inui, in: Proceedings of the 220th ACS National Meeting, Washington, August 20–24, 2000.
[4] E. Lecrenay, K. Sakanishi, I. Mochida, Catal. Today 39 (1997) 13.
[5] S.J. Sawhill, D.C. Phillips, M.E. Bussel, J. Catal. 215 (2003) 208.
[6] S.A. Ali, M.E. Biswas, T. Yoneda, T. Miura, S.H. Hamid, E. Iwamatsu, H. Al-Suaibi, Sci. Technol. Catal. 127 (1998) 407.
[7] E. Hayashi, E. Iwamatsu, M.E. Biswas, Y. Sanada, S. Ahmed, S.H. Hamid, T. Yoneda, Appl. Catal. 179 (1999) 203.
[8] M. Arai, Y. Minato, K. Torii, M. Shiraj, Catal. Lett. 61 (1999) 83.
[9] M.A. Ali, T. Kimura, Y. Suzuki, M.A. Saleh, H. Hamaid, T. Inui, Appl. Catal. 227 (2002) 63.
[10] M.A. Al Saleh, M.M. Hossain, M. Shalabi, T. Kimura, T. Inui, Appl. Catal. 253 (2003) 453.
[11] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, J. Catal. 156 (1995) 85.
[12] N.W. Hurst, S.J. Gentry, A. Jones, Catal. Rev. Sci. Eng. 24 (2) (1982) 233.
[13] T. Inui, Stud. Surf. Sci. Catal. 77 (1993) 131.
[14] M. Sugioka, F. Sado, T. Kurosaka, X. Wang, Catal. Today 45 (1998) 327.
[15] M. Sugioka, F. Sado, Y. Matsumoto, N. Maesaki, Catal. Today 29 (1996) 225.
[16] K. Fujimoto, in: B. Delmon, G.F. Froment, P. Grange (Eds.), Hydrotreatment and Hydrocracking of Oil Fraction, Elsevier, Amsterdam, 1999.