

Pd–Rh promoted Co/HPS catalysts for heavy oil upgrading

M.M. Hossain^{a,*}, M.A. Al-Saleh^b, M.A. Shalabi^b, T. Kimura^c, T. Inui^c

^aCREC, Chemical and Biochemical Engineering Department, University of Western Ontario, London, Ont., Canada N6A 5B9

^bCRP, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

^cJapan Petroleum Energy Center, Kanagawa, Japan

Received 21 June 2004; received in revised form 17 September 2004; accepted 18 September 2004

Abstract

This paper reports the promotional effects of Pd and Rh on hydrocracking (HC) and hydrodesulfurization (HDS) activity of Co/HPS catalyst. The catalysts were prepared by loading of noble metal followed by cobalt on the high porous saponite (HPS) support. The incipient impregnation technique was adapted for the loading of noble metal(s) while an ion exchange method was followed for cobalt loading on HPS. The catalysts were characterized by temperature-programmed reduction (TPR). Results showed that the reducibility of the catalysts was significantly improved in presence of the noble metals (Pd, Rh). The activity of the catalysts was tested in a batch autoclave reactor using vacuum gas oil as feedstock. Both the HC and HDS activity of noble metal-promoted Co/HPS catalysts were found to be higher than that of plain Co/HPS catalysts. Rh displayed higher promotional effects as compared to Pd in both HC and HDS purpose. This higher activity is consistent with the TPR results, which showed superior reducibility of Rh promoted catalysts. The most interesting part of this study pertained the effects of bi-noble (Pd–Rh) metal on Co/HPS. A trace amount of Rh along with Pd exhibited a significant enhancement of the catalytic activity of Co/HPS, which was comparable to what Rh alone did with a higher amount. The coke deposition on Pd–Rh promoted catalyst was also found lower than that of the plain and single noble metal promoted Co/HPS.

© 2004 Elsevier B.V. All rights reserved.

Keywords: HPS; Noble metal; Co; Pd; Rh; Heavy oil; HDS; HC

1. Introduction

The ever increasing demand for lighter engine fuel and higher price of light crude oil have stimulated the petroleum refining industry into looking for the possibility of processing heavy residues as well as the comparatively cheaper heavy crude oils. The main problem associated with the processing of residue/heavy oil is their high organic sulfur and nitrogen content, and the presence of other undesirable compounds, which must be removed before further processing due to their toxicity and environmental impact. In addition, current trends in environmental regulation are becoming increasingly stringent with regards to sulfur content in fuels. Therefore, to meet the growing

demand for lighter and cleaner fuel the need for more efficient hydrotreating process/catalysts becomes more evident. The after mentioned facts have spurred hydrotreating catalyst research into pursuing a more effective and stable catalyst for the production of sulfur free light fuels [1].

The key objective in developing a successful catalyst is to achieve maximum catalytic activity under milder reaction conditions. Conventionally, heavy oil upgrading catalysts applied in industry are derived from oxides of an element belonging to Group VIB (Mo or W) or Group VIII (Ni or Co) supported on alumina [1,2]. It is believed that in commercial Co–Mo/Al₂O₃ catalyst Co acts as promoter while Mo acts as the main active component for the catalyst activity. However, Co supported on alumina/carbon has also shown high HDS activity [2]. Some recent studies also suggested similar potentiality of Co as main active metal.

Ali et al. displayed high HC and HDS activity of Co-pillared high surface area saponite catalysts in a batch

* Corresponding author. Tel.: +1 519 661 211188357; fax: +1 519 661 3498.

E-mail address: mhossai4@uwo.ca (M.M. Hossain).

autoclave reactor using vacuum gas oil as feedstock [3]. Aoki and co-workers showed that mesoporous smectite-like materials containing cobalt can exhibit high activity of thiophene hydrodesulfurization [4]. Arai et al. also reported similar results in a supported Co-smectite clay catalysts [5]. In all the above papers, Co was used as active component instead of Mo, and clay (saponite, smectite, etc.) was used as support in place of alumina. The smectite clay materials such as high porous saponite (HPS), saponite, hectorite, stevensite have not been extensively investigated as support for heavy oil upgrading catalysts despite their high surface area and favorable pore structure. Recently, Kimura and co-authors reported highly active Co/HPS catalyst [6]. The catalyst was tested in a batch autoclave reactor using vacuum gas oil as feedstock. However, the coke formation on such catalysts was also reported to be high. Therefore, the enhancement of the catalyst stability was left as a challenge for the success of such catalyst. For decades, noble metals have been considered to hold promise minimizing coke deposition on hydroprocessing catalysts. On the other hand, highly efficient modern bi-metallic naphtha reforming catalysts owe their success to noble metal promotion [7]. The success of bi-metallic naphtha reforming catalyst has encouraged researchers to apply the same concept to hydroprocessing catalysts in an attempt to enhance catalyst activity, stability, and also to prevent coke deposition. Ali et al. displayed that the noble metal could significantly improve the catalytic activity of a high surface area saponite supported Co catalyst for processing vacuum gas oil in a laboratory scale flow reactor [8]. Al-Saleh et al. also investigated Pt–Rh modified Co-Clay catalysts in a batch autoclave reactor using vacuum gas oil (VGO) as feedstock. Both HC and HDS activity of Co-Clay was significantly increased when the catalysts were modified with a trace amount of Pt–Rh [9]. Hossain reported an extensive study on the effects of noble metals on catalytic activity of Co-Clay catalysts [10]. It has been explained that the noble metals are very effective in generating a sufficient amount of reactive hydrogen, which prevents coke deposition by reacting with the cracked reaction intermediates [8–13]. The present paper reports the investigation of the promotional effects of Pd, Rh and Pd–Rh on the catalytic activity of Co/HPS catalysts for heavy oil upgrading. The noble metal promoted catalysts were prepared and characterized by temperature-programmed reduction (TPR). The activities of the catalysts were tested in a batch autoclave reactor using vacuum gas oil for both HDS and HC activity test. Finally, the spent catalysts were also characterized for coke deposition.

2. Experimental methods

2.1. Catalyst preparation

Co/HPS and noble metal promoted Co/HPS catalysts were prepared and tested at the Catalytic Reaction

Engineering Laboratory, Center for Refining and Petrochemicals, RI-KUPUM, Saudi Arabia. The noble metal promotion of the catalyst was introduced in two different ways: (I) by single noble metal (Pd or Rh) and (II) by a Pd–Rh combination. In all catalysts Co loading was maintained at 18 wt.% (of the catalyst weight). For the single noble metal promoted catalysts the noble metal (Pd/Rh) loading was kept at 1 wt.% while in case of Pd–Rh promoted catalyst the Pd loading was still kept at 1 wt.% but the Rh loading was reduced to 0.1 wt.%. The synthetic HPS, originally received from Kunimine Kogyo Co. Ltd., Japan has a density of 2.5 g/cm³ and pH value of 9–10 in 2% suspension. Its composition was reported as 58.3% SiO₂, 32.9% MgO, 5.6% Al₂O₃ and 3.2% Na₂O on dry weight basis. The pore volume was 0.721 cm³/g; mean pore radius 30 Å; and multiple point BET surface area 600 m²/g.

Before metal loading the high porous saponite (HPS) was calcined in airflow at 600 °C for 5 h. The noble promoted catalysts were prepared by successive loading of noble metal followed by cobalt. A solution containing noble metal(s) was impregnated on HPS using the incipient wetness method. The resulting paste was dried at 120 °C followed by calcinations at 600 °C for 4 h. The Co loading was carried out by an ion-exchange technique, which consisted of the following steps: Co(NO₃)₂·6H₂O solution was prepared in distilled water and aged at 80 °C for 1 h. The noble metal(s) loaded HPS was added into the solution and the mixture was stirred at 80 °C for another 2 h. The precipitated product thus obtained was filtered and washed with distilled water followed by ethanol. The washed product was dried at 120 °C and calcined at 600 °C for 4 h and finally was pelletized for characterization and evaluation.

2.2. Catalyst characterization

2.2.1. Temperature-programmed reduction

The temperature-programmed reduction (TPR) was carried out in a Model TP-2000 TPR system, supplied by Ohkura Rikan Co. Ltd., Japan. The sample pre-treatment procedure and subsequent TPR measurements can be described as follows: 150 mg of catalyst sample were placed in a quartz tube reactor (8.0 mm OD), and held at the middle of the tube by using quartz wool plug. In order to remove the moisture, the sample was pretreated by flowing dry air (30 ml/min) at 400 °C at a heating rate of 10 °C/min and dwelled at 400 °C for next 2 h. The system was then allowed to cool down to ambient temperature by flowing argon (20 ml/min). For catalyst reduction a mixture of 5% hydrogen in argon was used at a flow rate of 20 ml/min. The temperature was programmed to increase linearly at 10 °C/min to 1030 °C and held at this temperature for 15 min. A 5A molecular sieve trapped the water that formed during the pretreatment process and/or reduction reaction. A thermal conductivity detector (TCD) measured the hydrogen concentration. Temperature was maintained at 50 °C in both TCD and molecular sieve. A NEC Model-PC9821-XE10

personal computer was connected in order to monitor the temperature of the catalyst and the TCD current response.

2.3. Catalyst evaluation

2.3.1. Batch autoclave reactor trials

The batch reactor experiments were carried out using vacuum gas oil (VGO, Arabian light gas oil) obtained from Saudi ARAMCO. This is an actual feedstock that has been used in an existing commercial hydroprocessing unit. The physical and chemical properties of the feedstock VGO are listed in Table 1. Prior to reaction, the catalyst was pre-sulfided separately in a tubular reactor at 400 °C for 1 h by flowing a mixture of 5% hydrogen sulfide and balanced hydrogen. For each batch, 3 g of pre-sulfided catalyst and 100 g of VGO were loaded into the reactor. The system was purged with hydrogen and then pressurized to 13,800 kPa with high-pressure hydrogen. Leak tests were carried out using a hydrogen detector. After leak test the reactor pressure was reduced to 6900 kPa and the temperature program was started (at 5 °C/min) in heat up mode. The stirrer was turned on when the temperature reached 60 °C and maintained at a speed of 800–900 rpm. When the reactor temperature reached 400 °C the hydrogen gas pressure was again adjusted to 13,800 kPa and maintained at this value throughout the experiment. The reaction time was counted from this point to onwards and each experiment was carried out for 90 min. After completion of the specified reaction time the system was cooled down to room temperature and gas, liquid product and spent catalyst samples were collected. Gas chromatography was used to analyze the gas sample, while the liquid product was analyzed for boiling point distribution using GC simulated distillation, hydrocarbon types by HPLC and elements by CHNS analysis.

Table 1
Properties of VGO feedstock (from Arabian light gas oil)

Properties	Value
Appearance	Soft but solid at room temperature
Color	Greenish dark brown
Density (g/cm ³ at 15 °C)	0.892
Molecular weight	442.7
Initial boiling point (IBP)	343 °C
Final boiling point (FBP)	641 °C
Elemental analysis (wt.%)	
Carbon	85.1
Hydrogen	11.95
Sulfur	2.667
Nitrogen	0.215
HPLC analysis (wt.%)	
Saturates	13.3
Aromatics	68.1
Polars	18.6

Since the initial boiling point of feed VGO was 343 °C (Table 1), the cracking activity of a catalyst was defined by the percentage of liquid product boiling below 343 °C. The weight percent of coke deposition on the spent catalyst was measured by CHNS analysis.

2.4. Characterization of feed VGO and liquid product

2.4.1. Gas chromatograph simulated distillation

The boiling range distribution of VGO feedstock and liquid products was measured by means of a simulated distillation analyzer using the ASTM D 2887 method. The analyzer consisted of a 5880A series HP gas chromatograph equipped with an automatic HP 7673A sample model, a flame ionization detector (FID) and a packed column coated with methylsilicone liquid phase (UCW-982). Prior to analysis the GC was calibrated by analyzing a mixture of *n*C₅ to *n*C₄₀ paraffins.

2.4.2. Elemental analysis

The feedstock VGO and liquid product samples were also analyzed for carbon, hydrogen, nitrogen, and sulfur using a CHNS analyzer, which was received from Elemental Model VARIOEL. This instrument allowed determining C, H, N, and S in a single operation. In this method, the liquid sample was introduced into the system where the combustion reaction took place in an oxygen–helium atmosphere followed by reduction. Consequently, the elements C, H, N and S in the sample were converted to CO₂, H₂O, N₂ and SO₂, respectively. Finally, these products were separated using separate adsorption columns and detected by a TCD detector.

The spent catalyst from the batch autoclave reactor was also analyzed for the amount of coke deposition after reaction using the same analyzer. The catalyst was washed with *n*-hexane to extract the coke and the resulting solution was analyzed for amount of coke.

2.4.3. Hydrocarbon group analysis

The hydrocarbon groups (saturates, aromatics and polars) that were present in the VGO feedstock and liquid products were analyzed using a high performance liquid chromatograph (HPLC) system, supplied by Waters Corporation, USA. The system consists of a solvent delivery pump, automatic sample injector and an automatic switching valve. It is also equipped with a photo diode array (PDA), UV–visible detector and a refractive index detector. The oven temperature is programmable and the HPLC system was operated and controlled by Millennium software. For each experiment, 5 mg liquid sample was mixed with 20 ml of HPLC grade *n*-hexane and the mixture was then stirred for 45 min at room temperature and finally it was filtrated by a 0.5 μm PTFE membrane to remove insoluble compounds. A 20 μl sample of filtrate was injected into the column (30 cm × 3.9 mm id). The column temperature was maintained at 25 °C

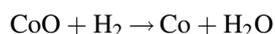
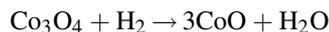
and elution of the components was carried out by flowing *n*-hexane (2 ml/min). The saturates were first eluted and detected by the refractometer, followed by aromatics by PDA. The column was then backflushed for 20 min to elute polars. The eluted fractions were quantified by using the response factor obtained by analyzing a standard sample (VGO).

3. Results and discussion

3.1. Temperature-programmed reduction

In the fresh catalyst, the metals are present in their oxide forms. Given that the metals are more active in their metallic/sulfide state, it is very important to characterize the catalyst so as to investigate the reducibility of the catalyst. The TPR characterization can help measuring the reducibility of the metal oxides before putting into the reaction. Furthermore, TPR helps in the study of the promotional effects of noble metals on the reduction of the main active species. Concerning hydrogen spillover effects, TPR can also provide insight into this phenomenon through the measurement of hydrogen consumption and shifting of the reduction temperature [9,10]. Fig. 1 illustrates the H₂ consumption profiles during the TPR of the different catalysts involved in this study. In case of plain Co/HPS, mainly two peaks evolved at 226 and 740 °C, respectively. The first peak, at 226 °C, was attributed to the reduction of trivalent Co oxide (Co₂O₃/Co₃O₄) to divalent Co oxide (CoO). The second peak, appearing at 740 °C, (i.e., the temperature at which most of the reduction occurred) was attributed to the reduction of divalent Co oxide (CoO) to the metallic Co (Co⁰) [14–17]. These observations are consistent with the following reaction scheme, which has been

proposed based on the TPR measurement of pure Co₃O₄ [18].



According to other researchers, the first peak is due to the easily reducible large particle of cobalt oxides (assumed as species I), while the second peak is due to the reduction of highly dispersed amorphous over layer of cobalt oxide (assumed as species II) [6,19]. The TPR profiles of both Pd and Rh promoted Co/HPS were also similar to that of unpromoted Co/HPS, which suggests no alloy formation between cobalt and the noble metals [20]. However, a small peak was observed due to the presence of Pd/Rh, which was considered as the leftover portion of the second peak of Co/HPS that was not affected by the noble metal [1]. It is interesting to note that the noble metal promoted catalysts exhibited a significantly low-temperature reduction. The shifting of the peak temperature, which occurred in the range of 140–215 °C, was clearly due to the promotional effects by the noble metals [17,21]. From a mechanistic point of view, this effect can be explained by so-called hydrogen spillover [8–10] phenomenon, which can be described as follows: the noble metal can dissociate molecular hydrogen to highly reactive hydrogen species, i.e. H⁺, H⁻, H₃⁺ or ion pair, and such reactive species can easily attack the cobalt oxide(s) and reduce them at comparatively lower temperatures [22]. This noble metal promotional effect also has been explained in the literature in the following ways: (a) noble metals might reduce the activation energy of the cobalt oxide reduction reaction; (b) the dispersion of cobalt oxide on HPS can also be enhanced in such a way that it is reduced at a comparatively lower temperature; (c) an increase in the number of nucleation sites for reduction [1,17,23]. Among the two noble metals used, Rh exhibited a more pronounced promotional effect compared to Pd in the reduction of Co species supported on HPS. In catalysts samples with equal loading, Rh shifted the peak temperature by 215 °C while Pd showed a shift of 140 °C, which reveals that Rh reduces cobalt oxide more readily than Pd.

Based on the study of the effects of Rh and Pd on Co/HPS, the following step was to investigate the Pd–Rh bi-noble metal effects on Co/HPS catalyst. It has been observed that Rh can promote Co/HPS more efficiently than Pd, on the other hand, its price is 2.5 times the price of Pd. Bearing this in mind, the next objective was set so as to achieve the similar effects (as obtained with Rh at its higher amount) by employing a Pd–Rh bi-noble metal combination using a trace amount of Rh. For comparison purpose, the TPR profile of this catalyst is also included into Fig. 1. It is clear from the TPR profile that a trace amount of Rh along with Pd can provide a similar temperature shift as Rh did alone at a higher amount of its loading. The bi-noble metal effect can be reasonably explained as follows: the presence of Rh

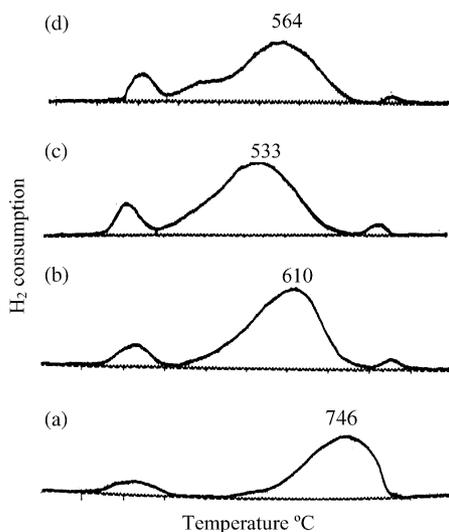


Fig. 1. TPR profiles of (a) Co/HPS, (b) Pd–Co/HPS, (c) Rh–Co/HPS and (d) Pd–Rh–Co/HPS catalysts.

Table 2
HC and HDS conversion of VGO in batch autoclave reactor

Catalyst description	Conversion (mol%)	
	HC	HDS
Co–Mo/Al ₂ O ₃	14.6	60.4
Co/HPS	15.0	58.6
Pd–Co/HPS	16.5	60.0
Rh–Co/HPS	20.0	69.5
Pd–Rh–Co/HPS	21.4	70.0

assisted in the reduction of Pd, which in turn assisted in the dissociation of more hydrogen molecules, thereby enhancing the reducibility of the cobalt oxide sites at a lower temperature [13]. The increased reducibility of noble metal promoted Co/HPS catalysts could also be due to superior dispersion of cobalt species on the support surface in presence of noble metals [24,25].

3.2. Catalyst evaluation

3.2.1. Batch autoclave reactor trials

The catalytic activity of Pd, Rh and Pd–Rh promoted Co/HPS as well as the plain Co/HPS catalysts were examined using vacuum gas oil as feedstock in a batch autoclave reactor. It is important to point out that this is a typical feedstock used in the industry. The experiments were carried out at typical industrial hydroprocessing conditions (400 °C, 13,800 kPa) and for 90 min in reaction. A standard CoMo/Al₂O₃ catalyst was also evaluated under identical reaction conditions and the activity data of this catalyst was also included in relevant figures of this report only for comparison purpose. However, given that the main objective of this study was to investigate the noble metal effects on the HC and HDS performance of Co/HPS catalysts, the CoMo/Al₂O₃ catalyst was not included in the subsequent discussion.

After 90 min reaction the liquid and gas products were collected and analyzed. The HC and HDS conversion data of

each catalyst are listed in Table 2. Fig. 2 shows the product gas analysis data of the evaluated catalysts. For all noble metal promoted catalysts, it can be clearly seen that the formation rate of gaseous hydrocarbon (C₁–C₅) was considerably lower than that of the unpromoted Co/HPS. Moreover, the Pd–Rh promoted Co/HPS showed the lowest rate of gas formation. This result was expected after analyzing the TPR data, which indicated the widespread availability of reactive hydrogen due to hydrogen spillover introduced by the noble metal(s) that help to suppress the formation of lighter gases. The presence of Pd/Rh or Pd–Rh helped maintain a sufficient amount of reactive hydrogen needed for the hydrogenation reaction that determines the termination of the cracking reaction, thus preventing the over cracking of the intermediates, which yields undesirable light gaseous products. In other literature reports it has been assumed that the addition of the noble metal introduces a better balance between the acidic function (for cracking) and hydrogenation function of the catalysts, which helps reducing the gaseous product formation by suppressing the over cracking of heavy hydrocarbon molecules [26,27]. This characteristic of a hydroprocessing catalyst is of great importance for its industrial application since deep cracking produces lighter gas, which is considered as waste [10]. The liquid product analysis data showed that the HC and HDS activity of Co/HPS were significantly higher with noble metal modification, as illustrated in Fig. 3(a) and (b). The order of activity was: Pd–Rh–Co/HPS > Rh–Co/HPS > Pd–Co/HPS > Co/HPS.

It is interesting to note that Pd–Rh promoted catalysts displayed the highest activity for both HC and HDS reactions. Such high activities were consistent with the reducibility data showed earlier in TPR studies of these catalysts. The higher HC and HDS activity of Pd/Rh and Pd–Rh promoted catalysts probably occurred due to the synergy effect introduced by the noble metals. Several authors have also reported similar high activities by using different noble metals (Pt, Rh, Pd, Ru, etc.) as well as their combination as promoters [8,9,28,29]. This promotional effects can be explained as follows: Sulfur bearing heteroatoms, as well as the heavy hydrocarbon molecules, crack on the acidic HPS sites to produce unstable reaction intermediates. Meanwhile, the noble metal(s) supply reactive hydrogen via the dissociation of molecular hydrogen. The cracked reaction intermediates react with the hydrogen species to produce stable products. As a result the rate of the reaction and the activity become higher. A mechanism consistent with the above explanation has been reported elsewhere [1,9]. A similar mechanism for hydrodesulfurization of thiophene over USY zeolite supported Pt, Pt–Pd catalysts have also been demonstrated by other authors [30,31]. The reasons of higher hydrogenation activity can be further confirmed from the H/C ratio and HPLC analysis data of liquid products, shown in Fig. 4(a) and 4(b), respectively. The H/C ratios of the noble metal promoted catalysts were shown to be significantly high as compared to those of unpromoted

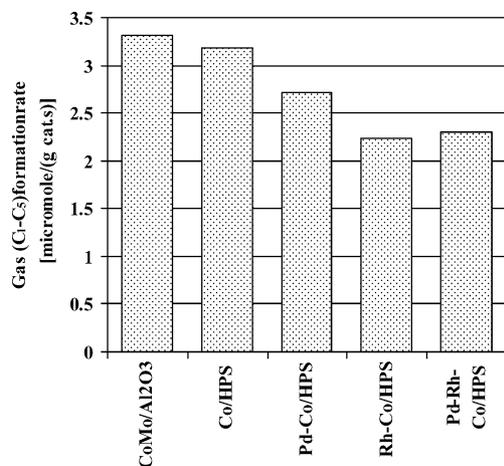


Fig. 2. Formation rate of gas (C₁–C₅) produced in batch autoclave reactor with VGO as feedstock.

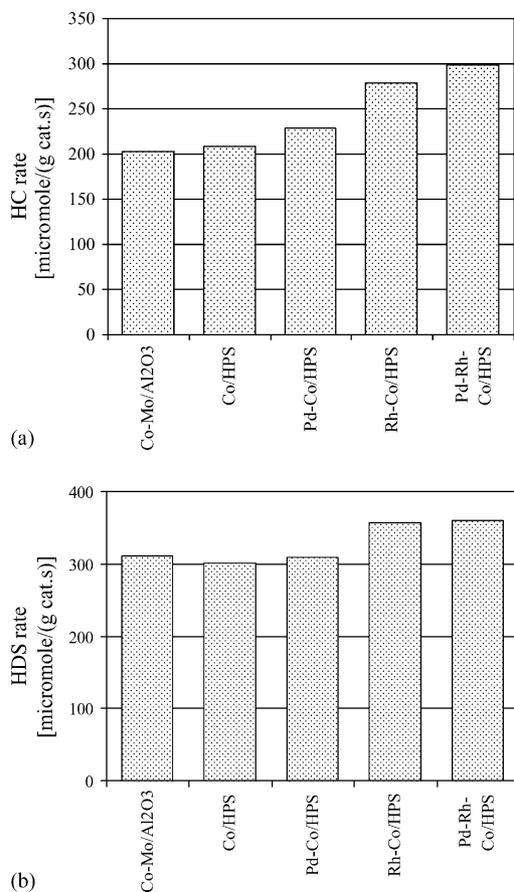


Fig. 3. (a) HC and (b) HDS rates of VGO using Co-Mo/Al₂O₃ and unpromoted, noble metal (Pd/Rh) and bi-noble metal (Pd-Rh) promoted Co/HPS catalysts in batch autoclave reactor.

Co/HPS catalysts. This result indicates the addition of hydrogen into the liquid products through subsequent hydrogenation of cracked intermediates, and also the removal of sulfur from the sulfur containing hydrocarbons [8]. The analysis for the types of hydrocarbons, also supports the higher hydrogenation activity of the noble metal modified Co/HPS. The presence of noble metal(s) resulted in higher saturates content in the liquid product, while yielding lower aromatics and polar content as compared to the plain Co/HPS. This result suggests that the addition of hydrogen to the liquid products during reaction due to the enhanced hydrogenation rate [9].

The higher HC and HDS activity of noble metal promoted catalysts can also be explained by the enhanced acidity introduced by the hydrogen spillover effects as observed in TPR [32]. This phenomenon has been explained by considering the acidic nature of hydrogen species involved in hydrogen spillover, which suggests that the hydrogen species give rise to protons that generate Brønsted acid sites on the Co sites, eventually leading to an increase in cracking as well as the hydrogenation activity. Other studies have also indicated such higher acidity and hydrogenation activity due to the presence of noble metal(s), although the term “hydrogen spillover” has not been used [1,27,33].

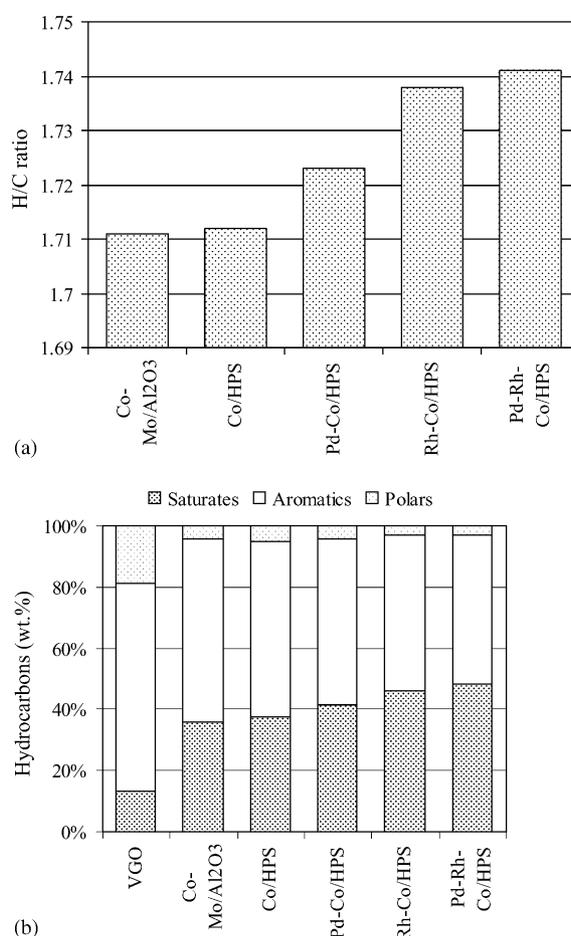


Fig. 4. (a) H/C ratio and (b) hydrocarbon types in liquid product from batch autoclave experiments.

The participation of spillover hydrogen was further demonstrated by the characterization of spent catalysts for the amount of coke deposition after the reaction. Fig. 5 displays the amount of coke deposition on different catalysts after reaction time of 90 min. The result showed that the coke deposition was reduced significantly (18–25 wt.%) on Pd/Rh and Pd-Rh promoted Co/HPS catalysts; particularly Rh and Pd-Rh displayed more pronounced effects in suppressing coke deposition. This observation can be explained by considering the following: gas phase hydrogen molecules are adsorbed on the noble metal sites and then dissociate to produce reactive hydrogen species (H^+ , H^- , H_3^+), which desorbs quickly. This reactive hydrogen species “spillover” to the Co sites (i.e., the main hydrogenation sites) as well as the acidic sites (HPS support) and react with the cracked intermediates to produce stable products. As a result, the deposition of the hydrocarbon intermediates on the active sites is significantly decreased, leading to a clean catalyst surface [9,32]. Another explanation is provided by the so-called the remote control mechanism by hydrogen spillover on noble metal promoted catalysts [9,10]. According to this mechanism the hydrogen involved in spillover influences the cracking of heavy hydrocarbon molecules by controlling the concentration of carbonium

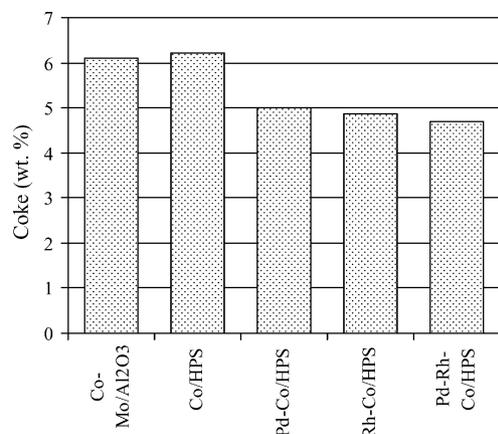


Fig. 5. Coke deposition on spent catalysts in batch autoclave experiments.

ions as well as the other unstable reaction intermediates, thereby hindering their deposition by converting them to stable products. Consequently, the catalysts remained active.

4. Conclusion

The reducibility of Co/HPS can be significantly enhanced by modifying the catalyst with noble metals (Pd, Rh) as well as their combination. Rh proved to be more effective than Pd in reducing the Co/HPS. A trace amount of Rh along with Pd showed a remarkable effect, which was much higher than that obtained with Pd alone. The enhanced reducibility of Co/HPS by noble metals also helped to increase the both HC and HDS activity of such catalysts, as shown by batch autoclave reactor experiments using vacuum gas oil as feedstock. Particularly, the Rh and Pd–Rh promoted catalysts were found to be very effective in both HC and HDS purpose. The analysis of the liquid products obtained from the batch reaction of VGO showed a considerable H/C ratio and higher saturates, which confirmed the higher hydrogenation activity of noble metal promoted Co/HPS catalysts. Furthermore, spent catalyst analysis also revealed a remarkable decrease in coke deposition on Co/HPS due to the addition of noble metals. Therefore, this study revealed that noble metal promoted Co/HPS holds great promise for hydrocracking and HDS of heavy oil.

Acknowledgements

The authors wish to acknowledge The Center for Refining and Petrochemicals, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia and Petroleum Energy Center, Japan, for supporting this work under the KFUPM-RI Project No. 21151. The authors also like to thanks Mr. Santiago Romero-Vargas for

his help in reviewing the manuscript for improving the English.

References

- [1] M.M. Hossain, M.A. Al-Saleh, M. Shalabi, T. Kimura, T. Inui, *Appl. Catal. A* 274 (2004) 43.
- [2] E. Hayashi, E. Iwamatsu, M.E. Biswas, Y. Sanada, S. Ahmed, S.H. Hamid, T. Yoneda, *Appl. Catal. A* 179 (1999) 203.
- [3] S.A. Ali, M.E. Biswas, T. Yoneda, T. Miura, S.H. Hamid, E. Iwamatsu, H. Al-Suaibi, *Sci. Technol. Catal.* 127 (1998) 407.
- [4] K. Aoki, Y. Minato, K. Torii, M. Shirai, M. Arai, *Appl. Catal. A* 215 (2001) 47.
- [5] M. Arai, Y. Minato, K. Torii, M. Shiraj, *Catal. Lett.* 61 (1999) 83.
- [6] 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*.
- [7] J.H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts and Applications*, Wiley, NY, USA, 1983.
- [8] M.A. Ali, T. Kimura, Y. Suzuki, M.A. Al-Saleh, H. Hamid, T. Inui, *Appl. Catal.* 227 (2002) 63.
- [9] M.A. Al-Saleh, M.M. Hossain, M. Shalabi, T. Kimura, T. Inui, *Appl. Catal.* 253 (2003) 453.
- [10] M.M. Hossain, M.S. Thesis, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, 2000.
- [11] J.M. Parera, E.M. Traffano, J.C. Musso, C.L. Pieck, *Stud. Surf. Sci. Catal.* 17 (1983) 101.
- [12] T. Inui, *Catal. Today* 51 (1999) 361.
- [13] T. Inui, *Stud. Surf. Sci. Catal.* 77 (1993) 17.
- [14] M. Voß, D. Borgmann, G. Wedler, *J. Catal.* 212 (2002) 10.
- [15] R. Lago, G. Bini, M.A. Peña, J.L. Fierro, *J. Catal.* 167 (1997) 198.
- [16] G. Jacobs, T.K. Das, Y. Zhang, J. Li, G. Racoillet, B.H. Davis, *Appl. Catal.* 233 (2002) 263.
- [17] F.B. Noronha, A. Frydman, D.A.G. Aranda, C. Perez, R.R. Soares, B. Morawek, D. Castner, C.T. Campbell, R. Frety, M. Schmal, *Catal. Today* 28 (1996) 147.
- [18] H.-K. Lin, H.-C. Chiu, H.-C. Tsai, S.-H. Chien, C.-B. Wang, *Catal. Lett.* 88 (2003) 169.
- [19] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, *J. Catal.* 156 (1995) 85.
- [20] M.G. Yang, I. Nakamura, K. Fujimoto, *Stud. Surf. Sci. Catal.* 112 (1997) 221.
- [21] C.L. Bianchi, *Catal. Lett.* 76 (2001) 155.
- [22] T. Kusakari, K. Tomishige, K. Fujimoto, *Appl. Catal.* 224 (2002) 219.
- [23] N.W. Hurst, S.J. Gentry, A. Jones, *Catal. Rev. Sci. Eng.* 24 (2) (1982) 233.
- [24] Z. Cheng, Q. Wu, J. Li., Q. Zhu, *Catal. Today* 30 (1996) 147.
- [25] Y. Chen, K. Tomishige, K. Yokoyama, K. Fujimoto, *Appl. Catal.* 165 (1997) 335.
- [26] S.P. Elangovan, C. Cischof, M. Hartmann, *Catal. Lett.* 80 (2002) 35.
- [27] E. Blomsma, J.A. Martens, P.A. Jacobs, *Catal. J.* 165 (1997) 241.
- [28] L.I. Ali, A.-G.A. Ali, S.M. Aboul-Fotouh, A.K. Aboul-Gheir, *Appl. Catal.* 205 (2001) 129.
- [29] L. Leite, E. Benazzi, N. Marchal-George, *Catal. Today* 65 (2001) 241.
- [30] M. Sugioka, F. Sado, Y. Matsumoto, N. Maesaki, *Catal. Today* 29 (1996) 225.
- [31] M. Sugioka, F. Sado, T. Kurosaka, X. Wang, *Catal. Today* 45 (1998) 327.
- [32] K. Fujimoto, in: B. Delmon, G.F. Froment, P. Grange (Eds.), *Hydro-treatment and Hydrocracking of Oil Fraction*, Elsevier, Amsterdam, 1999.
- [33] T. Wada, K. Kaneda, S. Murata, M. Nomura, *Catal. Today* 31 (1996) 113.