Hydrogen spillover effects on Pt–Rh modified Co–clay catalysts for heavy oil upgrading

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Abstract

Hydrogen spillover effects on noble metal-promoted Co/HPS (high porous saponite) catalysts have been investigated by temperature-programmed reduction (TPR) studies and batch autoclave reactor trials. Pt and Rh noble metals were used to introduce hydrogen spillover on Co/HPS. TPR studies showed that Pt–Rh combination has more significant effects on the reducibility of Co species on HPS catalysts than the unpromoted and single noble metal (Pt, Rh individually)-promoted catalysts. The Pt–Rh combination shifts the TPR peaks to lower temperatures. Two Pt–Rh-promoted catalysts were evaluated in batch autoclave reactor (at 400 °C and 140 kg/cm^2) using vacuum gas oil (VGO) as the feedstock. Pt–Rh-promoted catalysts showed higher activity for both hydrocracking and hydrodesulfurization of the heavy feed than the unpromoted Co/HPS catalyst.
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1. Introduction

Catalytic activity, stability, lifetime, and selectivity are the main aspects in the development of heavy oil upgrading catalysts (also called hydrocracking/hydrotreating catalysts). The activity and lifetime of these catalysts mainly depend on support type, hydrogen transfer function (metal/metals oxides), and type of feed to be processed. The optimum performance of a catalyst can be achieved by appropriately balancing these two functions. Cracking of heavy hydrocarbon molecules on an acidic support provides free radicals and olefins that need to be hydrogenated to produce stable products. The hydrogenation reac-

tions are facilitated by loading a suitable element from Groups VIB (Mo or W) and VIII (Co or Ni) [1]. Conventionally, SiO$_2$–Al$_2$O$_3$ and/or zeolites have been used as support in heavy oil upgrading catalysts. Due to the limited pore structure of these support materials to access the bulky molecule of the heavy feeds, research is underway to investigate the possibility of utilizing clay as an alternative support. Clays are amorphous materials having large-sized pore structure compared to the conventional supports. Co- and Ni-pillared high surface area saponite clay displayed comparable activity to treat vacuum gas oil in a batch autoclave reactor [2]. Smectite clay minerals when loaded with Pt show high ethylene hydrogenation activity [3]. Co oxide-supported smectite clay was found to be very promising for hydrodesulfurization (HDS) catalyst [4]. Recently, Kimura et al. [1] investigated

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highly active Co high porous saponite (HPS) catalyst, which was exposed in a batch autoclave reactor for 60 min reaction using vacuum gas oil as feed. The activity of such catalysts declined when the reaction time extended to 90 min. Large molecules present in the heavy feed, upon cracking, probably produce reaction intermediates, which deposited on the catalyst surface as coke. This decreased catalyst activity. The reaction intermediates might be hydrogenated to stable products by supplying sufficient amounts of reactive hydrogen, which can decrease coke deposition.

Usually noble metals (Rh, Pd, Pt and Ru) are employed to generate sufficient amounts of reactive hydrogen (called spill over hydrogen) on the catalyst surface. Parera et al. [5] was probably the first group that reported the involvement of hydrogen spillover to remove coke from the surface of a Pt/Al_2O_3 catalyst. Rh can play the role of a porthole of reactive hydrogen that reduces coke deposition on a rhodium-modified ultra-rapid reforming catalyst [6–8]. Most of the work on the effects of hydrogen spillover available in the literature are related to reforming catalysts; only a very limited number of papers have concentrated on the catalysts for the hydrocracking/hydrogenation of model compounds [9–11]. Hydrogen spillover effects on heavy oil upgrading catalysts have not been studied extensively. However, this effect might be utilized effectively to find new catalysts with higher activity and lifetime as well as to improve the existing commercial catalysts. This work aimed to improve the activity and lifetime of Co/HPS catalyst by introducing hydrogen spillover effects. The noble metals Pt and Rh were used in this regard. TPR measurement demonstrated the hydrogen spillover effects by measuring the reducibility of Co oxides supported on HPS. Batch evaluation displayed the activity of the modified catalyst with vacuum gas oil as feed stock.

2. Experimental

High porous saponite (HPS) clay supplied by Kunimine Kogyo Co. Ltd., Japan was used as support; it was calcined at 600 °C for 4 h. For catalyst preparation, cobalt was loaded by ion-exchange technique after the addition of noble metals on the support. The ion-exchange technique is described below.

A required amount of cobalt nitrate solution ($Co(NO_3)_2 \cdot 6H_2O$ in distilled water) was aged at 80 °C for 2 h. Then, noble metal-modified HPS was added to the solution and the mixture was stirred at 80 °C for one and half hours. After cooling down to room temperature, the solution was filtered and washed with distilled water, followed by the addition of ethanol, and this was dried at 120 °C. Finally, the dried powder was calcined at 600 °C for 4 h and this resulting material was pelletized.

For the present work, the hydrogen concentration during TPR was measured by using a thermal conductivity detector (TCD). The same amount of catalysts (150 mg) was used for each experiment and the catalyst was heated at 400 °C for 2 h in air before starting the TPR measurement. Temperature was programmed to increase at a rate of 10 °C/min from 30 to 1030 °C and hydrogen consumption was recorded.

Catalysts were evaluated in a batch autoclave reactor by using vacuum gas oil (VGO) as the feed stock. The physical and chemical properties of the feedstock VGO are listed in Table 1. For each batch, 3 g of pre-sulfided catalysts (sulfided by using a microflow reactor) and 100 g of VGO were loaded into the batch reactor. The system was pressurized up to 140 kg/cm^2 by high-pressure hydrogen to check for leakage, using a hydrogen detector. After completion of the leak test, the system was depressurized to 80 kg/cm^2 and the temperature program (temperature increasing rate 5 °C/min) was started for heating. The

Table 1
Properties of vacuum gas oil (VGO) feed

Property	Value
Color	Greenish dark brown
Appearance	Solid at room temperature
Density (g/cm^3 at 15 °C)	0.8917
Molecular weight	442.70
HPLC analysis (wt.%)	
Saturates	13.3
Aromatics	68.1
Polars	18.6
Elements (wt.%)	
Carbon	85.09
Nitrogen	0.215
Sulfur	2.666
Hydrogen	11.95
C/H ratio	1.68

stirrer was started at 50 °C temperature with a speed of 800–900 rpm. When the internal temperature of the reactor reached 400 °C, the system was again pressurized to 140 kg/cm^2 and the reaction was continued for the specified time (30, 60 or 90 min). The gas, liquid product and the spent catalyst samples were collected after cooling the system to room temperature. The gas sample was analyzed with a gas chromatograph (GC) while a simulated distillation gas chromatograph and a CHNS analyzer analyzed the liquid product. The weight percent of coke deposition on the spent catalyst was found from CHNS analysis.

The feedstocks VGO and the liquid product of the batch autoclave reactor were analyzed for the different hydrocarbon groups (saturates, aromatics and polars) present by using a high performance liquid chromatograph (HPLC) system supplied by Waters Corporation, USA. The HPLC system was operated and controlled by Millennium software. At first, a 0.5 g liquid sample was mixed with 20 ml filtered HPLC grade n-hexane and the resulting mixture was stirred at ambient temperature for 45 min. The n-hexane insoluble parts of the mixture were separated out by using a 0.5 μm PTFE membrane filter. An amount of 20 μl of the filtrate sample was injected into the HPLC aminopropyle column (30 cm × 3.9 mm i.d.), which fractionated the sample into saturates, aromatics and polars. The column temperature was maintained at 25 °C and the elution of the components was carried out using n-hexane at a flow rate of 2 ml/min. The saturates were first eluted and detected with a refractometer, followed by the aromatics which were detected with PDA detector. Finally the column was backflushed for 20 min to elute polars. The quantification of the eluted fractions was achieved by using the response obtained by analyzing a standard VGO sample.

3. Results and discussion

3.1. Temperature-programmed reduction

The TPR spectra of Co/HPS catalyst and the noble metal-promoted Co/HPS catalysts are presented in Fig. 1. For the Co/HPS catalyst, the major peaks were found at 226 and 746 °C. The first phase (peak at 226 °C) has been assumed to be the large particles of cobalt oxide (species I), while the second phase (peak
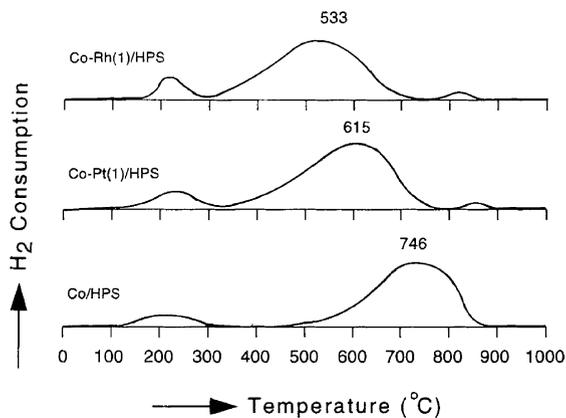

Fig. 1. TPR spectra of noble metal promoted and unpromoted Co/HPS.

at 746 °C) has been described as highly dispersed cobalt oxide (species II) [12]. When the catalyst was modified with noble metal, the TPR profile was unchanged; only the second peak was significantly shifted to lower temperature, keeping a portion of this phase as the third peak (assumed species III). The similarities between the TPR profiles of the promoted and unpromoted catalysts indicate that no metal alloy was formed with the modification of the noble metal [13]. The shifting of the second peak occurred in the range of 125–200 °C. This is attributed to the effect of hydrogen spillover lowering the reduction temperature of cobalt oxides in this phase. Fig. 1 shows that the first phase of the TPR peak was not shifted by noble metal addition. Therefore, it is clear that hydrogen spillover took place at temperatures higher than the first peak. Hence, only the species II were affected by the hydrogen spillover. For unpromoted catalysts, initially the reduction starts by spontaneous activation of hydrogen and reduces a very small amount of Co oxide; the reduced Co thus takes part in the further activation of hydrogen [14]. Usually, this type of reduction occurs at comparatively high temperatures and it also depends on the types of metal and support involved. In the cases of noble metal-promoted catalysts, the scenario is totally different. The promoter aids the initiation of the reduction of the Co oxides. Hydrogen can be dissociated on the noble metal sites at comparatively lower temperatures; such hydrogen spills to the cobalt oxide sites and reduces them. In case of Rh-promoted Co/HPS, the second peak occurred at

lower temperature (by 82 °C) than that of Pt-promoted Co/HPS, which indicates that Rh has higher strength for facilitating hydrogen spillover than Pt does.

We observed the higher activity of Rh as compared to Pt for enhancing the hydrogen spillover. We also kept in mind the higher price of Rh (10 times more than Pt). So our next attempt was to employ bi-noble metal-promotional effects on Co/HPS with the aim of using less amount of Rh. The Rh loading was varied in such a way that the use of it was reduced but at the same time the amount of hydrogen spillover effects remained unchanged. In this context, a trace amount (0.1–0.2 wt.%) of Rh was loaded with 1 wt.% of Pt on Co/HPS. The TPR profiles of such a catalyst are similar to those of the catalysts when the same noble metals were loaded individually (Fig. 2). Here, less amount of Rh with 1 wt.% Pt caused almost the same shifting of the main peak (phase II) to the lower temperature as 1 wt.% Rh did previously. This result can be explained as follows. Pt (also other noble metals) reduced more easily in presence of Rh and the reduced Pt thus plays the role of porthole for hydrogen spillover toward cobalt oxide (main active sites) and such spillover reduced them at lower temperature [7]. The reduction peak temperature was decreased with increasing Rh loading; however, after 0.2 wt.% of loading, it did not further significantly decrease. Therefore, only 0.1 and 0.2 wt.% Rh loaded catalysts were selected for evaluation in the batch autoclave reactor.

As the next step, an attempt was made to quantify the hydrogen spillover effects by measuring the
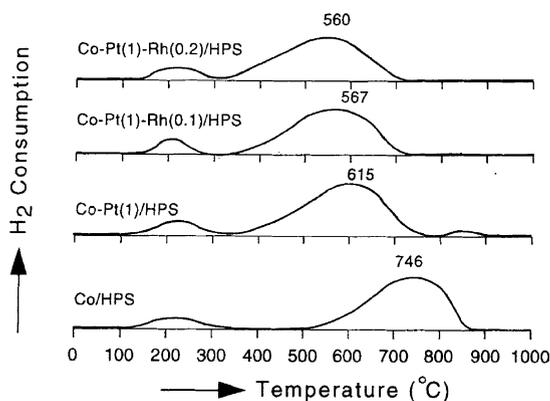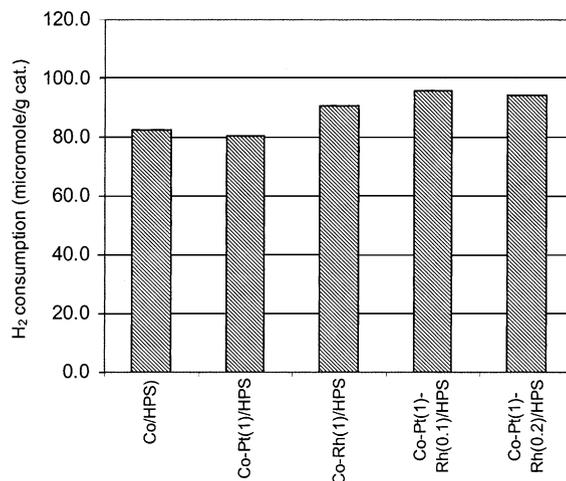

Fig. 3. H_2 consumption in first peak of the TPR spectra.

amount of hydrogen consumed by each peak per gram of catalyst. The first peak and second peak were considered in these measurements; because the area under the third peak was almost negligible, it was not considered. Figs. 3 and 4 display the amount (μmol/g catalyst) of hydrogen consumed by the first peak and the second peak respectively for unpromoted, noble metal-promoted and bi-noble metal-promoted catalysts. For both peaks, it was noticed that the amount of hydrogen consumption was slightly increased in cases of noble metal-promoted catalysts as compared to the results for unpromoted Co/HPS. Therefore, in this study it can be safely concluded that the number
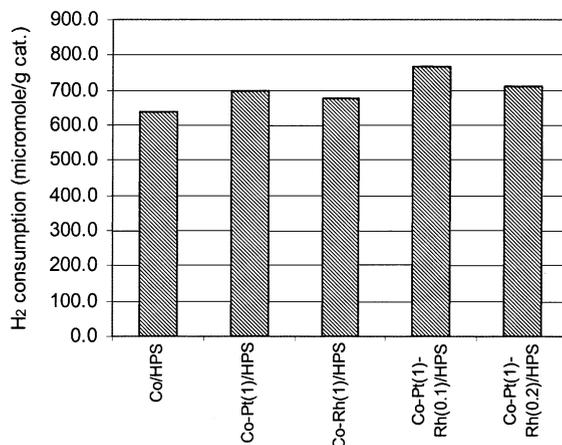

Fig. 2. TPR profile of Pt–Rh-promoted Co/HPS catalysts.

Fig. 4. H_2 consumption in second peak of the TPR spectra.

of Co oxide species reduction of the catalysts were not significantly increased with the presence of noble metals. Their presence only promoted the shifting of the reduction temperature of the Co oxide particles in the second peak.

3.2. Batch autoclave trials

Initially all the catalysts were evaluated for 30 min in the batch autoclave reactor. It was found that all the catalysts displayed almost the same activity. The next two runs were carried out for 60 and 90 min. For each of the Pt–Rh-promoted Co/HPS catalysts, mole percent values of the total hydrocarbons (C_1–C_5) were significantly less than that of the unpromoted Co/HPS (Fig. 5). This indicates that the higher hydrogenation activity was achieved by the noble metal-promoted catalysts. The presence of noble metals provides sufficient amounts of reactive hydrogen to the Co metal sites and instantaneously hydrogenates the cracking intermediates produced by the cracking reaction and prevents further cracking to produce lower hydrocarbons. Such types of catalytic activities are highly desirable to suppress the production of gaseous products. The higher hydrocracking (HC) and hydrodesulfurization (HDS) activities calculated from the liquid product analysis, are another strong support of the higher hydrogenation activity offered by the noble metal-promoted cobalt catalysts, as shown in Fig. 6a and b, respectively. From these figures it is clear that both bi-noble metals-promoted catalysts displayed higher HC and HDS activities
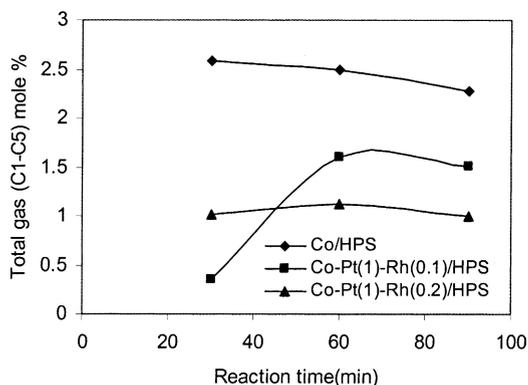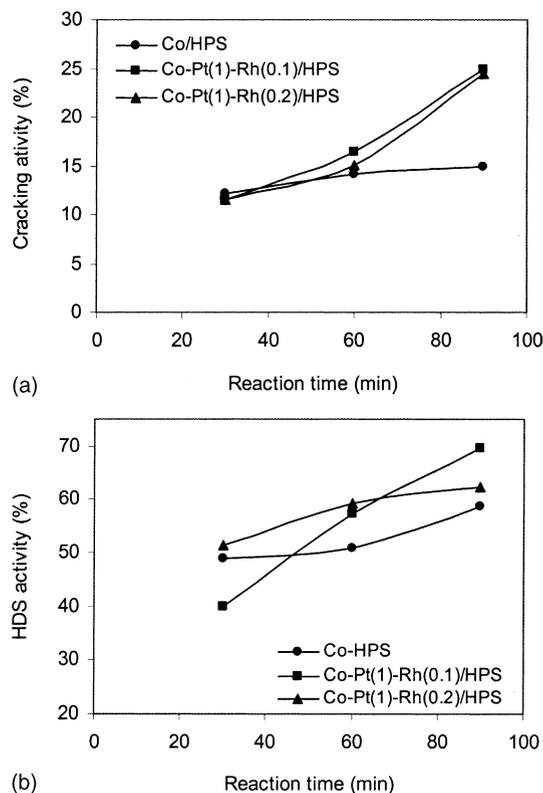

Fig. 6. (a) Hydrocracking activity and (b) HDS activity in batch trial.

in comparison with that of the plain Co/HPS itself. With the increasing reaction time, both the activities sharply increased in the presence of Pt–Rh, while they remained almost the same in the case of the unpromoted catalyst. Another way of showing the higher hydrogenation activities is by HPLC analysis results of the liquid product, as presented in Table 2. In the case of the Pt–Rh-promoted Co/HPS, the amount of saturates is significantly higher, while aromatics and polars were significantly lower, than those of the plain Co/HPS. This analysis result indicates that the spillover hydrogen enhanced the hydrogenation activity of the catalysts [15]. The batch reactor evaluations presented above are well correlated to the TPR studies of the same catalysts, where noble metals displayed hydrogen spillover effects by shifting the reduction temperature. These higher activities were attributed to the enhanced acidity due to spillover hydrogen from noble metal sites to the acidic support

Fig. 5. Total gas (C_1–C_5) produced during reaction in batch autoclave reactor.

Table 2
Batch reactor evaluation results and product analysis

Catalyst	Reaction time (min)	HC (%)	HDS (%)	Product analysis		
				Saturates	Aromatics	Polars
Co/HPS	30	12.2	49.0	30.4	60.1	9.5
	60	14.1	51.0	35.0	58.6	6.4
	90	15.0	58.6	37.5	57.2	5.3
Co–Pt(1)–Rh(0.1)/HPS	30	11.5	40.0	42.1	50.1	7.8
	60	16.5	57.0	41.7	53.1	5.2
	90	25.0	69.6	47.8	50.1	2.1

sites. This phenomenon can be explained reasonably by the acidic function of spillover hydrogen [16]. It has been suggested that spillover hydrogen can give rise to protons, which gives rise to Bronsted acid sites on the supported cobalt oxide sites, increasing the hydrogenation activity as well as the acidity.

Another possible reason of higher activity might be less coke deposition on the catalysts. The amount of coke deposition on the Pt–Rh-promoted catalysts was less compared to that on plain Co/HPS. It further decreased with increasing the reaction time (Fig. 7). The less coking was probably due to the availability of reactive hydrogen through spillover from noble metal sites. Hydrogen present in the gas phase at first adsorbed and dissociated on the noble metal sites to produce reactive hydrogen [16], which spilled over to Co sites as well as to the acidic sites and reacted with the cracking intermediates. Hence, the catalyst surface remained clean and active for further reactions. Further explanation can be made by positing a remote control mechanism, where the reactive hydrogen generated on Pt–Rh sites spilled over to the acidic surface
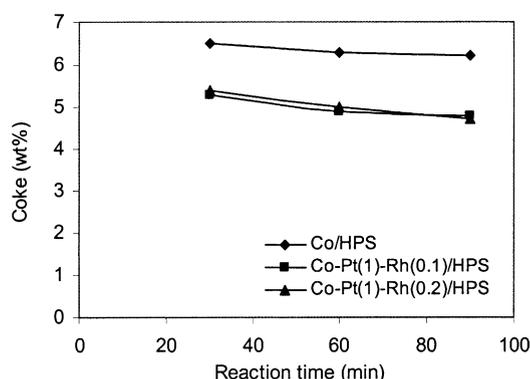

Fig. 7. Carbon deposition on spent catalysts in batch trial.

and influenced the reaction by controlling the concentration of reaction intermediates, carbonium ions, and finally prevented their deposition by hydrogenating them. Consequently the activity of catalysts was sustained for a longer period of time.

On the basis of this study, a possible mechanism for hydrocracking of heavy oil is shown in Fig. 8. The
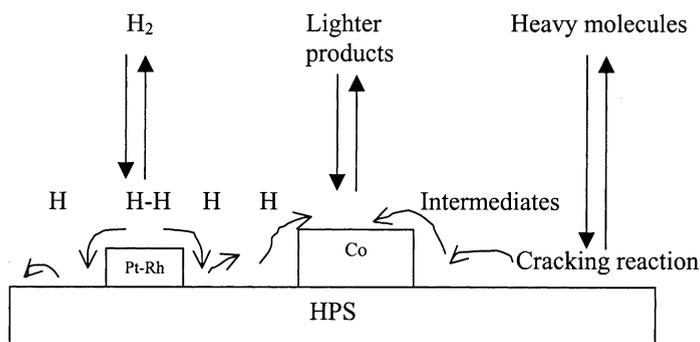

Fig. 8. A possible mechanism of hydrogen spillover on a Co–Pt–Rh/HPS catalyst.

gas phase hydrogen adsorbed and dissociated on the noble metals (Pt–Rh) sites, that supply the reactive hydrogen species (spillover hydrogen); on the other hand, the heavy hydrocarbon molecules crack on the acidic support sites. Finally, the cracked intermediates react with the hydrogen species on the hydrogenation sites (Co). Hence the catalyst surface remains clean from deposition of cracked intermediates (coke).

4. Conclusion

The addition of noble metal/metals on Co/HPS significantly decreased the reduction temperature of the cobalt oxides present on the support surface. The increased reducibility was due to the hydrogen spillover effect as evidenced by the TPR measurements. Batch reactor evaluation revealed that Pt–Rh-promoted catalysts showed higher hydrocracking and HDS activity than unpromoted Co/HPS catalysts. The coke deposition was also decreased by employing bi-noble metal hydrogen spillover effects on the Co/HPS catalyst. Therefore, the possibility of using bi-noble metal-promoted Co–clay catalysts is promising for heavy oil upgrading purposes.

Acknowledgements

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