

# Influence of noble metals (Rh, Pd, Pt) on Co-saponite catalysts for HDS and HC of heavy oil

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## Abstract

The promotional effects of trace amount of noble metal (Rh, Pd, Pt) on Co-saponite (high surface area) catalysts were studied by different characterization and evaluation techniques. BET experiments showed that the specific surface area and the pore volume of the noble metal promoted catalysts remained almost unchanged. The reduction/adsorption characteristics of the catalysts were significantly influenced by the presence of the noble metals as revealed by the temperature programmed studies. The main reduction peak was shifted remarkably to the lower temperature due to the noble metal effects. It also increased the amount of cobalt oxide phase reduction. Pulse chemisorptions and H<sub>2</sub>-TPD kinetics studies revealed that the improved metal dispersion and the lower desorption activation energy have combined effects on the enhanced reducibility of the modified Co-saponite catalysts. The reactivity experiments showed that all of the noble metal promoted catalysts exhibited higher hydrodesulfurization (HDS) and hydrocracking (HC) activities as compared to the unpromoted Co-saponite and among those the Rh promoted catalyst provides superior performances. The coke deposition on the catalyst was also considerably decreased due to the noble metals. These superior activities were attributed to enhanced reducibility and metal dispersion of cobalt due to the influence of the noble metals.

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## 1. Introduction

The ever increasing demand for lighter engine fuel and the recent escalation of the price of oil confronted the refining industry with the problem of maximizing the processing of the heavy fraction of crude oil to produce lighter products. The main problem associated with heavy oil processing is their high sulfur and nitrogen content, which must be removed before further processing because of their toxic characteristics and environmental impact. In addition, environmental regulations are getting increasingly stringent with regards to sulfur composition in engine fuels. To meet the increasing demand for lighter and cleaner fuel, it is necessary to develop more efficient hydrotreating catalysts and processes. The after mentioned facts emphasize the development of catalysts with relatively large pore sizes, which will allow the bulky molecule of heavy hydrocarbons to be processed efficiently. The search for such catalysts resulted in

growing interest on different alternative support materials and the appropriate active metal components. In recent years the suitability of amorphous and pillared clay materials has been explored, because of their favorable acidic and textural properties [1,2]. Conventionally, a suitable transition metal from Group VIB (Mo/W) or VII (Ni/Co) has been applied as the main active component, which is deposited on the acidic support. In many commercial catalysts a second metal (Co, W, V, Pt, etc.) is often used as a promoter to enhance the catalyst activity and stability and in some cases to increase the selectivity of a certain product fraction [3–6]. For instance, vanadium promoted Ni-V catalysts displayed better hydrogenation properties than that of the conventional MoS<sub>2</sub> catalysts. However, this catalyst is less selective towards on dehydrogenolysis of the C–S bond of the sulfur bearing hydrocarbons. The noble metals demonstrated excellent promotional effects in both activity and stability in some supported metal catalysts applied in different reaction systems, such a steam/dry reforming of methane and naphtha reforming [7,8]. Usually, a trace of the noble metals is used because of the rare availability and the high cost. In earlier papers the present author and his co-worker reported

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### Nomenclature

$E_{\text{des}}$	energy of desorption (kJ/mol)
$k_{\text{deso}}$	frequency factor
$n$	order of desorption
$R$	the universal gas constant
$T$	desorption temperature (K)
$T_p$	temperature at maximum desorption rate (K)
$\theta_{\text{des}}$	concentration of adsorbed $\text{H}_2$ on the surface (mol/cm <sup>3</sup> )
$\alpha$	rate of temperature increase (K/min)

comparable HDS and HC activities of bi-noble metal promoted Co-clay catalysts [9–12]. The presence of noble metals influenced to improve the stability of the Co-clay catalyst for longer period of time during hydrotreating of vacuum gas oil. The coke deposition of the catalyst was significantly reduced due to the noble metals effects. Many researchers have explained the noble metal promotional effects by so-called hydrogen spillover [11–14].

This article attempts to elucidate the role of noble metals on Co-saponite catalysts by using different characterization techniques. Various catalyst characterization methods allow determining the active element/phase, and the influence of various factors on the active phase generation [15]. Finally, the resultant characteristics of the noble metal promotion were compared with the HDS and HC activities using heavy oil feedstock.

## 2. Experimental

### 2.1. Preparation of catalyst

The support material, synthetic high surface area saponite clay was received from Kunimine Kogyo Co. Ltd., Japan. The composition (dry weight basis) of the material was reported as 58.3%  $\text{SiO}_2$ , 32.9%  $\text{MgO}$ , 5.6%  $\text{Al}_2\text{O}_3$  and 3.2%  $\text{Na}_2\text{O}$ . It has a density of 2.5 g/cm<sup>3</sup> and pH value of 9–10 in 2% suspension. The clay material has a BET surface area of 600 m<sup>2</sup>/g, pore volume of 0.47 cm<sup>3</sup>/gm and average pore radius of 30 Å. Before metal loading, the support material was calcined at 600 °C for 5 h in airflow. In catalyst preparation, the calcined support material was first modified with noble metal by using the incipient wetness impregnation of noble metal chloride solution on the calcined saponite support. The resulting paste was dried at 120 °C followed by calcination at 600 °C for 4 h. The Co loading was achieved by an ion-exchange technique, which consisted of the following steps:  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution was prepared in distilled water and aged at 80 °C for 1 h. The noble metal(s) loaded saponite 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. Finally the product was pelletized for characterization and evaluation.

### 2.2. Sample characterization

#### 2.2.1. $\text{N}_2$ isotherm

The surface area, average pore radius and pore volume of the samples were determined in a Micromeritics ASAP 2010 analyzer by using  $\text{N}_2$  adsorption at 77 K. For each experiment 0.1–0.2 g of sample was degassed at 573 K for 2.5 h before analysis. The adsorption isotherms were measured in  $10^{-6}$  to 1 relative pressure ranges. The total pore volume was determined from the amount of adsorption at a relative pressure close to unity. The average pore size was estimated assuming cylindrical pore geometry and by using the relation,  $D_p = (4 \times \text{pore volume}/S_{\text{BET}})$ .

#### 2.2.2. Temperature programmed desorption

Temperature programmed desorption (TPD) experiments were carried out in a Micromeritics AutoChem II 2920 analyzer. For the characterization experiments 0.1–0.2 mg of catalyst sample was loaded in a U-shaped quartz reactor tube and the reactor was placed into the sample port, which was located inside a heating element. Before starting TPD, the pre-reduced catalyst sample was degassed at 500 °C for 2 h under argon flow. The sample was saturated with hydrogen at 40 °C by flowing a mixture of gas containing 10%  $\text{H}_2$  and 90% Ar. Physically adsorbed hydrogen was removed by flowing argon gas at a rate of 50 mL/min for one hour. The temperature of the sample was increased at a linear heating rate under argon gas flow. A TCD detector analyzed the gas leaving the sample. For each sample, chromatograms were collected for pre-specified heating rates and after each experiment the sample was purged with argon flow at 500 °C for 1 h.

#### 2.2.3. Temperature programmed reduction

Temperature programmed reduction (TPR) experiments were carried out in a Micromeritics AutoChem II 2920 analyzer. Experiments were carried by placing a 0.1–0.15 g of catalyst sample in a quartz tube reactor (8.0 mm o.d.), and held at the middle of the tube by using quartz wool plug. Before TPR measurement, the sample was completely dried by flowing dry air (30 mL/min) over the sample and increasing the temperature at a heating rate of 10 °C/min until a temperature of 500 °C was reached. The temperature was then held at 500 °C for next 2 h. The sample was then brought back to the room temperature under 20 mL/min argon flow. A reducing gas mixture (10%  $\text{H}_2$ –90% Ar) was flown through the catalyst bed with a rate of 20 mL/min. The temperature increased linearly at 10 °C/min up to a maximum of 1000 °C and held at this temperature for 15 min. A cold trap was installed to absorb the water that formed during the pretreatment process and reduction reaction. The change of hydrogen concentration in the exit gas stream was determined via a thermal conductivity detector. Finally, the area of the resulting peak was integrated numerically to calculate the hydrogen consumption.

#### 2.2.4. Pulse chemisorption

Hydrogen pulse chemisorption experiments were performed to understand the metal dispersion on the saponite support sur-

Table 1  
Physical and chemical properties of feedstock (VGO)

Properties	Value
Appearance	Soft but solid at room temperature
Color	Greenish dark brown
Density (g/cm <sup>3</sup> 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

face. The particle size of the metal precursors can also be determined by this experiment. The sample was pretreated with an argon flow (50 mL/min). A series of hydrogen pulse (1.0 mL) were injected into the system at ambient temperature. A TCD detector analyzed the exit gas from the reactor. As hydrogen gas was adsorbed by the sample, peaks were created in the TCD reading of the outlet stream. The test was complete when two consecutive peaks had the same area.

### 2.3. Catalysts performances for HDS and HC activities

#### 2.3.1. Batch autoclave evaluations

The catalytic performance of the catalysts was conducted in a batch autoclave reactor using vacuum gas oil (VGO) as feedstock. The physical and chemical properties of the feedstock are listed in Table 1. The experiments were carried out at 400 °C and 13,800 kPa; these conditions are within the range of commercial hydroprocessing units. Before reaction, the catalysts were presulfided at 400 °C with a mixture of hydrogen sulfide gas (5%) and hydrogen gas (95%). In each batch, 300 mg catalyst and 100 g VGO was loaded into the reactor vessel, which was connected to a hydrogen cylinder. To remove air, the system was purged with hydrogen flow. A leak test was carried out at elevated reactor pressure (13,800 kPa) using a hydrogen detector. In order to attain the reaction temperature (400 °C) a temperature program was started from the system control panel

with a heating rate of 5 °C/min. To minimize the reaction during the heating period a low reactor pressure (6900 kPa) was maintained. When the reactor reached to 60 °C the stirrer was turned on at a speed of 800–900 rpm. At 400 °C the hydrogen gas pressure of the system was again increased to 13,800 kPa and maintained this level throughout the experiment. The reaction time was counted from this point to onwards and each experiment was carried out for next 90 min. After completion of the pre-specified reaction time the reactor was opened to cool down to room temperature and gas, liquid product and spent catalyst samples were collected for analysis. Gas chromatography was used to analyze the gas sample, and the liquid was analyzed for boiling point distribution by GC simulated distillation. HPLC and CHNS analysis of the liquid product was also conducted for the boiling point distribution of different hydrocarbon groups (saturates, aromatics and polars) and for elements, respectively. The amount of coke deposition on the spent catalyst was determined from an elemental analysis of the deposited material on the catalysts. The HDS activity of the catalysts was determined from the CHNS analysis data and the cracking activity was counted by the percentage of liquid product having boiling point below 343 °C (since the initial boiling point of the feed VGO was 343 °C).

## 3. Results and discussion

### 3.1. Catalysts bulk composition

In hydrotreating catalysts, the acidic support offers the cracking activity while the hydrogenation reactions take place on the metal components. Therefore, it is very important to maintain the balance between the cracking and hydrogenation functionalities. An elemental analysis of fresh catalysts provided 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. The elemental analysis of fresh catalysts showed that the Co loading was slightly varied in the presence of the noble metal and the maximum loading (18.5 wt.%) occurred on unpromoted Co-saponite (Table 2). This variation is probably due to the occupation of ion-exchange sites (mainly Na and Mg) on saponite 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 the scope of the present work.

Table 2  
Composition and physical characterization of Co-saponite catalysts

Catalyst description	Metal loaded (wt.%)				BET surface area (m <sup>2</sup> /g)	Total pore volume (mL/g)	Pore size (Å)
	Co	Rh	Pd	Pt			
Saponite	–	–	–	–	600	0.47	31.3
Co-saponite	18.5	–	–	–	514	0.44	29.3
Co-Rh-saponite	18.3	1.0	–	–	512	0.41	27.3
Co-Pd-saponite	18.3	–	1.0	–	507	0.40	26.7
Co-Pt-saponite	18.1	–	–	1.0	511	0.40	26.7

### 3.2. Catalysts characterization

#### 3.2.1. BET surface area

BET surface area and the pore volume of the bare saponite and those of the prepared catalysts samples are reported in Table 2. It was noticed that the specific surface area, pore volume and average pore diameter were moderately affected upon the introduction of Co on the high porous saponite support. It can be deduced from this observation that the cobalt oxides were possibly distributed uniformly on the pore surface of the support, and this decreased pore volume and the surface area. This uniform metal dispersion possibly helped minimize the blockage of the pore, which is very important for the catalysts activity. On the other hand, the addition of the promoter (noble metals) did not change the specific surface area and the pore volume of the catalysts. There could be two possible reasons of this unchanged surface area and pore volume. First the quantity of the noble metal loading was very small as compared to Co and secondly the small amount of impregnated noble metal atoms were mostly dispersed on the outer layer of the support. Therefore, the physical characteristics of the catalyst were unchanged due to the addition of noble metals. On the basis of this specific surface area, average pore volume and pore size measurement results, it can be stated that the prepared catalysts can offer high surface area and large pores to access a major fraction of the heavy molecules during the hydrotreating reactions.

#### 3.2.2. H<sub>2</sub>-TPD and energy of desorption

TPD characterization is a powerful tool for studying the adsorption steps in heterogeneous catalytic reaction system. The surface reactivity of the prepared catalysts was assessed by investigating the energetics and kinetics of metal and support interaction using temperature programmed H<sub>2</sub> desorption technique. The following assumptions were made for these estimations:

- (i) The surface was homogeneous for adsorption of H<sub>2</sub>, that is,  $k_{\text{des}} = k_{\text{des}0} \exp(-E_{\text{des}}/RT)$ , is not a function of surface coverage ( $\theta$ ).
- (ii) Re-adsorption of the desorbed gas does not occur.
- (iii) Concentration of H<sub>2</sub> (adsorbate) in the gas phase is uniform throughout the bed.
- (iv) Desorption of hydrogen atom is second-order.
- (v) Linear temperature increases with time.

In order to prevent the re-adsorption (assumption ii) a high flow rate of gas was maintained through the small bed of solid sample. Assumption (iv) holds correct because hydrogen desorption is generally limited by the rate of recombination of two atoms of hydrogen to form molecular hydrogen [16]. Assumptions (iii) and (v) were satisfied by choosing the appropriate experimental conditions.

The kinetics of the desorption process follow a simple power law which can be expressed as [16]:

$$r_{\text{des}} = - \left( \frac{d\theta_{\text{des}}}{dt} \right) = k_{\text{des}0} \theta_{\text{des}}^n \exp \left( \frac{-E_{\text{des}}}{RT} \right) \quad (1)$$

Table 3  
Heat of desorption of hydrogen

Sample ID	$E_{\text{des}}$ (kJ/mol)	Correlation coefficient ( $R^2$ )
Co-saponite	90.3	0.99
Co-Rh-saponite	55.1	0.99
Co-Pd-saponite	72.0	0.94
Co-Pt-saponite	73.8	0.97

$$\text{at a linear heating rate } (\alpha), \quad \frac{dT}{dt} = \alpha \quad (2)$$

The linear heating rate can be related to the rate of desorption by

$$\frac{d\theta_{\text{des}}}{dt} = - \left( \frac{d\theta_{\text{des}}}{dT} \right) \left( \frac{dT}{dt} \right) = - \left( \frac{d\theta_{\text{des}}}{dT} \right) \alpha \quad (3)$$

Therefore, Eqs. (1) and (3) yields:

$$\begin{aligned} \frac{d^2\theta_{\text{des}}}{dT^2} = & - \left( \frac{k_{\text{des}0}}{\alpha} \right) \left[ (n\theta_{\text{des}}^{n-1}) \frac{d\theta_{\text{des}}}{dT} \exp \left( \frac{-E_{\text{des}}}{RT} \right) \right. \\ & \left. + \theta_{\text{des}}^n \left( \frac{E_{\text{des}}}{RT^2} \right) \exp \left( \frac{-E_{\text{des}}}{RT} \right) \right] \quad (4) \end{aligned}$$

$$\text{at maximum desorption rate } (T = T_p), \quad \frac{d^2\theta_{\text{des}}}{dT^2} = 0 \quad (5)$$

Substituting Eqs. (3) and (5) into Eq. (4) and after mathematical steps, the following equation can be obtained:

$$\left( \frac{T_p^2}{\alpha} \right) = \left( \frac{E_{\text{des}}}{k_{\text{des}0} R n \theta_{\text{des}0}^{n-1}} \right) \exp \left[ \frac{E_{\text{des}}}{R} \left( \frac{1}{T_p} - \frac{1}{T_{p0}} \right) \right] \quad (6)$$

Using Eq. (6), the heat of desorption can be estimated by performing a nonlinear regression of TPD experimental data with varying the heating rate linearly and keeping the initial surface coverage same ( $\theta_{\text{des},0}$ ) for every experiment. The centering temperature ( $T_{p0}$ ) was used to minimize the cross-correlation between parameters. For each catalysts the H<sub>2</sub>-TPD experiments were carried out at a set of linear heating rates (30, 20, 15, 10, and 5 °C/min) and the maximum desorption peak temperature recorded for each case. Table 3 lists the estimated heat of desorptions values and the correlation coefficients. The energy of desorption for the plain Co-saponite was found 90.3 kJ/mol while the values were 55.1, 72.0, and 73.8 for Rh, Pd and Pt promoted Co-saponite, respectively. Thus, the H<sub>2</sub>-TPD study shows that the noble metal modification play a significant role on the adsorption and desorption processes of the promoted catalysts by reducing the activation energy. The reduced activation energy has a great importance in hydrocracking catalysts to generate sufficient amount of reactive hydrogen for hydrogenation of the cracking intermediates leading to substantially higher activity and stability for longer period of time.

#### 3.2.3. Metal reduction and dispersion

In supported catalysts, the metals are present in their oxide forms. Before reaction the metal oxides are required to be

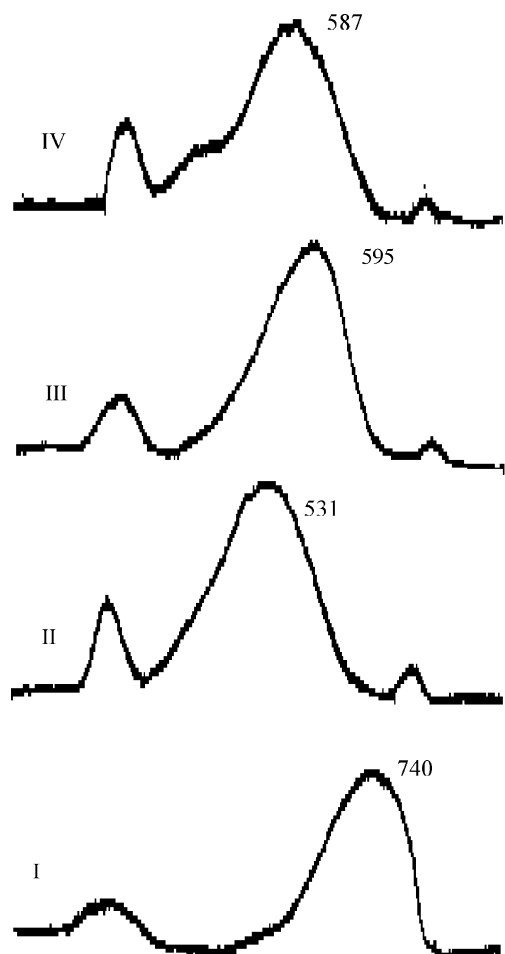
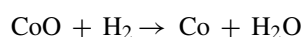
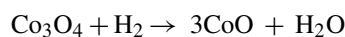


Fig. 1.  $H_2$ -TPR spectra of saponite supported (I) Co, (II) Co-Rh, (III) Co-Pd and (IV) Co-Pt catalysts.

reduced to their metallic/sulfide states, because the reduced phase is more active than that of the metal oxides [17]. Therefore, it is very important to characterize the catalyst in order to investigate the reducibility of the catalyst. Temperature programmed reduction (TPR) provides the information about: the formation of metal oxide phase(s), interaction between those phase(s), the interaction between metal oxide and support material, and the reduction characteristics of the catalysts. Furthermore, TPR helps in the study of the promotional effects of noble metals on the reduction of the main active cobalt species. Concerning hydrogen spillover effects (will be explained latter), TPR can also provide insight into this phenomenon through the measurement of hydrogen consumption and shifting of the reduction temperature [12,13]. Fig. 1 illustrates the reduction curves of various catalysts studied in this investigation. For all the catalysts, the TPR profiles are similar, which indicates that the same types of metal oxides are present in both unpromoted and noble metal promoted catalysts. The structures of these TPR curves can be analyzed by comparing the structures of the known substances that have been reduced under the same conditions. The small first peak occurred at a temperature of about 225 °C and attributed to the reduction of trivalent Co oxide ( $Co_2O_3/Co_3O_4$ ) to divalent Co oxide (CoO). Voß et al. [18] reported a similar

temperature for the reduction of pure species  $Co_3O_4$ . They also proved the formation of such species on a supported system by XRD analysis. Noronha et al. [19] confirmed the reduction of  $Co_3O_4$  by TPR study of noble metal promoted and unpromoted Co catalysts. The major peak, appearing between 525 and 750 °C, was believed to be the reduction of divalent Co oxide (CoO) to the metallic Co ( $Co^0$ ) [18–20]. Some researcher also called it amorphous over layer of CoO, which interacted firmly with the support surface [12,21]. Accordingly, the overall TPR reduction steps on raising the temperature of the sample can be represented by the following reaction steps:



The similarities between the unpromoted and noble metal promoted Co-saponite suggested no alloy formation between cobalt and the noble metals [11]. The only exception is a small peak, which was noticed with all the noble metal promoted catalysts. This peak considered to be a small fraction of the second peak, which was unaffected by the noble metal or possibly a complex between the support and the cobalt species [9]. Another important observation is the shifting of the second peak towards a lower temperature due to the presence of the noble metals. The shift occurred in the range of 140–215 °C, and was clearly due to the promotional effects of the noble metals [19,22]. From a mechanistic point of view, this effect can be explained by the so-called hydrogen spillover phenomenon. This effect can be described as follows: the noble metal can dissociate molecular hydrogen to highly reactive hydrogen species (i.e.  $H^+$ ,  $H^-$ ,  $H^{3+}$ ) or ion pair. Such reactive species can easily attack the cobalt oxide(s) and reduce them at comparatively lower temperatures [14]. The noble metal promotional effects can also be explained in the following ways: (I) the decreased activation energy of the cobalt oxide reduction reaction due to the presence of noble metal which has been revealed by the  $H_2$ -TPD study; (II) the dispersion of cobalt oxide on saponite can also be enhanced in such a way that it is reduced at a comparatively lower temperature; (III) an increase in the number of nucleation sites for reduction [9,19,23]. Among the three noble metals used, Rh exhibited a more pronounced promotional effect compared to Pt and Pd in the reduction of Co species supported on saponite. In catalysts samples with equal loading, Rh shifted the peak temperature by 215 °C while Pt and Pd showed a shift of 120 and 140 °C, respectively, which reveals that Rh reduces cobalt oxide more readily than Pt and Pd.

A quantitative analysis of hydrogen consumption during TPR can also be made since there is a direct relation between the amount of hydrogen consumption and the amount of metal reduction. Table 4 lists the amount of hydrogen consumed in each peak of TPR profiles of different catalysts. The values were determined from the area measurement of the peaks. For both peaks, it was noticed that the amount of hydrogen consumption was fairly increased in cases of noble metal-promoted catalysts as compared to the results for unpromoted Co-saponite.

Metal dispersion determined by pulse chemisorption of hydrogen on Co-saponite catalysts with and without the addi-

Table 4  
Hydrogen uptake during TPR

Catalyst description	Hydrogen consumed (mmol/g cat.)		
	Peak I	Peak II	Peak III
Co-saponite	0.234	2.695	0
Co-Rh-saponite	0.352	3.144	0.023
Co-Pd-saponite	0.327	2.917	0.026
Co-Pt-saponite	0.295	2.791	0.026

tion of noble metals is compared in Table 5. The modification of the saponite support with noble metal results in a significant improvement in metal dispersion. The possible reason an increased metal dispersion obtained with the addition of noble metal is the lower reduction temperature of the catalyst limiting sinterings [24]. The average Co particle size on modified catalysts was also slightly smaller than that of the unpromoted Co-saponite catalyst. The each of noble metal modified catalysts was subjected to repeated reduction–oxidation cycles after subsequent pretreatment. The metal dispersion was determined after each reduction cycles. A consistent metal dispersion was observed in the subsequent reduction cycles. This result indicates that the stable metal support interaction and metal redispersion and during the catalytic processes.

### 3.3. Catalyst performances in batch reactor

Both the HDS and hydrocracking (HC) activities of the catalysts were tested in batch autoclave reactor experiments using VGO as feedstock, which is the real feed in a heavy oil hydrotreating unit. The experimental temperature and pressure was selected as 400 °C and 13,800 kPa, respectively. These values are within the range of typical hydrotreating units in the refinery processes. The experiments were carried out for 90 min. After reaction, the gas and liquid products and the spent catalysts were collected for analysis. A standard Co-Mo/Al<sub>2</sub>O<sub>3</sub> 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-saponite catalysts, the Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was not included in the subsequent discussion. The results show that the gas formation rates were considerably decreased with the modification of Co-saponite by the noble metals (Fig. 2). The availability of reactive hydrogen due to the presence of the noble metals might have controlled the over cracking of the hydrocarbons which produces the lighter gases. It has been explained in the TPR studies

Table 5  
Metal dispersion and metal crystal size

Catalyst description	Dispersion (%)	Crystal size (nm)
Co-saponite	12.1	7.93
Co-Rh-saponite	14.2	6.76
Co-Pd-saponite	13.7	7.01
Co-Pt-saponite	12.5	7.68

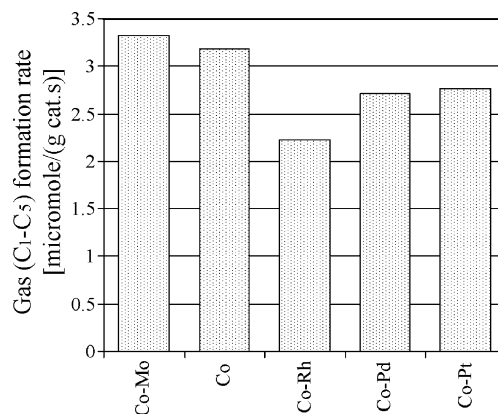


Fig. 2. Light gas (C<sub>1</sub>–C<sub>4</sub>) formation rate in batch autoclave reactor using VGO as feedstock.

that the noble metals can generate reactive hydrogen species at lower temperature, which maintained sufficient amount reactive hydrogen for the hydrogenation reaction. Therefore, the cracked intermediates immediately hydrogenated to produce stable product and the cracking reaction thus terminated before producing more gaseous hydrocarbons [24,25]. Lower rates of gas production is preferable for the petroleum refineries because the excessive gas production can create operational problems and some times the gaseous products are considered as waste. Thus the addition of noble metal has positive impact on minimizing the gas formation during the hydrotreating reactions. The liquid product analysis results also indicate favorable characteristics of the noble metal promoted catalysts. Fig. 3a and b displays the HC and HDS activity data of various catalysts evaluate for this study. The presence of the noble metals considerably improved the HC activity of Co-saponite. Compared to the unpromoted Co-saponite catalyst, the HC activity were increased by 33.3, 9.7 and 6.3% for Rh, Pt and Pd promoted catalyst, respectively. The HDS activity of Co-Rh-saponite catalyst was also increased significantly (18.6%). However, the HDS activity of the Pd and Pt promoted Co-saponite was marginally improved (5.8% for Pt promoted catalyst and 2.4% for Pd promoted catalyst). The order of reactivity of the catalysts was Co-Rh > Co-Pd > Co-Pt > Co supported on saponite materials. Expectedly, the Rh promoted catalysts displayed superior activity in comparison to the rest of the catalysts.

The batch reactor evaluation results are consistent with the hydrogen reduction results in the TPR studies. All the noble metal promoted catalysts showed a reduced reduction temperature and higher reducibility, which have been helped enhancing the catalytic activities of the catalysts. This is called the synergy effects of the promoter and the main active species (Co). A similar synergic phenomenon also presented by many authors in the literature [10,12]. The overall catalytic steps of noble metal promoted Co-saponite can be explained as shown in Fig. 4. The heavy hydrocarbon molecules, including the sulfur bearing organic compounds first adsorb and crack on the acidic support sites to generate lighter hydrocarbon intermediates. At the same time the hydrogen from the gas phase also adsorbs and dissociated on the noble metal sites to form reactive hydrogen species. Finally, the cracked hydrocarbon intermediates react with the

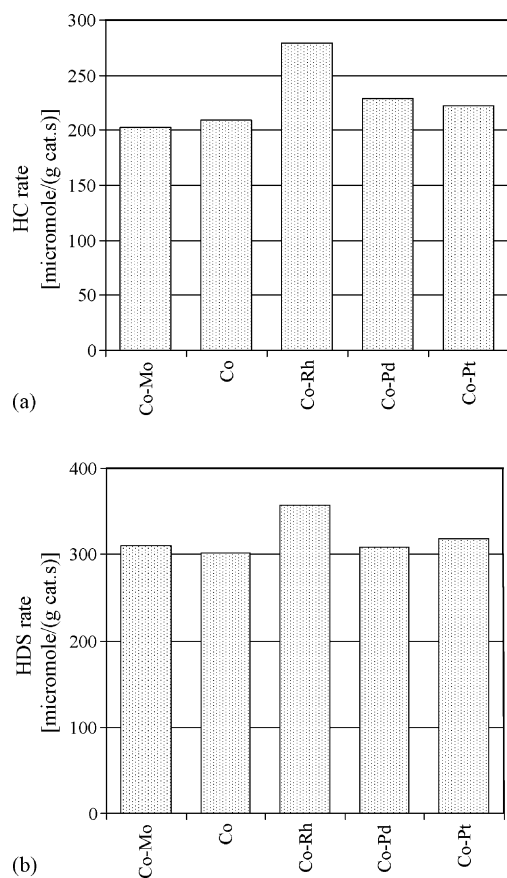


Fig. 3. (a) HDS and (b) HC activities of Co-Mo/Al<sub>2</sub>O<sub>3</sub> (reference catalyst), saponite supported (I) Co, (II) Co-Rh, (III) Co-Pd and (IV) Co-Pt catalysts in batch autoclave reactor for VGO hydrotreating.

hydrogen on the hydrogenation sites (Co) to produce stable lighter products. Thus the presence of even a small amount of noble metal influence the overall reaction steps and consequently the reaction rates increase significantly. A similar mechanism for a bi-noble metal promoted Co catalyst has been reported for VGO hydrocracking [10]. Sugioka et al [3,4] also proposed a consistent mechanism for thiophene HDS over USY zeolite sup-

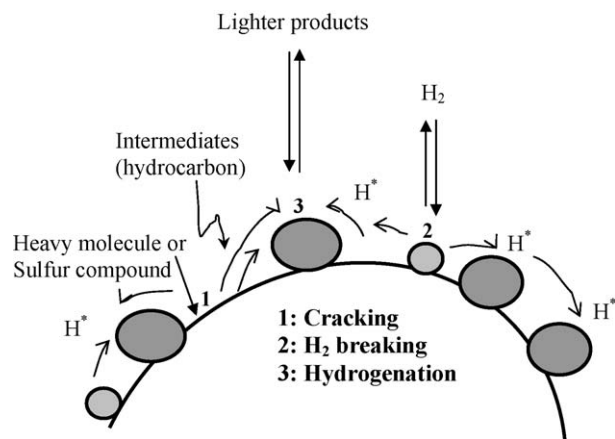


Fig. 4. Hypothetical reaction mechanism of heavy oil hydrocracking over noble metal promoted Co-saponite catalysts [arc: acidic support surface; larger circles: Co atoms; smaller circles: noble metals].

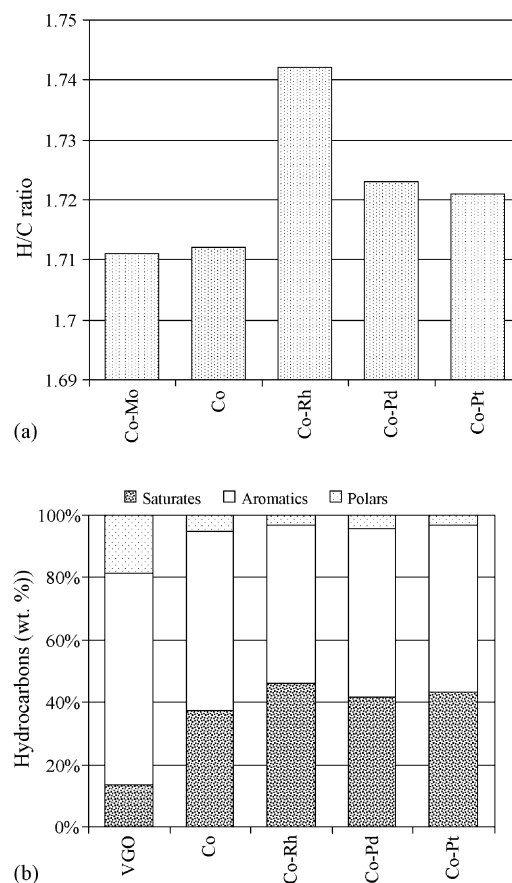


Fig. 5. (a) H/C ratio and (b) hydrocarbon groups in the liquid product from batch reactor experiments.

ported Pt and Pt-Pd catalysts. The above hypothesis was verified further by the hydrogen to carbon ratio and the HPLC results of the liquid product as shown in Fig. 5a and b, respectively. As it can be seen in the relevant figure, the hydrogen to carbon ratio was significantly improved in the case of the noble metal modified catalysts. This result indicates that more hydrogen was added to the liquid products through subsequent hydrogenation of cracked intermediates as well as the removal of sulfur atoms from the sulfur bearing organic compounds. The HPLC data also supports the higher hydrogenation activity due to the presence of noble metals. It shows that the saturated hydrocarbon fraction has been increased while the aromatics and polar fraction has been decreased considerably.

The enhanced catalytic performance of the noble metal promoted catalysts has been explained in different ways. The overall effect was explained by considering the acidic nature of the spillover hydrogen species, which gave rise to protons to generate Brønsted acid sites for cracking reactions and provide enough reactive hydrogen for the hydrogenation reaction. Eventually, both the cracking and hydrogenation activities were increased. Similar explanation also have been presented by some other researchers to describe the promotional effects of the noble metals on hydrotreating catalysts, although the term “hydrogen spillover” was not used [9,24,25]. On the basis of energy of hydrogen desorption as found in the H<sub>2</sub>-TPD study, it is clear that extent of reactive hydrogen generation can be increased

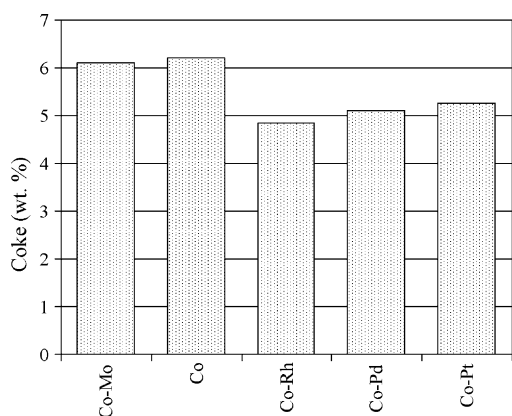


Fig. 6. Carbon analysis on spent catalysts from batch reactor experiments.

by noble metal modification. Consequently, the availability of spillover hydrogen will be increased to react with the cracking intermediates. Spent catalyst characterization results also suggested the participation of the spillover hydrogen, introduced by the noble metals. The coke deposition on the noble metal promoted Co-saponite catalysts was considerably decreased due to the effect of hydrogen spillover (Fig. 6). During the reaction, the gas phase hydrogen adsorbed on the noble metal sites to produce enough reactive hydrogen species ( $H^+$ ,  $H^-$ ,  $H_3^+$ , etc.) and desorbed quickly. This desorbed species spillover to the hydrogenation (Co) as well as the cracking (support) sites and reacted with the hydrocarbon intermediates to produce more stable molecules. As a result, the deposition of the intermediates decreased, leaving the active sites clean for further reaction. Some other researcher explained the reduced coke deposition by remote control mechanism of the spillover hydrogen [10,11,26]. According to the remote control interpretation, the noble metals (Rh, Pt, Pd) are hydrogen donor through spillover mechanism. The spillover hydrogen influenced the cracking reaction by controlling the concentration of carbonium ions and other unstable reaction intermediates, thereby hindering the deposition of carbons/hydrocarbons by converting them to stable products. Consequently the catalyst surface remained clean and active for further reaction.

#### 4. Conclusion

Compared to unpromoted Co-saponite, the noble metal modified Co-saponite catalysts are superior bifunctional (cracking and hydrogenation) catalysts for heavy oil upgrading purpose. The introduction of noble metal leads to a higher catalytic activity and reduced carbon deposition on the catalyst. This improved performance is due to a better balance between the cracking and hydrogenation functionalities of the catalysts. The noble metals are more active towards creating more reactive hydrogen species compared to Co, which enhanced the hydrogenation reaction and reduced the carbon deposition, and maintained active sites during the reaction. TPR experiments indicate that the promotional effect of noble metals is due to the increased amount of active Co species and high metal dispersion. The  $H_2$ -TPD study suggested that the reduced energy of activation for hydrogen adsorption on

the catalyst surface is due to the presence of the noble metals. Finally, Rh showed superior activity as a promoter in comparison to the other noble metals (Pt and Pd), which is possibly its ability of generating more reactive hydrogen species in the hydrocracking environment.

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