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Rejuvenation of Residue Hydroconversion Catalysts by H-donor Solvents

Yingxian Zhao · Murray R. Gray · Feng Wei

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Abstract The spent hydroprocessing catalyst from conversion of bitumen was extracted with hydrotreated gas oil, tetralin and tetralin-pyrene as solvents at 400 °C and 10 MPa hydrogen pressure in order to remove coke and rejuvennate catalyst activity. The reactive extraction of solvents partially removed the coke on catalyst with the order of effectiveness: gas oil $<$ tetralin $<$ tetralin-pyrene. Tetralin showed higher ability than the gas oil for the coke removal by donating hydrogen in situ to hydrogenate the coke. Binary tetralin/pyrene solvent mixture gave synergism for removing coke on the catalyst due to the ability of pyrene to shuttle hydrogen to form more active H-donors, hydropyrenes. HDS activity of the spent catalyst was enhanced after the coke removal.

Keywords Residue hydroconversion · Coked catalyst · Rejuvenation · H-donors

1 Introduction

Catalytic hydroconversion is one of the process options for upgrading of petroleum residue. During hydroconversion processes, catalyst deactivation is often caused by the deposition of coke and metals on the catalyst surface [1–4]. Several studies have shown that the activity of residue hydroconversion catalysts is proportional to the coke concentration [4, 5]. In processing highly asphaltenic bitumen residue, the decay of catalyst activity due to coking may be dominant, which severely reduces the lifetime of catalyst. Methods to either control deposition of coke on catalyst, or remove coke from catalyst could rejuvenate catalyst activity and extend its life-time of service.

Regeneration of deactivated hydrotreating catalysts is normally carried out by burning off the deposited coke with air. In oxidation of spent hydroconversion catalysts, however, the vanadium accumulated in the catalyst could destroy the mechanical strength of the alumina catalyst pellets [6], making the oxidative regeneration unacceptable for vanadium-rich spent catalysts from residue hydroconversion. An interesting alternative is to remediate the spent catalyst by solvent treatment in situ or outside reactor. Previous studies have shown that heteroatomic solvents such as pyridine and quinoline were not suitable for coke removal due to the deposition or adsorption on the catalysts, while the hydrotreated gas oil was a good solvent for removing tender coke deposited on fresh catalyst in early stage of operation, but not effective for removing aged coke from catalyst with long service hours [7].

The ability of hydrogen-donor solvents to promote coal conversion has been well recognized [8–11]. Most often tetralin has been used as a hydrogen donor reagent for coal conversion [12–15]. Dihydropyrene and hexahydropyrenes exhibited higher activity of donating hydrogen than tetralin [16, 17]. Binary hydrogen donor and acceptor solvent mixtures such as tetralin-pyrene showed synergism in coal conversion [18], because pyrene has high ability to shuttle hydrogen to form hydropyrenes. It was also reported that hydrogen-donor solvents enhanced conversion of residues to distillable liquids without forming coke [19–21], but little has been reported in literature on remediation and

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Y. Zhao (✉) · F. Wei
Ningbo Institute of Technology, Zhejiang University, Ningbo, Zhejiang 315100, People's Republic of China
e-mail: zyx@nit.zju.edu.cn

M. R. Gray
Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, Canada T6G 2G6

rejuvenation of spent residue hydroconversion catalysts by removing coke with hydroaromatic solvents.

The purpose of this work was to study the ability of H-donor solvents for rejuvenating the activity of spent residue hydroconversion catalysts by removing coke from the catalysts. In comparison with gas oil, tetralin was used to treat a spent hydroprocessing catalyst under certain conditions. The mechanism of the coke removal by hydrogenation reaction was investigated. In addition, extraction of the spent catalyst with binary tetralin-pyrene solvent mixtures was conducted to reveal the synergism of H-donor and H-acceptor in removing coke on catalyst. The HDS (hydrodesulfurization) activities of the original and treated spent catalysts were determined by measuring sulfur removal from bitumen at standard reaction conditions.

2 Experimental

2.1 Materials

A commercial Ni/Mo on γ-alumina catalyst for residue hydroconversion was used in this study. The fresh catalyst contained 2–4% NiO and 10–15% MoO_3, supplied as 1 mm cylindrical extrude. Surface area was 150–200 m^2/g by nitrogen adsorption and the BET equation, pore volume was 0.4–0.8 mL/g and mean pore diameter was 7–15 nm, as determined by nitrogen desorption. The spent catalyst sample was obtained after service over 30 days in an industrial hydroprocessing unit. This reactor operates at 425–450 °C at a pressure of 10–15 MPa with 55–85% hydrogen in the feed gas. At least 1% of the catalyst in the reactor is replaced daily, and the study sample was from such routine withdrawls of catalyst. The sample was Soxhlet extracted for 24 h with methylene chloride, then vacuum dried at 65 °C, to remove soluble oil from the catalyst pores.

Hydrotreated gas oil was produced in a commercial refinery, and selected as a clean, high boiling solvent material in this study. The original oil,bitumen coker distillate,had been subjected to two stages of catalytic hydrotreating to reduce concentrations of sulfur and nitrogen [7]. The properties of the gas oil were presented in Table 1. Other chemicals, including tetralin, pyrene and hexahydropyrene, were supplied by Fisher Scientific, and used as received.

Athabasca bitumen was used as a feed for testing HDS activity of the original and treated spent catalysts. Its properties are listed in Table 1.

2.2 Coke Removal by Reactive Extraction

The gas oil, tetralin, and tetralin-pyrene mixture were used as solvents to extract the coke from the spent catalyst in a 15 mL micro-batch reactor. A typical single-step run was carried out at 400 °C and 10 MPa H_2 pressure for 1 h. Multi-step extraction used a series of 1-h reactions, with replacement of the solvent after each step for up to 8 h cumulative time. After the extraction, the catalyst samples were Soxhlet extracted with toluene for 24 h, followed by drying at 110 °C for 2 h, and then kept for elemental analysis or HDS activity test.

Table 1 Properties of feed bitumen and gas oil solvent

	Athabasca bitumen	Gas oil solvent
Sulfur (wt %)	4.89	0
Nitrogen (ppm)	4500	25
Nickel (ppm)	73	0
Vanadium (ppm)	191	0
Aromatic C (mol %)	36	14.9
Asphaltenes (wt %)	16.0	0
Micro carbon residue (wt %)	13.7	0
Boiling range (°C)	~300–524+	213–516

2.3 HDS Activity Test

HDS activities of the original and treated spent catalysts were examined by reacting Athabasca bitumen in a 15 mL micro-batch reactor. Typically, a sample of 0.5 g catalyst was mixed with 3 g bitumen in the reactor, and then pressurized with nitrogen to leak-test the reactor. After the nitrogen was released, the reactor was pressurized with hydrogen and purged twice before adding hydrogen to obtain the desired cold pressure. The reactor was then immersed in a fluidized sand bath at 430 °C for 1 h. After the reaction was completed, the reactor was cooled in water. The detail information for collection, separation and analysis of products can be found in previous paper [22].

2.4 Analysis

Elemental analyses of catalyst samples were performed on a Carlo Erba Stumentazione Elemental Analyzer. Prior to the analysis, the catalyst samples were treated with the similar procedure in Sect. 2.2. To ensure representative sampling, a 100-mg portion of the dried sample was crushed to a powder and vacuum heated at 110 °C for 1.5 h, and a 2-mg sample was used for analysis. This analysis was done by combusting the sample, followed by GC column separation, and then thermal conductivity detection. Metal contents of the spent catalyst was determined after ashing by ion-coupled plasma determination. The analysis of the extracts from the reactive extraction of spent catalyst was conducted with MS-GC. Sulfur in the liquid samples was determined by combustion of the sample followed by fluorescence detection.

3 Results and Discussion

3.1 Characterization of the Spent Catalyst

The data of Table 2 give the C, S, N, V, Fe and Ca contents per unit of alumina in the catalyst, as well as the Ni content per unit of initial Ni in the catalyst, thereby correcting for both coke and metal sulfide content. As indicated, the catalyst contains significant amounts of coke and metals after use in residue hydroconversion. The analyses of scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) by Carruthers et al. [23] showed that the concentration of V was approximately twice as high at the exterior as in the center of the spent catalyst pellets, and that Ca and Fe were concentrated in a thin skin at the outer edges of the pellets. Therefore, the outer surface of spent catalyst was coated with a skin of Ca and Fe minerals.

3.2 Coke Removal from the Spent Catalyst

Coke removal was tested with the gas oil, tetralin and tetralin-pyrene as solvents in a micro-batch reactor at 400 °C and 10 MPa H_2 pressure. The data of Table 3 list the C, H, N and S contents of the original and solvent-extracted spent catalysts. In addition to a high carbon content, sulfur content of the original spent catalyst was high due to the accumulation of metal sulfides from demetallization of the bitumen [6, 7]. The carbon content of the spent catalyst dropped from 11.84 to 10.62, 8.48 and 7.67 by 1-h extraction of gas oil, tetralin, and tetralin-pyrene, respectively. In parallel with a reduction in carbon content, these solvents gave similar trends in reduction of nitrogen and sulfur contents. On the other hand, H/C ratio of the catalyst increased from 0.58 to 0.59 by gas oil, to 0.68 by tetralin, and to 0.71 by tetralin-pyrene, indicating that the deposits on the catalysts became less carbonaceous.

In Fig. 1 the carbon contents of catalysts are plotted as a function of cumulative reaction time. By the extraction of each tested solvent,the carbon content of catalyst dropped more significantly during the first 1-h reaction time, and then decreased more slowly to reach a stable level with increasing cumulative extraction time. The stable levels of carbon content of catalysts are 10.2, 7.3 and 5.8 corresponding to the extraction of gas oil, tetralin and tetralin/pyrene respectively. These data suggest that different solvent system possess different power to the removal of coke in the order of tetralin/pyrene > tetralin > gas oil, a significant amount of coke can be removed from the aged

Table 2 C, S, N and metal contents of the spent catalyst

Element	Elemental composition	
	g/g initial alumina	g/g initial nickel
C	0.22	
S	0.21	
N	0.006	
V	0.20	
Fe	0.006	
Ca	0.023	
Ni		3.3

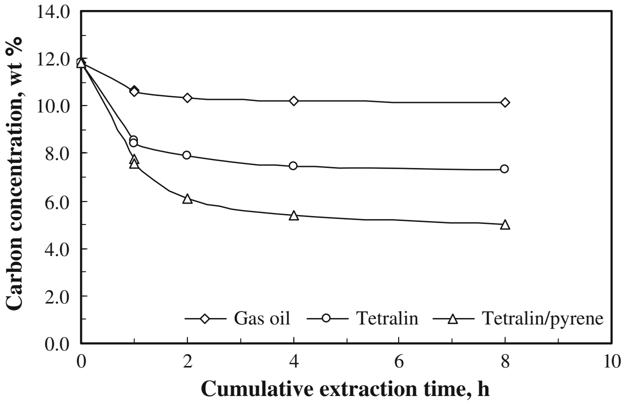


Fig. 1 Carbon removal from spent catalyst using gas oil, tetralin and tetralin/pyrene at 400 °C and 10 MPa H_2 pressure with 1 h per step, extraction with methylene chloride after each step

Table 3 Characteristics of original and remedied spent catalysts

Properties	Samples			
	Original[a]	Extracted by gas oil	Extracted by tetralin	Extracted by tetralin-pyrene
Carbon (wt %)	11.84	10.62	8.48	7.67
Hydrogen (wt %)	0.575	0.522	0.483	0.479
Sulfur (wt %)	11.57	10.34	9.09	8.96
Nitrogen (wt %)	0.341	0.289	0.266	0.241
H/C (atomic)	0.58	0.59	0.68	0.71

[a] Service time: >30 days

spent catalyst by hydrogenation. The hydrogen from an H-donor solvent is more effective to hydrogenate the carbonaceous deposits on catalyst, while molecular hydrogen seems not reactive to the coke. For removing the deposits, the gas oil with low aromaticity is less effective than tetralin with high ability of hydrogen donor. The binary solvent mixture of tetralin (H-donor) and pyrene (H-acceptor) shows synergism in removing coke on catalyst, due to the ability of pyrene to shuttle hydrogen from the gas or tetralin in situ to form more active H-donors, hydropyrenes.

3.3 HDS Activities of the Catalysts

To compare the activity of original and remedied catalysts for residue hydroconversion, the whole Athabasca bitumen was cracked over these catalysts in a micro-batch reactor at 430 °C and 10 MPa H_2 pressure for 1 h. As illustrated in Fig. 2 the fresh catalyst gave a sulfur removal of 80% under the reaction conditions, in comparison to the removal of 58% from the original spent catalyst. After 1-h extraction by gas oil, tetralin and tetralin-pyrene, the catalysts gave the sulfur removal of 67, 71 and 74 respectively.

In Fig. 3 the HDS activities of catalyst are plotted as a function of carbon/alumina ratio in the catalyst. The carbon/alumina ratio of the original spent catalyst decreased from 0.22 to 0.19–0.20 by gas-oil extraction, to 0.14–0.16 by tetralin extraction, and to 0.09–0.14 by tetralin/pyrene extraction. With increasing the carbon/alumina ratio in catalyst from 0 to 0.22, the HDS activity of the catalyst decreased slightly at the ratio <0.1, and dropped rapidly at the ratio >0.1. Since the deactivation of catalysts for bitumen conversion is mainly caused by deposits of coke and metals on the catalysts, it was expected that the spent catalysts were rejuvenated by removing the deposits with reactive extraction of gas oil and aromatic solvents. Considering the fresh catalyst gave a sulfur removal of 80%, the recovery of HDS activity from 58% of the original spent catalyst to 74–77% of the remedied catalyst with tetralin-pyrene is very significant. In other words, the reactive extraction with H-donor solvent may provide an effective and economic way to rejuvenate the deactivated hydroconversion catalyst, which could overcome defects of oxidative regeneration method.

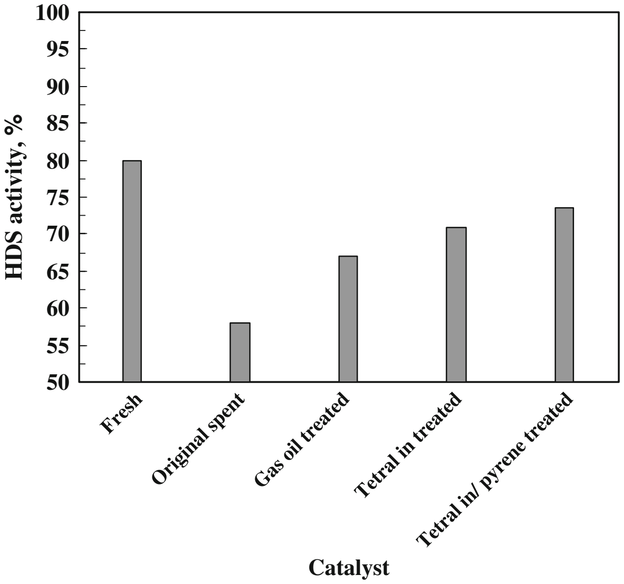


Fig. 2 HDS activity of fresh, spent and remedied Catalyst Catalytic hydroconversion of Athabasca bitumen in microbatch reactor at 430 °C and 10 MPa H_2 for 1 h

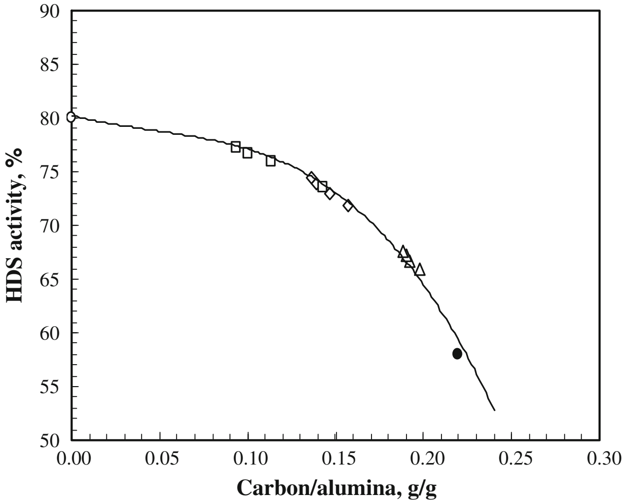


Fig. 3 HDS activity of catalyst as a function of carbon content: (○) fresh catalyst; (●) original spent catalyst; (□) extracted by tetralin/pyrene; (◇) extracted by tetralin; and (Δ) extracted by gas oil

3.4 Mechanism and Consequence of Solvent H-transfer

The different abilities of various solvent systems for removing coke on the spent catalyst arouse some interests to uncover the mechanism of H-donor solvent rejuvenating the coked catalyst. The MS-GC analysis on the extracts (the used solvents) from reactive extraction of the original spent catalyst solvents may provide an insight to the mechanism.

As illustrated in Fig. 4a, the reactive extraction by pure tetralin at 400 °C and 10 MPa H_2 pressure for 1 h gave a tetralin conversion of 28.4%, and the key compounds in the produced extract included tetralin ($C_{10}H_{12}$), naphthalene ($C_{10}H_8$), decahydronaphthalenes ($C_{10}H_{18}$), 2,3-dihydro-1-methylindene ($C_{10}H_{12}$) and butyl benzene ($C_{10}H_{14}$). Obviously, the tetralin must have been involved the following reactions: decomposition to form butyl benzene

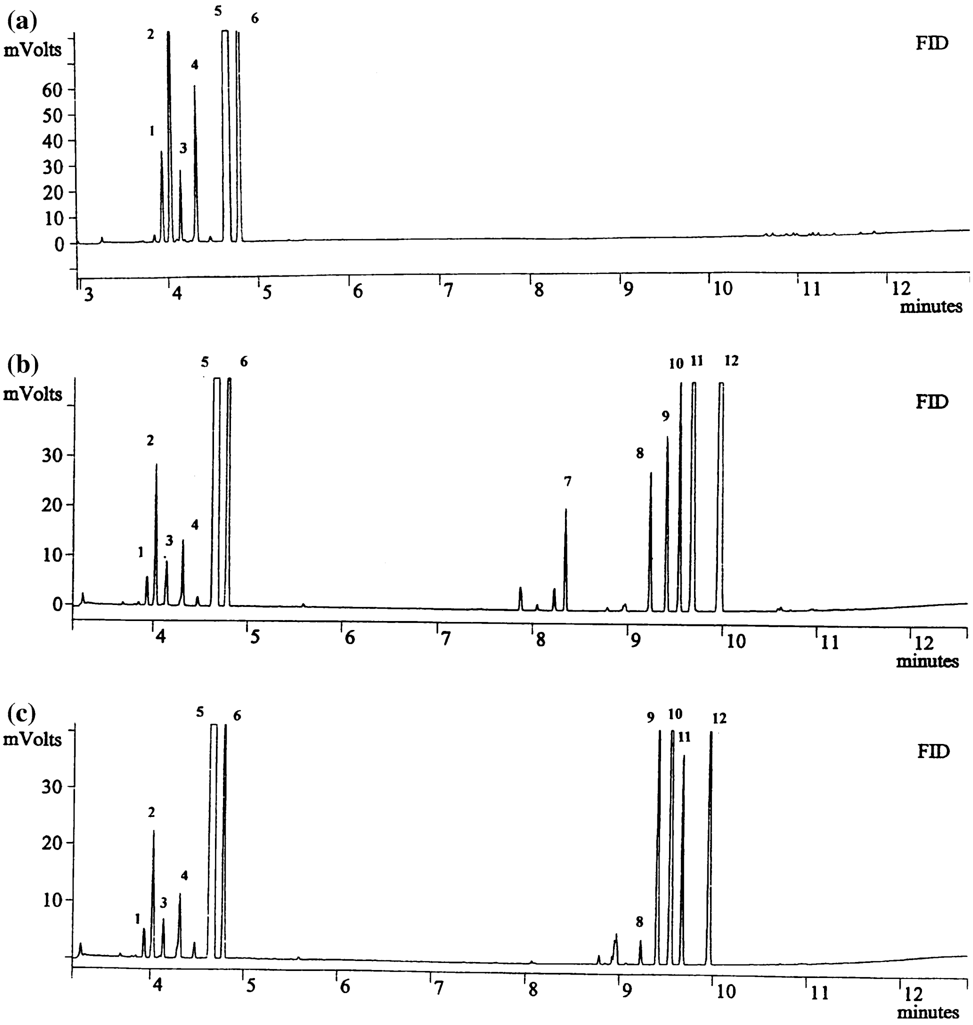
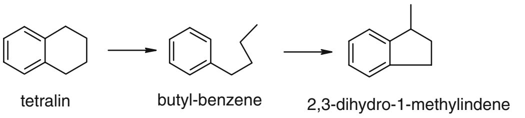
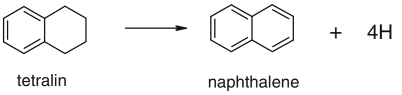


Fig. 4 GC analyses of the extracts from reactive extraction of the spent catalyst at 400 °C and 10 MPa H_2 pressure for 1 h, with the following solvents. (**a**) Tetralin/catalyst: 5.0 (volume) Tetralin conversion: 28.4%. (**b**) Tetralin-pyrene (25%)/catalyst: 5.0 (volume) Tetralin conversion: 15.9% Pyrene conversion: 52.4%. (**c**) Tetralin-hexahydropyrene (15%)/catalyst: 5.0 (volume) Tetralin conversion: 7.5% Hexahydropyrene conversion: 56.0%

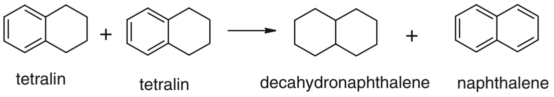
($C_{10}H_{14}$) and 2,3-dihydro-1-methylindene ($C_{10}H_{12}$) (Eq. 1), dehydrogenation to form naphthalene (Eq. 2) with transferring hydrogen to the coke on catalyst or other compounds, as well as hydrogenation to form decahydronaphthalenes by accepting hydrogen from another tetralin molecule (Eq. 3) or molecular hydrogen.



(1)



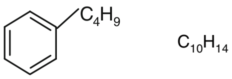
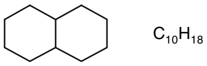
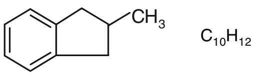
(2)



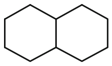
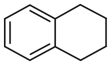
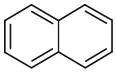
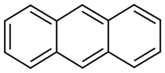
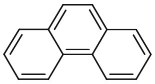
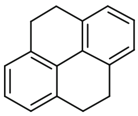
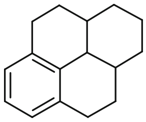
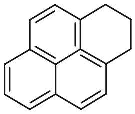
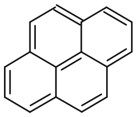
(3)

For the extraction by tetralin (75%)-pyrene (25%) at the same conditions as shown in Fig. 4b, the conversions of tetralin and pyrene are 15.9 and 52.4%, respectively.

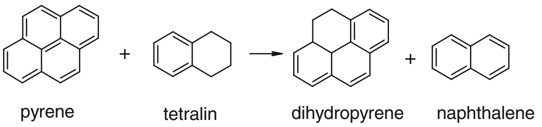
Key compounds identified by MS-GC

GC peak No	Compound	
1	Butyl benzene	
2	*trans*-Decahydronaphthalene	
3	2,3-Dihydro-1-methylindene	

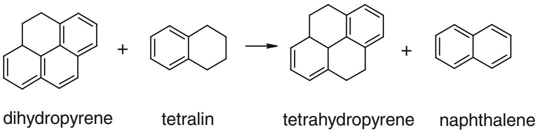
continued

GC peak No	Compound	
4	*cis*-Decahydronaphthalene	 $C_{10}H_{18}$
5	Tetrahydronaphthalene (Tetralin)	 $C_{10}H_{12}$
6	Naphthalene	 $C_{10}H_8$
7	Anthracene or phenanthrene	  $C_{14}H_{10}$
8	4,5,9,10-Tetrahydropyrene	 $C_{16}H_{14}$
9,10	Hexahydropyrenes	 $C_{16}H_{16}$
11	Dihydropyrene	 $C_{16}H_{12}$
12	Pyrene	 $C_{16}H_{10}$

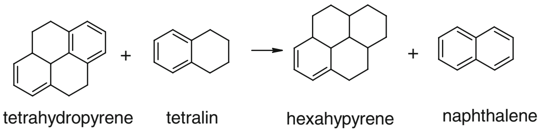
Besides those compounds appeared in pure tetralin extraction, the extract contained dihydropyrene ($C_{16}H_{12}$), tetrahydropyrene ($C_{16}H_{14}$), hexahydropyrene ($C_{16}H_{16}$), and other minor components such as anthrancene ($C_{14}H_{10}$),. Doubtless pyrene has high ability to accept and shuttle hydrogen from either tetralin or molecular hydrogen to form more effective H-donors, hydropyrenes (Eq. 4). Also pyrene does not undergo significant decomposition under the used conditions.



(4a)

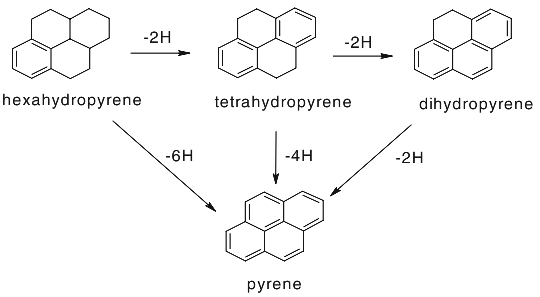


(4b)



(4c)

To further examine the ability of H-donating by hydropyrenes, the additional extraction of the original spent catalyst with tetralin-hexahydropyrene (15%) under the same conditions. As illustrated in Fig. 4c, hexahydropyrene gave much higher conversion than tetralin (56% versus 7.5%), and also has a high ability of dehydrogenation to form dihydropyrene and pyrene (Eq. 5) with a negligible decomposition.



(5)

Based on the above GC-MS analysis, the mechanism of the coked catalyst rejuvenation by H-donor solvent becomes more interpretable. In pure tetralin extraction, part of tetralin was dehydrogenated into naphthalene (Eq. 2) by donating hydrogen to hydrogenate the coke on catalyst. In binary tetralin-pyrene solvent extraction, the pyrene enable to accept hydrogen from tetralin (Eq. 4) or shuttle molecular hydrogen to form in situ highly active H-donor, hydropyrenes which donate hydrogen to the coked catalyst and change back into pyrene at the same time. The tetralin in this binary solvent system could dissolve pyrene, facilitate the H-transfer, and give synergism with pyrene to the coke removal of catalyst. Under the ideal circumstances, a proper H-acceptor such as pyrene would undergo a H-acceptor → H-donor → H-acceptor recycle. As the recycle repeated, the coke on the deactivated catalysts would be removed and the activity of catalyst would be regenerated.

Finally, it should be pointed out that phase splitting of pyrene-tetralin mixtures has been observed by John et al. under coal liquefaction conditions [24]. The effects of the phase-splitting and diffusion on the rejuvenation of the coked hydroconversion catalysts have not been fully defined so far. More fundamental studies are needed to be done before an innovative technology is established to industrial application. Nevertheless, this study showed a great potential in developing a novel technology for rejuvenation of the deactivated residue hydroconversion catalysts by H-donor solvents.

4 Conclusions

1. The carbonaceous deposits on the spent industrial catalyst for residue hydroconversion can be partially removed by the reactive extraction of solvents with the order of effectiveness: gas oil < tetralin < tetralin-pyrene.
2. Tetralin has a higher activity than the gas oil for removing the deposits due to its ability of donating hydrogen in situ to hydrogenate the coke on catalyst.
3. Binary H-donor/H-acceptor solvent mixture, tetralin/pyrene shows synergism for removing the coke on catalyst due to the ability of pyrene to shuttle hydrogen to form very active H-donors, hydropyrenes.
4. Removal of coke on the surface of catalyst rejuvenates the spent catalyst, as indicated by the enhancement of its HDS activity.

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