

Effect of Re on product yields and deactivation patterns of naphtha reforming catalyst

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Abstract

The effect of rhenium concentration on the activity and stability of Pt–Re/Al₂O₃ catalysts used in naphtha reforming were studied by varying the rhenium concentration. The samples were prepared by the co-impregnation method on chloride alumina. The platinum content was 0.3 wt.%, and the rhenium loading was varied to obtain Re/Pt weight ratios of 1.0, 1.5, 2.0, 2.5 and 3. Re loading greatly influenced the catalytic properties and product yields in naphtha reforming. TPR profiles indicated the increase in hydrogen uptake, but decrease in reducibility of rhenium with increase of rhenium loading. At low rhenium loadings, the catalyst exhibited the presence of two groups of rhenium reduced at two different temperatures, while the peaks are merged in to a single sharp peak at higher rhenium loadings. Increase in aromatic yields and decrease in cracking yields was observed up to 0.6 wt.% rhenium loading (Re/Pt weight ratio = 2.0). Further increase of Re caused decrease in xylene and C₉+ with simultaneous increase of benzene, toluene, methane and ethane yields. The catalyst with 0.6 wt.% rhenium exhibited best aromatic yields and highest hours-on-oil performance.

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1. Introduction

Naphtha reforming is one of the important processes in the petroleum refinery [1–3]. There has been a continuous effort in catalyst development for the production of aromatics from the naphtha. Acidic alumina in combination with one or two noble metals dispersed on it can catalyze all the important reactions of reforming. Pt–Re/Al₂O₃ is well known among the bi-metallic catalysts, where the ratio of Re/Pt plays vital role [4,5]. The excess rhenium (Skewed) catalysts were reported to exhibit better performance when compared to the equal rhenium (Balanced) catalysts [6,7]. The superiority of the Skewed catalyst in terms of longer catalyst life and aromatic yields is ascribed to the change in electronic properties of the Pt. However, the Skewed metal catalyst was also observed to cause high gas formation due to the hydrogenolysis reactions [7]. Pre-sulphidation of the Skewed catalyst is widely practiced to control the hyper-activity

towards hydrogenolysis reactions [8–11]. It is also advised to operate the Skewed metal catalyst at lower severity conditions for obtaining the maximum aromatic yields with low gas formation [7]. Another strategy applied for taking the beneficial effect of excess rhenium with minimizing the side reactions is by using the different concentrations of rhenium in the first and last reactors of the multi-stage catalytic reforming process [12].

Nature and composition of hydrocarbons is also reported to influence the product selectivities in reforming. Skewed metal catalyst is observed to be better for the reforming of C₉–C₁₀ hydrocarbons, whereas relatively lower rhenium amount is good for the C₆–C₈ paraffins [7]. The formation of gas product increases with the chain length of the hydrocarbon reactant on the lower rhenium containing catalyst, whereas the opposite is true for the higher rhenium catalyst. These findings clearly indicate the influence of rhenium amount on the reaction pathways of reforming and the importance of selection of rhenium amount for the production of aromatics from a desired feedstock. That means the designing of catalyst needs to be conducted based on the hydrocarbon composition of the feed.

The present study is aimed at the development of a Pt–Re bi-metallic reforming catalyst for the conversion of an industrial

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naphtha feedstock containing C₆–C₉ hydrocarbons. The catalyst with 0.3 wt.% Pt and 0.3 wt.% Re on Al₂O₃ is taken as standard (Balanced catalyst) and the concentration of rhenium is varied from 0.3 wt.% to 0.9 wt.% (Skewed catalysts). Effect of rhenium content on the properties of catalysts, product yields, selectivity to individual aromatic compounds and time-on-oil stability aspects of the catalyst were studied. The studies indicated the need for optimizing the rhenium concentration of the catalyst for the maximization of aromatics with higher stability in catalytic activity.

2. Experimental

2.1. Catalysts

Alumina support with desired properties such as acidity, porosity and mechanical strength was prepared by mixing two types of Pural SB alumina, namely, (1) pural SB alumina peptized with nitric acid and (2) pre-calcined Pural SB alumina. The mixture was extruded to obtain cylindrical extrudates of 1.5 mm diameter. The alumina support thus contains alumina hydrate (70 wt.%) as well as gamma alumina (30 wt.%). The support is dipped in 2.5 wt.% N/15 HCl solution for 24 h followed by decanting the excess solution from the catalyst. The wet catalyst is dried at 110 °C for 16 h and calcined at 450 °C for 4 h. Adsorption capacity of Re on the chlorided alumina support was studied to estimate the concentration of HReO₄ solution, and the solution containing both Pt and Re salts was used for simultaneous impregnation of the metals using excess impregnation method. After 6 h the solution was decanted from the catalyst and the catalyst was dried at 110 °C for 16 h and calcined at 550 °C for 4 h under controlled airflow.

Several catalysts were prepared by varying the concentration of Re from 0.3 wt.% to 0.9 wt.% in the bi-metallic catalysts. The amount of Pt is always kept constant (0.3 wt.%) on all the catalysts. For the five catalysts PR-1 to PR-V, the Re/Pt weight ratio obtained is 1, 1.5, 2, 2.5, and 3, respectively. The samples were dried and calcined before using them for the reaction. Reduction is conducted at 500 °C for 8 h, followed by sulphidation with 0.2 wt.% dimethyl disulphide (DMDS) at 370 °C for 90 min.

2.2. Physico-chemical characterization

The catalysts were tested for surface area, pore volume, pore size distribution, temperature-programmed reduction (TPR) and acidity.

Surface area and pore size distribution of samples were determined volumetrically by physisorption of nitrogen at liquid nitrogen temperature (77 K) in static mode using ASAP-2010 Micromeritics (USA) instrument. For measuring surface area, 0.2010 g of sample is taken in a specially designed sample tube and degassed at 573 K under vacuum of 10⁻³ Torr for 4 h. A frit is attached to the mouth of the sample tube, so that when the sample tube is removed from preparation mode, it does not allow sample to expose in atmosphere. Sample is cooled to room temperature under vacuum and the sample tube is removed from preparation port and attached to analysis port of the instrument. For all the

samples, N₂ adsorption–desorption isotherms were obtained at 77 K and the temperature was maintained constant by using liquid nitrogen, whereas helium gas was used for measuring dead space.

Temperature-programmed reduction (TPR) measurements were conducted in a flow system consisting of a quartz tube (10 mm × 30 mm) filled with about 0.5 g catalyst. This tube was heated in a temperature-programmed furnace from ambient to 600 °C with heating rate of 100 °C/min. A gas mixture of H₂ and N₂ consisting 8 vol.% H₂ was used as a reducing gas. The H₂ consumption as a function of reduction temperatures was continuously monitored with a TCD cell and recorded.

Acidity was characterized by a Setaram C-80 heat flow micro calorimeter which was attached to a volumetric adsorption unit for probe delivery. 0.1 g of catalyst was out-gassed at 723 K under vacuum. The micro calorimetric measurement of ammonia adsorption was carried out at 448 K. Differential heat of ammonia adsorption was determined by introducing small quantities of ammonia on to the out-gassed sample, till the neutralization of all acid sites occurred on the catalyst surface. The heat of adsorption evolved for each dose was calculated from the resulting thermograms and the amount of ammonia adsorbed was calculated from the pressure change.

2.3. Catalyst evaluation

The paraffinic naphtha with boiling range of 90–140 °C is used as feed. The physico-chemical properties of the feed are given in Table 1. The reforming reaction is conducted in a fixed bed down flow reactor of 100 cc volume capacity loaded with 25 g of catalyst. CCl₄ equivalent to 1 ppm chloride was also mixed with the feed in order to nullify the moisture effect. Before starting the experiments, the catalyst was stabilized under the following conditions:

Pressure: 20 bar, temperature: 460 °C, WHSV: 3 h⁻¹ and H₂/HC: 10.

In order to check the stability of the catalysts in shorter duration, accelerated ageing tests were conducted at higher severity. These tests were performed by raising the reactor temperature so as to maintain the RONC of reformat at around 98, keeping other process variables same. However, the recycle rate

Table 1
Physico-chemical properties of feed

Boiling range	90–140 °C
Density at 15 °C	0.7270 cc/g
ASTM distillation (°C)	
IBP	82.7
10%	97.2
30%	102.1
50%	108.4
70%	115.2
90%	126.8
FBP	150.7
Sulphur (ppm)	0.82
Nitrogen (ppm)	<1
RONC	46.6

Table 2
Carbon number wise PNA analysis of feed

Carbon number	Paraffins	Naphthenes	Aromatics	Total
C6	6.2	6.1	0.5	12.8
C7	25.4	2.4	4.4	32.2
C8	16.7	9.7	5.6	32.0
C9	12.9	1.3	8.8	23.0
Total	61.2	19.5	19.3	100.0

$N+2A=58.1$.

was adjusted to get H_2/HC ratio around 4.5 during the experiments.

3. Results

The component wise analysis of the feed indicates the presence of major amount of paraffins, followed by naphthenes and aromatics (Table 2). Among the hydrocarbons, C_8 and C_7 components are major (~ 65 wt.%) followed by C_9 and C_6 . Among the paraffins, the C_7 paraffins are higher followed by C_8 and C_9 . Naphthenes are higher in C_8 and aromatics are higher in C_9 . The feed exhibits $N+2A$ of 58 with 0.727 g/cc density and 46.6 RON. The feed also contains 0.82 ppm of sulphur.

Table 3
Catalyst properties and product yields in naphtha reforming

Catalysts	PR-I	PR-II	PR-III	PR-IV	PR-V
Physico-chemical properties of catalysts					
Bulk density (g/cc)	0.57	0.61	0.59	0.57	0.58
Platinum (wt.%)	0.30	0.30	0.29	0.30	0.30
Rhenium (wt.%)	0.30	0.45	0.60	0.75	0.90
Chlorine (wt.%)	1.10	0.94	1.00	1.04	1.00
Pore volume (cc/g)	0.745	0.750	0.742	0.728	0.730
Metal dispersion (%)	77.0	82.0	80.0	77.0	75.0
Surface area (m^2/g)	200.00	205.00	200.00	181.00	198.00
Total acidity (m mol/g)	0.40	0.42	0.39	0.38	0.34
Strong ($\Delta H > 100$ kJ/mol)	0.20	0.19	0.18	0.12	0.11
Medium ($\Delta H = 100-75$ kJ/mol)	0.12	0.14	0.13	0.15	0.14
Weak ($\Delta H < 75$ kJ/mol)	0.08	0.09	0.08	0.11	0.09
Relative H_2 uptake (TPR)	1.0	1.27	1.25	1.08	0.78
Product yields in naphtha reforming (wt.%)					
Cracking (C_1-C_4)	18.0	15.4	14.1	15.3	14.7
(A) Fuel gas ($C_1 + C_2$)	2.4	3.3	4.2	6.2	5.9
C_1	0.1	0.8	1.4	2.2	2.1
C_2	2.3	2.5	2.8	4.0	3.8
(B) LPG ($C_3 + C_4$)	15.6	12.1	9.9	9.1	8.8
C_3	9.8	6.7	6.1	4.8	5.0
C_4	5.8	5.4	3.8	4.3	3.8
C_5+ hydrocarbon	82.0	84.6	85.9	84.7	85.3
Aromatics in C_5+	59.1	64.9	66.5	66.1	64.0
Benzene	4.3	5.4	5.6	6.8	7.2
Toluene	21.6	24.6	25.5	27.2	28.7
Xylenes	27.3	31.2	31.6	28.5	24.8
C_9+ aromatics	5.9	3.7	3.8	3.6	3.3
H_2	1.4	1.9	2.5	2.6	2.4
RONC	93.2	87.4	98.8	97.2	97.0

The properties of catalysts used in reforming reaction are given in Table 3. All the catalysts have been prepared following the similar method of support preparation and metal loadings. However, the amount of metal was varied (Re/Pt ratio) as discussed in the experimental session. The catalysts exhibited nearly the same values of bulk density, chlorine content and surface area, while there is a slight difference in pore volume, acidity and metal dispersion. Overall, the catalyst does not exhibit significant change in the fundamental properties with rhenium loading.

The TPR profiles of the catalysts are given in Fig. 1. At 0.3 wt.% rhenium loading, the catalyst exhibited the reduction peak at 270 °C with a shoulder at about 230 °C. With increasing rhenium loading from 0.3 wt.% to 0.9 wt.%, there are three changes observed in the TPR profiles, (1) the peak area corresponds to hydrogen uptake is increased, (2) the reduction peak is gradually shifted to higher temperatures and (3) the shoulder peak is merged with that of the main peak to give a single reduction peak at about 330 °C.

Performance of catalysts in reforming reaction is given in Table 3. Based on their nature, the products obtained can be classified as (1) cracking products and (2) aromatic products. Among the cracking products, LPG ($C_3 + C_4$) is more and the fuel gas ($C_1 + C_2$) is less on all the catalysts. This may be due to the preferential cracking of the paraffins at the middle of the

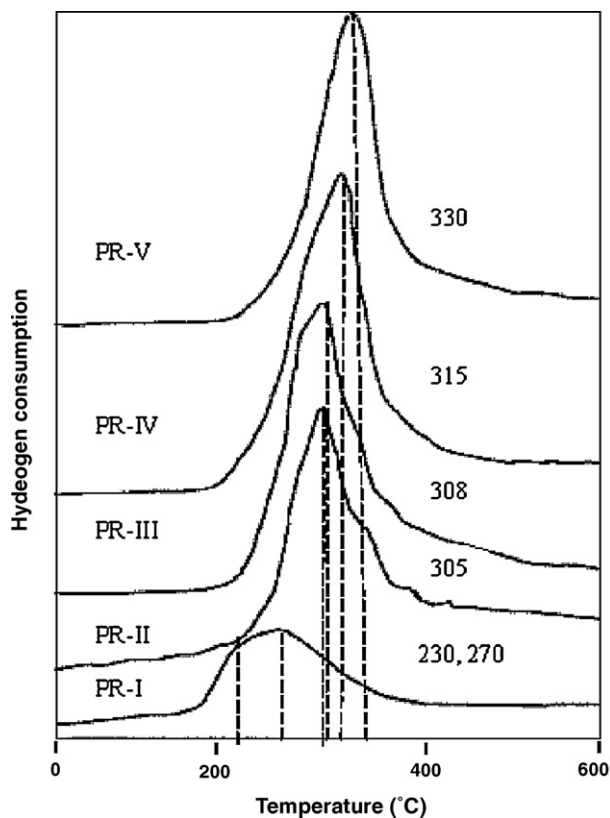


Fig. 1. TPR profiles of Pt–Re/Al₂O₃ catalysts with variation in rhenium loading.

molecule rather than the cracking at the end. Among the aromatics, xylenes are major products followed by toluene. Benzene and C₉ + aromatic products are low with all the catalysts. Since, the feed contains almost equal amount of C₇ and C₈ hydrocarbons, the higher yield of xylenes compared to toluene observed may be due to the higher aromatization activity of C₈ hydrocarbons. The high amount of naphthenes in C₈ hydrocarbons in the feed may also be the reason for high aromatic production of xylenes.

In general, the cracking yields are slightly decreased while those of aromatics are increased with rhenium loading (Fig. 2). The total aromatic production is increased from Re/Pt wt. ratio of 1 to 1.5 and attained a peak at 1.5. This is also reflected in the increase of RON and H₂ yields. Further increase of rhenium could not cause any significant increase in total aromatic production. Among the cracked products, the yield of LPG is increased and that of fuel gas is decreased with rhenium loading.

Among the aromatics, the selectivity towards individual compounds is varied. Effect of rhenium loading on the aromatic yields is shown in Fig. 2. All the catalysts exhibited highest selectivity towards xylenes followed by toluene. It is interesting to see that the yields of benzene, toluene, xylenes and C₉+ aromatics are not following the similar trends with the total aromatics. The yields of xylenes and C₉+ aromatics are decreased, while that of benzene and toluene is increased at higher rhenium loadings.

Effect of Re content on the stability in activity of the catalysts is shown in Fig. 3. The catalyst PR-III with Re/Pt wt. ratio of

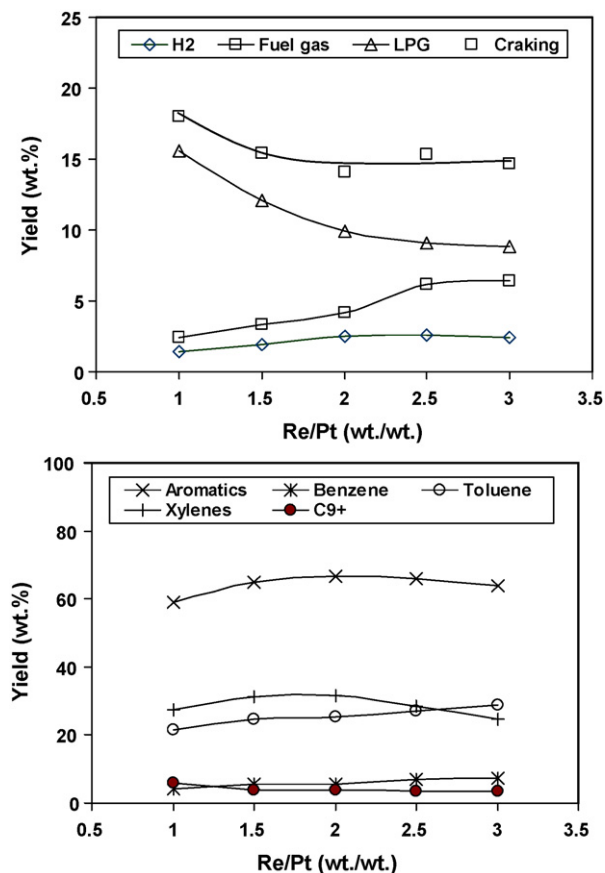


Fig. 2. Performances of catalysts in naphtha reforming.

2 exhibited the highest stability (400 h) and further increase in rhenium caused decline in stability (280 h). This may be due to the variation in amount of coke formed on the catalyst. However, the coke analysis studies indicated that the amount of coke on the catalysts with Re/Pt > 1.5 is constant (6 wt.%). This observation suggests the low activity of the surface active sites in high rhenium containing catalysts. Further, the catalyst PR-III exhib-

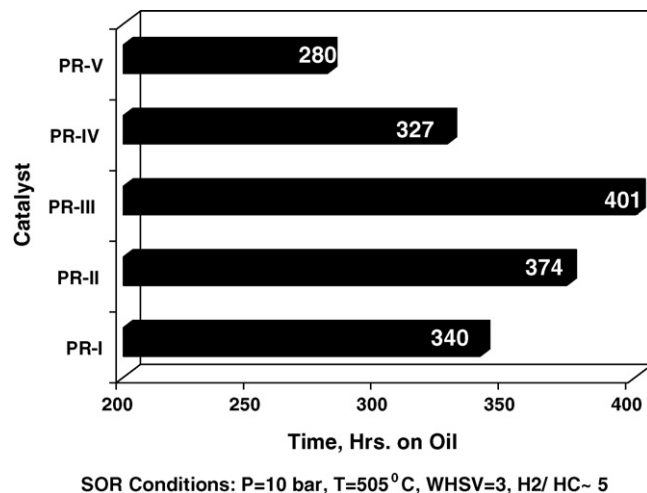


Fig. 3. Hours-on-oil performances of catalysts at accelerated ageing.

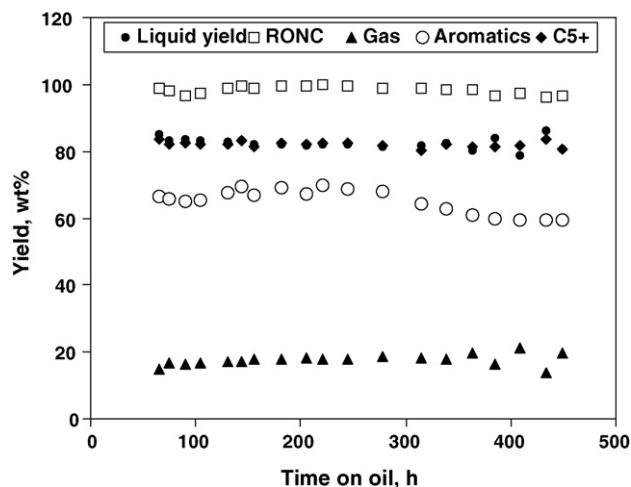


Fig. 4. Stability in product yields over of PR-III (Re/Pt=2) catalyst.

ited stability in product yields such as aromatics, C₅+, liquid, gas and product RON (Fig. 4).

4. Discussion

4.1. Effect of Re loading on the catalytic properties of Pt–Re/Al₂O₃

Rhenium in Pt–Re/Al₂O₃ catalyst is known to exist in two types of active sites, namely, (1) Pt–Re ensembles and (2) support (Al₂O₃) interacted rhenium [13]. The strong interaction between rhenium and support is expected to cause decrease in reducibility of rhenium in the later case.

The TPR profiles of the PR-I show a high temperature peak with a shoulder at lower temperature, clearly supports the existence of rhenium reducible at two different temperatures. Increase in rhenium loading improved the hydrogen uptake measured by peak area in TPD. The shifting of the TPR high temperature peaks in PR-II to PR-V clearly suggests the increase of acid interacted rhenium species. The samples also exhibited decrease in strong acidity at higher rhenium loadings (Table 3) supporting the formation of more acid interactive rhenium in these samples. This is in agreement with the earlier findings of Sachtler on the acid interaction of rhenium in Pt–Re/Al₂O₃ catalysts [14].

Overall, rhenium loading above 0.3 wt.% caused increase in hydrogen uptake and decrease in reducibility of the rhenium in Pt–Re/Al₂O₃ catalysts. However, careful analysis of the TPR profiles indicates that the hydrogen uptake is significantly increased from 0.3 wt.% to 0.45 wt.% rhenium, whereas, the increase is only moderate at above 0.45 wt.% rhenium loading. That means, the loading of rhenium up to 0.45 wt.% is responsible for the formation of highly dispersed rhenium interactive with Pt as well as acidity of the catalyst. Above this loading, the formation of rhenium (Re⁰) segregates may be responsible for low increase in the hydrogen uptake. Earlier, Nacheff et al., proposed the co-existence of Re⁰ and Re⁴⁺ in the reduced Pt (0.3)–Re (0.2)/Al₂O₃ catalyst [15]. Since, the rhenium loading in samples PR-IV and V of the present study is much higher

(0.75 wt.% and 0.9 wt.%, respectively) than those studied by Nacheff et al., our samples are thus expected to have higher percentage of Re⁰ segregates and Re⁴⁺ interacting with Al₂O₃. A slight decrease in pore volume also supports the possible formation of rhenium segregates occupying the pores of the alumina at higher rhenium loading. Presence of rhenium in segregates is also expected to contribute less towards the hydrogen spill over and aromatization reactions.

4.2. Effect of Re loading on performance in naphtha reforming

It is known that the main reforming reactions are acid controlled and the mechanism involves the protons, hydride ions and hydrogen. But, the metal sites can also influence the reactions such as mono-functional dehydrogenation of naphthenes, bifunctional paraffin dehydrocyclization, isomerization and more importantly the hydrogen spill over. Hence, the interaction of rhenium with Pt and Al₂O₃ support can greatly influence the catalytic properties such as concentration of Pt–Re ensembles, acidity, acid interactive rhenium and rhenium segregates that can facilitate the variety of reforming reactions. The *n*-pentane dehydrocyclization studies of Parera et al. and deactivation studies of several others also indicated the operation to two types aromatization reactions on Pt–Re/Al₂O₃, namely, mono-functional metal mechanism controlled by Pt–Re and bifunctional mechanism controlled by rhenium associated with acid sites [13,16–18]. In the present study, increased rhenium loading is expected to cause increased formation of support (Al₂O₃) interacted rhenium that can enhance the bifunctional aromatization reaction responsible for enhanced aromatic yields. As from results given in Table 3, the aromatic yields are indeed increased with the simultaneous decrease of cracking yields up on rhenium loading from 0.3 wt.% (PR-I) to 0.45 wt.% (PR-II). Decrease in cracking yields support the conversion of acid sites into acid interacted rhenium, and the conversion of cracking sites into aromatization sites. This is in agreement with the observations of Grau and Parera regarding the lower acid activity of the high rhenium catalysts compared to the balanced one [13].

Further increase of rhenium (PR-III) could not cause any significant increase in aromatic yields. But, there is a change in other product yields, such as decrease in LPG and increase in fuel gas yields. The increase in fuel gas yields may be due to increased hydrogenolytic activity and the formation of C₁ and C₂ fragments through dealkylation of C₉+ aromatics and xylenes. This aspect can be analyzed in the light of changes in yields of individual aromatics (Table 3). The decrease in C₉+ aromatics and xylenes with simultaneous increase of benzene and toluene observed in PR-IV and PR-V also support the possible occurrence of dealkylation reaction at higher rhenium loadings. That means the hydrogenolytic activity of the catalyst at high rhenium loadings is responsible for the conversion of C₉+ and xylenes or their precursors into benzene and toluene. This reaction is also expected to produce C₁ and C₂ hydrocarbon gases, which is indeed observed at higher rhenium loadings, supports the occurrence of dealkylation reaction. Studies of Trafano and Parera indicated the importance of hydrogen spill over

and hydrogenolytic activity of Pt–Re/Al₂O₃ catalyst, where, the rhenium loading was observed to increase hydrogenolytic activity but decrease the hydrogen spill over capacity of the catalyst [19]. Further studies of Parera indicated the possible formation of higher concentration of Re⁰ species rather than Pt–Re ensembles at high rhenium loadings that are responsible for increased hydrogenolytic activity [13].

The hydrogen uptake measurements also indicate the importance of hydrogen spill over capacity of the catalysts on the aromatic yields. These changes can strongly influence the reaction mechanism involving protons, hydride ions and hydrogen that eventually change the product yields. Improvement in aromatic yields observed up to the rhenium loading of 0.6 wt.% and changes in LPG, fuel gas and individual aromatics observed above the 0.6 wt.% metal loading in the present study may be due to the increase in hydrogenolytic activity and decrease in hydrogen spill over capacity of the catalysts at higher metal loadings. The TPR profiles of samples also indicated that the hydrogen uptake is not increased with the rhenium loading above 0.6 wt.% rhenium. Hence, the decrease in hydrogen uptake and hydrogen spill over capacity of high rhenium catalysts PR-IV and PR-V (0.75 wt.% and 0.9 wt.% Re, respectively) can be ascribed to the probable formation of Re⁰ segregates in these samples.

Earlier findings in literature also indicated that rhenium is necessary for the enhanced yields of aromatics, but lower metal loadings are better for aromatization of short chain hydrocarbons [7]. That means, the optimum amount of rhenium for aromatization depends on the hydrocarbon composition of the feedstock under study. This phenomenon seems to be true in the present case, where, increase in rhenium loading could not give continuous increase in aromatics. At the reaction conditions studied for the reforming of naphtha feed stock, the Re/Pt wt. ratio of about 2 (PR-III) seems to be optimum for the production of aromatics with minimum gases. This catalyst (PR-III) also exhibited constant activity in the studied period of 450 h, where, liquid yields, aromatic yields, gas yields and C₅₊ yields were comparable through out the time period. The catalyst also exhibited the consistency in product RONC.

The time-on-stream performance of the catalysts also indicated relatively faster deactivation of the catalysts above 0.6 wt.% rhenium loading (in spite of same amount of coke formation). That means, relatively small amount of coke is sufficient to deactivate the active sites related to acidity present in the high rhenium catalysts. This is in agreement with the studies of Grau and Parera indicating the formation of segregates of Re⁰ and Re⁴⁺ interacted on Al₂O₃ surface at higher rhenium loadings, which exhibit lower catalytic activity and can be deactivated at a greater degree when compared to low rhenium loaded catalysts [13].

Overall, the loading of rhenium above 0.3 wt.% resulted in the formation of more support interactive rhenium which enhanced the aromatic yields by facilitating bifunctional mechanism in addition to mono-functional aromatization on Pt–Re ensembles [16–18]. The increased formation of Re⁰ may be responsible for increase in hydrogenolytic activity and fuel gas yields at higher rhenium loadings. Above the rhenium loading of 0.6 wt.%, the

formation of rhenium segregates may be responsible for decrease in hydrogen spill over and decrease in aromatic yields. The rhenium concentration in Pt–Re/Al₂O₃ catalyst eventually influenced the catalyst stability.

5. Conclusions

Increase in rhenium loading above the 50% of Pt contributed to the improvement in catalytic properties such as hydrogen uptake and enhancement in aromatic yields up to the level of 0.6 wt.% (67% Re and 33% Pt) rhenium (catalyst PR-III). Rhenium content also altered the yields of other products such as fuel gas, LPG, benzene, toluene, xylenes and C₉₊ aromatics. Though the differences in product yields are not significant over various rhenium loaded catalysts, yet the stability in activity of the catalysts is greatly influenced by the rhenium content. Among the catalysts, the one with 0.6 wt.% rhenium (catalyst PR-III) is exhibited highest hours-on-oil stability. The studies indicate the importance of optimization of rhenium for achieving higher aromatic yields and life of reforming catalyst.

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References

- [1] V.A. Mazzieri, J.M. Grau, C.R. Vera, J.C. Yori, J.M. Parera, C.L. Pieck, *Catal. Today* 107–108 (2005) 643.
- [2] R. Mariscal, J.L.G. Fierro, J.C. Yori, J.M. Parera, J.M. Grau, *Appl. Catal. A* 327 (2007) 123.
- [3] B.C. Gates, J.R. Katzer, G.C.A. Schit, *Chemistry of Catalytic Processes*, McGraw-Hill, New York, 1979, p. 184.
- [4] J.P. Frank, G. Martino, in: Oudar, H. Wise (Eds.), *Deactivation and Poisoning of Catalysts*, Marcel Dekker, New York, 1985, p. 205.
- [5] J.A. Anabatawi, S.A. Ali, A.M. Al-Zahrani, M.A. Siddiqui, *React. Kinet. Catal. Lett.* 63 (1) (1998) 143.
- [6] P.A. Larsen, in: H.Th. Rijnten, H.J. Lovink (Eds.), *Ketjen Catalysts Symposium on Question and Answer Session-Hydroprocessing*, AKZO Chemie Ketjen Catalysts, The Netherlands, 1986, p. 75.
- [7] J.M. Grau, J.M. Parera, *Ind. Eng. Chem. Res.* 28 (1989) 1596.
- [8] C. Laiyuan, N. Yueqin, Z. Jingling, L. Liwu, L. Xihui, C. Sen, *Appl. Catal.* 97 (1993) 133.
- [9] R.W. Coughlin, K. Kawakami, A. Hasan, *J. Catal.* 88 (1984), pp. 150 and 163.
- [10] V.K. Shun, J.M. Butt, W.M.H. Sachtler, *J. Catal.* 96 (1985) 371.
- [11] P.J.M. Reek, A. den Hartong, V. Ponc, *Appl. Catal. Appl. Catal.* 46 (1989) 213.
- [12] H.C. Chen, C.M. Detz, P.W. Tamm, US Patent 4,764,267 (16 August, 1988).
- [13] J.M. Grau, J.M. Parera, *Appl. Catal.* 70 (1991) 9.
- [14] W.M.H. Sachtler, *J. Mol. Catal.* 25 (1984) 1.
- [15] M.S. Nacheff, L.S. Kraus, M. Ichikawa, B.M. Hoffman, J.B. Butt, W.M.H. Sachtler, *J. Catal.* 106 (1987) 263.
- [16] P.S. Nix, P.B. Weisz, *J. Catal.* 3 (1964) 179.
- [17] J.H. Sinfelt, H. Hurwitz, J.C. Rohrer, *J. Catal.* 1 (1962) 481.
- [18] A.J. Silvestri, P.A. Naro, R.L. Smith, *J. Catal.* 14 (1969) 386.
- [19] E.M. Traffano, J.M. Parera, *Appl. Catal.* 28 (1986) 193.