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NAPHTHA CATALYTIC UPGRADING FOR PRODUCTION OF ENVIRONMENTALLY- FRIENDLY GASOLINE

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Abstract

The recent economic climate, impact of government regulation, and new market trends have impacted the catalyst designers to improve the performance of catalyst. To achieve this goal, a series of experiments were conducted to focus on the influence of Ga and Re addition on the catalytic activity of Pt–Re/Al_2O_3 naphtha reforming catalysts. To supported γ-Al_2O_3 the Ga-Re-Pt prepare by using incipient wetness impregnation method. Many characterization tests are used such as scanning electron microscopy, temperature programmed desorption, X-ray diffraction and BET surface area. The liquid product yield tested by PONA method. In this study the benzene content is used as main performance criteria throughout many experiments performed at different liquid hourly space velocity, hydrogen/hydrocarbon ratios and different operating temperature. According to the catalyst characterization tests the co-impregnation method showed good result in term of performance and properties. The catalyst exhibited good liquid product distribution and significant minimization of benzene content.

Keywords: Gallium; octane number; catalyst; naphtha reforming.

1. Introduction

Now-a-days industries are searching for alternatives such as bio-based composites to contribute in reducing global warming by reducing the use of petroleum based products. Bio-composites are composite materials that are made from natural fibers and matrix. Gasoline is subject to more demands and expectations than ever before. Regulatory agencies around the world are increasingly exercising their powers to regulate motor gasoline characteristics and mandate the use of deposit control additives. The main goals are to increase octane number without the addition of aromatics and to reduce emissions. The quality of gasolines can vary widely, depending on the crude source, sulfur content and octane number. It is desired to improve octane number, which is a measure of resistance to impregnation, by using organic additives.

Trimm *et al.* [1] have reported on the use of a Pt/CeO_2 and a Pt-Ni commercial catalyst for the autothermal reforming of gasoline. Use of commercial gasoline resulted in heavy coking of the commercial catalyst and was abandoned in favor of analogous mixtures. The reactor was arranged to have an oxidation section containing the Pt/CeO_2 catalyst and a reforming section containing the Pt-Ni commercial catalyst, separated by a quartz wool plug. Villegas *et al.* [2] used a Pt/CeO_2-ZrO_2 catalyst for isooctane autothermal reforming. Villegas *et al.* [2] concluded that catalyst worked well at a steam to carbon ratio of 2 and an oxygen to carbon ratio of 1. Deactivation was observed under pure partial oxidation conditions, although carbon deposition was light at 23 mg C/g catalyst. Pino *et al.* [3] have reported on a Ce(Pt)O_2 catalyst for partial oxidation of methane at an oxygen to carbon ratio of 1.0. Increasing Pt loading from 0.5 wt% to 2.0 wt% increased the methane conversion, which approached equilibrium. The catalyst was stable over 100 hours of operation, evidencing no carbon deposition [3].

Due to the vast growth of environmental regulation in various countries, many organizations give massive attention towards health and pollutants, in different area, air, water, soil, fuel. These organizations, like word bank and EPA (Environmental Protection Agency) legalize many rules, and these rules become worldwide accepted. Refinery processes for the upgrading of gasolines aim at the conversion of other hydrocarbons into aromatics and iso-paraffins. Benzene has long been known to be a human carcinogen and has been classified as such by the International Agency for Research on Cancer [4]. High exposure levels of benzene are particularly prominent in workers employed in the oil, shipping, auto repair, and petrochemical industries, as well as shoe- and rubber-manufacturing plants [5-7]. Benzene has a high vapor pressure at ambient temperatures, therefore exposure occurs mainly through inhalation, although contamination of drinking water or dermal exposure can also occur [8-9]. Due to the known carcinogenic and toxic effects of high levels of benzene, progressive reduction in the occupational exposure limits has occurred in North America and Europe.

Therefore, the main objective of this work is to prepare a Ga-Re-Pt catalyst supported alumina and evaluate the performance of this catalyst in naphtha reforming reactions at different operating conditions of temperature, hydrogen/ hydrocarbon ratios (H_2/HC) and liquid hourly space velocity (LHSV) to produce an environment friendly gasoline with less benzene content.

2. Experimental work

2.1. Catalyst preparation

The catalyst was prepared by incipient wetness impregnation method using hexachloroplatinic acid ($PtCl_6H_2$, 8% Sigma Company, Germany) as a stock solution of active metal. γ-Al_2O_3 (99.9%, 0.62 gm/cm^3, 195 m^2/gm) is used as received from Aldrich Company. The stock solution is used to prepare 0.3% Pt solution; γ-Al_2O_3 is impregnated with that solution after evacuation using a vacuum pump, drying at 150◦C overnight, and calcined at 450°C in muffle furnace (Humboldt, H 30160) for 4 h. Meanwhile, Re (10%) and Ga (4%) solutions are prepared using rhenium sulphate ($Re_2(SO_4)_3.5H_2O$) and Ga_2SO_4 salts. Throughout 5 trials of co-impregnation and testing, they doped concentration by atomic absorption spectroscopy, 0.3% Pt, 1 % Re and 0.25% Ga are impregnated on alumina and the calcination is performed at temperature of 600◦C.

Fresh samples of the catalysts are exposed to a flowing gas mixture of pure H_2 at 650◦C for 12 h. This treatment is made to simulate accelerated ageing of the catalyst under reduction conditions in refineries during ATR (i.e., high-temperatures and reducing atmospheres) [10]. The total acidity of the prepared catalyst is measured according to Alemdarouglu [11] and it was 0.683 mmol/gm. The chemical composition of the prepared catalyst is examined in Atomic absorption spectrophotometer manufactured by Perkin-Elmer (Optima 2000 DV Inductively Coupled Plasma/Optical Emission Spectrometer (ICP/OES). Analytical Expert, pro multi-purpose diffractometer, (MPD Philips X-Pert, Netherlands) which is equipped with a pixel detector for data collection and both a Pt and Ga heating strip operate at 1500◦C and 2300$_o$C respectively. Textural properties of the catalyst are determined by Hitachi Scanning Electron Microscope (S-570, Japan) at 7-124 kV after coating the rubbed particles with polyethylene cover.

2.2. Catalyst evaluation

The prepared catalyst has to be evaluated, this evaluation is achieved in a trickle bed reactor rig consists of a surge tank for heavy naphtha. Heavy naphtha is fed to a jacketed 73 cm reactor length and 1.6 cm diameter S.S 316 L modified tube loaded with 15 gm fresh catalyst (for each test) and inert glass bead. The reactor is heated by an electrical coil controlled with a preset auto program. The catalyst reduction is performed by hydrogen at 520◦C for 4 hours at 12 bar, followed by 30 minutes sulfidation with 500 ppm H_2S in hydrogen stream, naphtha feed is charged to the reactor through a GC pump at 371◦C. The catalyst is reduced in hydrogen at 500ºC for 4 h. It needs 20 minutes to start naphtha feeding through a dosing pump at 1, 1.25, 1.5, and 2 $hr^{-1}$to 480, 500, 520 and 540 ºC controlled reactor (temperature increment is set at 10ºC/min). Hydrogen is fed at 69 bar and different H2/HC, 4, 4.5, 5.0 and 5.5. The product leaves the catalytic reactor to a flush drum where the unconsumed hydrogen is separated and recycled to the gas mixer to be mixed with fresh hydrogen, the liquid reformate product is taken every 1 hour and analyzed in high performance liquid chromatography (HPLC) (LTA 302 Butler): the system composed with two model P600 pumps, a model UV600 UV-Vis absorbance detector, a Spark model 840 auto-sampler, and a column oven manufactured by Labtech America and has to be used for analysis of compounds absorbing UV-Vis light at a wavelength range of 190nm-600nm using water/hexane (HPLC grade) a mobile phase, the mobile phase flow rate is 1 ml / min, and the HPLC retention time for benzene is 1.2 min. The commercial gasoline product (4 % benzene) standard sample was brought from Shell Global. Peak assignment in the sample spectrum is conducted by a careful comparison with the standard gasoline spectrum. Research Octane Number (RON) of the reformate sample is measured in duplication due to the ASTM D2700 procedure. The API (density) test is performed on Mettler (METTLER TOLEDO DM45).

3. Results and discussion

3.1. Catalyst characterization

The results of catalyst composition analysis for metal elements Ga, Re, and Pt are considered as a guide for ensuring accurate co-impregnation on alumina support during catalyst preparation. The results of tri-metallic dispersion of the fresh catalyst prepared in our laboratory (Catalyst x) are presented in Figure 1. The XRD pattern for Ga-Re-Pt /γ-Al_2O_3 has detected the entire elements and ensures that these elements are imbedded on the support structure in a good metal distribution pattern. It is obvious that Pt has the highest diffraction and the other promoters (Ga and Re) are impregnated at less loading. This pattern also ensures that a trimetalic structure is achieved after incipient wetness impregnation on alumina.

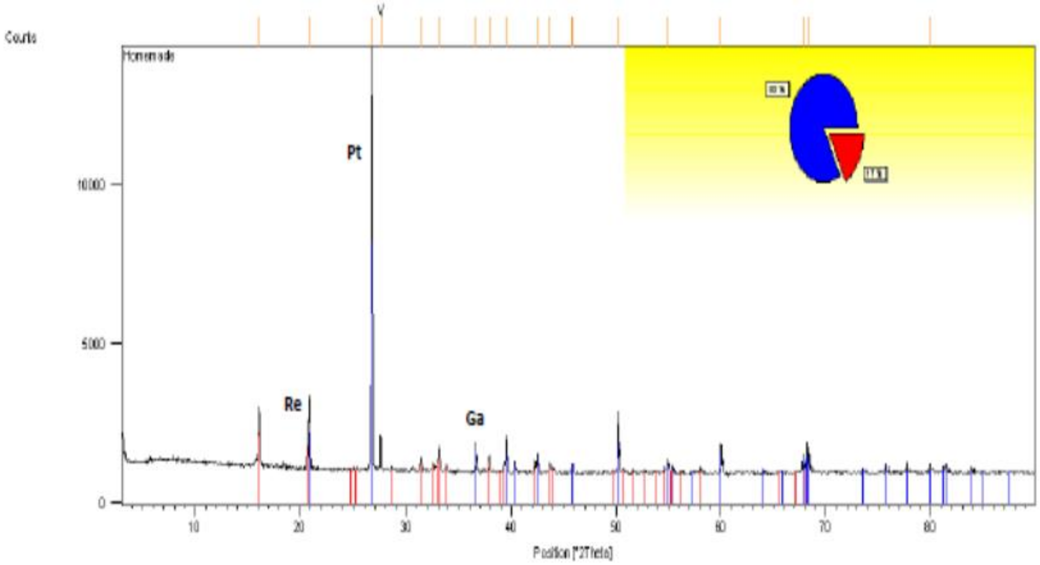

Figure 1. XRD patterns for fresh Ga-Re-Pt/Al_2O_3 laboratory prepared catalyst sample

Figure 2, shows the TPR traces of the tri-metallic catalyst. Pt/Al_2O_3 has a large hydrogen consumption peak centered at 320ºC. The total hydrogen consumption (TPR area) corresponds to the total reduction of Pt(IV) to Pt(0) [12]. The TPR trace of Re is steeper and has a maximum peak of 680ºC, with a similar one for Ga at 840ºC. This is an indication of an interaction between Pt, Re, and Ga oxides and alumina. The three peaks are attributed to metals oxides reduction at certain temperatures. Figure 3, presents a surface map obtained by SEM. This figure shows a good distribution of active metals (Pt, Re, and Ga) which represents while particles of Pt, Re and Ga in different particle sizes, alumina support represents large particle, furthermore. The agglomeration of active metals in some regions in the surface results in decreasing activity of catalyst and may be a seed for early sintering.

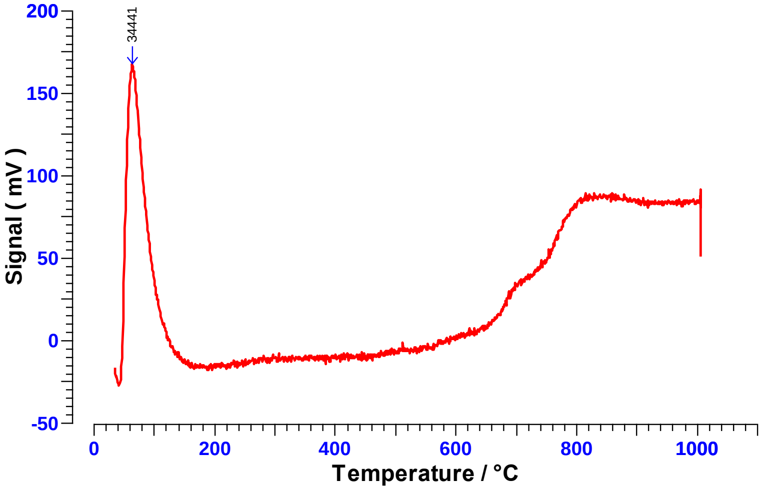

Figure 2. TPR for fresh Ga-Re-Pt/Al2O3 laboratory prepared catalyst sample

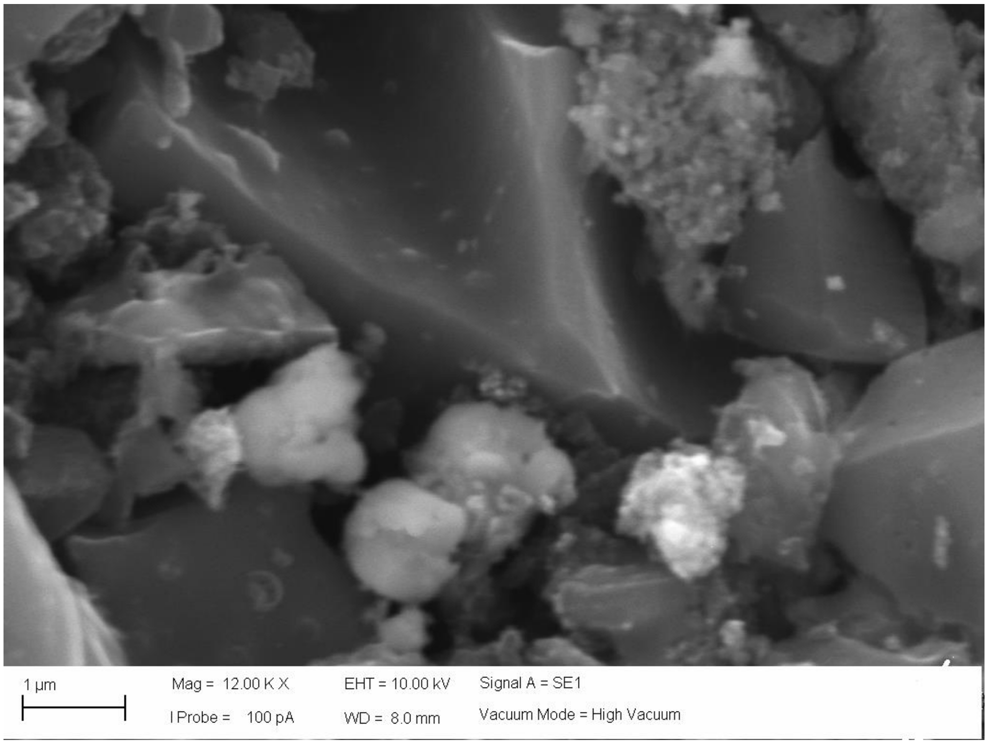

Figure 3. SEM image for fresh Ga-Re-Pt/Al_2O_3 laboratory prepared catalyst sample

3.2. Effect of temperature

Several trade-offs could occur regarding the effect of temperature on the promotion of desirable and undesirable reactions. Although the benefits of controlling temperature are evident, this is a very challengeable task in light of the highly endothermic nature of the dehydrogenation reactions [13]. Throughout this study the reactions were conducted at temperature range of 480-540°C to verify the optimum temperature progression. The reforming experiment is performed 6 hours with 1 hour as a time increment, with no chlorine addition throughout the experiments. Pt-Re-Ga catalyst is capable of operation over a wide range of temperature with high improvement of Research Octane Number (RON) and this is obvious in figure 4. This figure, Pt-Re-Ga exhibited a distinguished improving in RON with increasing of temperature and a good stability of the prepared catalyst is achieved (there is no RON decay throughout the time duration). In the lowest ratios of H_2/HC, the RON tends to settle at certain values of 76 and 84 for 4 and 4.5 ratios respectively this inhibition may be attributed to coke formation on the surface of the catalyst at low rate of hydrogen feeding. In contrast, the higher temperatures resulted in progressive RON improvement at highest H_2/HC ratio (5 and 5.5). Generally the inhibition of coke formation does not result in lowering RON even at low values of H_2/Hc ratios. As a result, the amount of hydrogen entering the reactor is an effective parameter which determines the H_2/HC ratio. H_2/HC molar ratio is one of the main parameters in the reforming units which should be controlled frequently and properly.

Low values accelerate the polymerization of the coke on the catalyst surface [14] hence, Incipient Wetness Impregnation resulted in good catalyst stability at the operating temperatures, it can be also concluded that 5 ppm injection of chlorine is sufficient to retard further coke deposition [15]. Figure 5, shows how benzene content progressively decreases with increasing temperatures. The reforming at the highest temperature results in the lowest benzene content of 1.88% at the highest H_2/HC ratio of 5.5. The other ratios also exhibit reasonable benzene content of 2.81, 2.35, and 2.05 for H_2/HC 4.0, 4.5, and 5.0. In addition, the temperature difference obviously accelerates catalyst deactivation at lower H_2/HC but there is no evidence that sintering starts early at the tested temperatures; thereby, there are no unexpected exothermic reactions that occur at these temperatures [16]. These finding are in good agreement with [12,17-20]

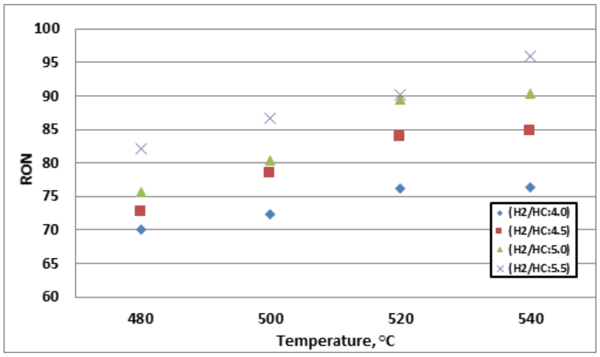

Figure 4. Effect of operating temperature on research octane number of the treated gasoline

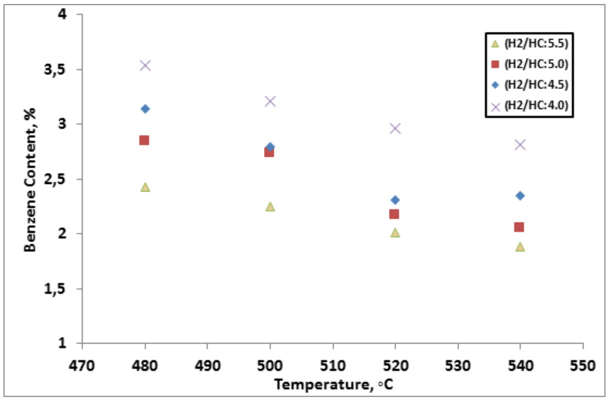

Figure 5. Effect of operating temperature on benzene content of the treated gasoline

3.3. Effect of LHSV

Figure 6, shows that the effect of space velocity (expressed as LHSV) is dramatically significant on benzene content. Operating at 1, 1.25, and 1.5 hr^{-1} resulted in a significant decrease in benzene content and is proven via many researchers, that enhancement of naphtha octane number in reformates is conventionally achieved by lowering LHSV or raising inlet temperature [21]. Operating at a higher LHSV from 1.5 through 2.0 hr^{-1} played synergistic role and resulted in an increase in benzene content, this can be attributed to the reduction of space / time of reactants (i.e. reducing the time required for reforming reaction with hydrogen over the catalyst). Moreover, higher liquid flow rates give greater liquid hold up which evidently decreases the contact of liquid and gas reactants on active site by increasing the film thickness. While at low liquid flow rate, the liquid resides in the reactor for longer time, and therefore undergoes more conversion and agrees with [22-23].

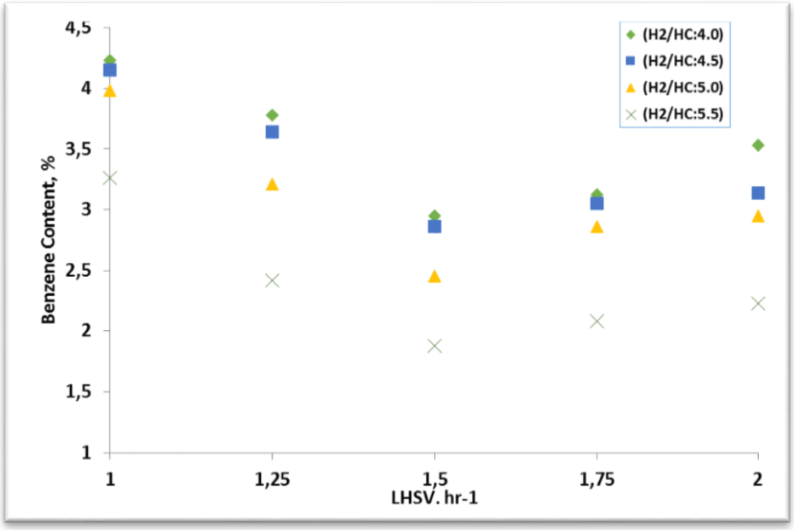

Figure 6. Effect of space velocity on benzene content of reformate

3.4. Effect of time on stream

PONA test is a detailed analysis of reformate hydrocarbon and it is considered in this study to assess the liquid products. $C5^+$% is the main parameter in this test. Table 1 shows a sample of PONA test for heavy naphtha and reformate which are based on ASTM D6293-98. The impregnation with Ga and Re increase the activity of the catalyst. With this catalyst at the operating temperature range of 480-540°C the selectivity is higher than with the commercial catalyst according to routine test in the Baiji Refinery (Iraq) as shown in table 1. The product distribution varies obviously with temperature. Table 1, shows that 540°C has the optimum liquid product distribution and the highest percentage of liquid products. This finding agrees with [16], they concluded that the gas producing selectivity of the commercial catalyst is sensitive towards the reaction temperature, while on the modified catalysts the liquid product yield is nearly constant. The laboratory prepared catalyst shows an average C_{5+} yield at 71.8%. Full analysis of the hydrocarbon composition of the reformate at different temperature shows that every 20°C increase in temperature results in about 0.5 wt% less aromatics and 0.21–0.34 wt.% higher isoparaffins. This yield can be attributed to the inhibition of hydrocracking and/or hydrogenolysis side reactions and agrees with [10,17].

Table 1. PONA test for heavy naphta and reformate by commercial and laboratory prepared catalysts

Com. name	Heavy naphtha A+O= 7.0%		Reformate (commercial catalyst) A+O= 51.0%		Reformate (laboratory prepared catalyst) A+O= 49.61%		1.5 LHSV, 5.5 H_2/HC wt.% ratio			
	Conc.	RT	Conc.	RT	Conc.	RT	480°C	500°C	520°C	540°C
PC3	0.139	2.908	0.015	0.373	0.023	0.436	0.0858	0.0428	0.036	0.023
PC4	0.930	3.547	0.95	1.173	1.114	1.381	0.9502	0.972	1.086	1.114
NC5	3.348	6.29	0.116	2.62	0.102	3.162	1.759	1.286	0.926	0.102
PC5	14.492	7.467	6.69	3.17	7.127	3.329	11.709	9.709	8.302	7.127
NC6	8.059	11.222	0.585	5.817	0.431	4.724	4.151	2.693	1.421	0.431
PC6	21.231	12.688	14.48	6.840	15.78	7.536	15.603	17.603	18.682	21.78
NC7	6.257	16.763	0.587	10.25	0.525	10.681	2.905	1.841	0.737	0.525
PC7	18.986	18.342	16.232	11.707	15.392	12.261	17.019	16.206	16.87	15.392
NC8	3.921	22.117	0.047	15.693	0.0528	16.032	2.032	2.289	1.043	0.0528
PC8	12.224	23.583	7.729	17.067	6.495	16.806	9.257	9.625	7.937	6.495
NC9	0.595	28.258	0.074	20.433	0.096	21.419	0.308	0.274	0.117	0.096
PC9	2.819	29.58	1.494	22.53	1.257	20.63	1.783	1.716	1.646	1.257
Total	93.00		49.00		50.394		67.562	64.3	58.803	50.394

RT- retention time, conc. in wt%

4. Conclusions

It can be concluded that gallium and rhenium interacted with platinum on alumina support successfully and can be used as a tri-metallic catalyst in reforming reactions. The characterization test proved that co-impregnation method works with this kind of catalyst. High reformate yield may be caused by a reduction in hydrocracking and/or hydrogenolysis side reactions. There is no significant early sintering at the early life of this catalyst due to operating at 480-540°C. This catalyst results in 1.88 % benzene and 1.6% higher reformate yield at the optimum operating conditions of 540°C, liquid hourly space velocity of 1.5 h^{-1} and 5.5 hydrogen/hydrocarbon ratio according to PONA test which compared the performance with the refinery yield. It is realized that Ga and Re addition greatly improves the selectivity, activity and stability of the catalyst. The addition of Ga and Re to the Pt/Al_2O_3 catalyst reducing the benzene/i-C7 ratio yielding environmentally friendly gasoline.

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Conflict of Interest

The authors declare no conflict of interest.

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