

PERFORMANCE ENHANCEMENT OF Pt-RE/ Al_2O_3 NAPHTHA REFORMING NANOCATALYSTS USING MICROEMULSION TECHNIQUE

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Received January 4, 2016; Accepted February 16, 2016

Abstract

Bimetallic Pt-Re supported nanocatalysts for naphtha reforming were prepared by impregnation and microemulsion techniques with water/surfactant (W/S) ratios of 0.3, 0.5, 0.66, 0.72, and 1 on gamma alumina. The catalysts were characterized by ICP-AES, BET, NH_3 -TPD, CO chemisorption, TPR, and TEM. The nanocatalysts were assessed in terms of their activity and products' yield in a fixed bed micro reactor for n-heptane reforming as model compound. The catalysts produced with microemulsion technique have smaller particles with very narrow particle size distributions and the reducibility of nanoparticles increased. The nano-particles synthesized by the proposed microemulsion technique increased catalyst activity (g HC/g cat. hr) and the yields of benzene and toluene, from 26.94, 4.36% and 16.92% to 50.04, 5.60% and 21.75%, respectively. The yield methane decreased from 2.65 to 0.99%. During 360 hrs continues reaction, the catalyst prepared with microemulsion (water to surfactant ratio of 0.3) showed 5% deactivation whereas the catalyst prepared with impregnation showed 30% deactivation.

Keywords: n-Heptane Reforming; Pt, Re, Microemulsion; Deactivation; Activity; Yield.

1. Introduction

Catalytic reforming is one of the processes aiming to increase the octane number of virgin naphtha. Catalytic reforming is the main route of hydrogen production in refineries and is an important route for aromatic intermediates production (benzene, toluene and xylenes). Side reactions (hydrogenolysis and hydrocracking) produce light gases such as propane and butane. There has been a continuous effort in catalyst development for the production of aromatics from the naphtha [1].

Alumina support has important industrial applications in the petroleum industry in reforming and hydrotreating processes [2]. The naphtha reforming reactions occur through bifunctional catalysis. Reactions, such as paraffin cracking and isomerization, are catalyzed by materials with acidic properties. The metal dehydrogenates the saturated hydrocarbons (alkylcyclopentanes or paraffins), producing more reactive olefin compounds. Therefore, the reaction to produce aromatic compounds is bifunctional since it uses both the metal and the acid sites [3]. In the catalytic reforming processes, platinum is the active component which disperses on the surface of γ -aluminum as support. The catalyst acidity promotes by addition of chlorine [4-6]. In the late 1960s, the monometallic catalysts were replaced by bimetallic Pt-Re/ Al_2O_3 -Cl catalysts [7], which were promising catalysts for low pressure operation. Bimetallic catalysts improved the length of the operation cycles due to their higher coking deactivation resistance, higher selectivity to aromatic compounds, and lower gas formation [8]. Acidic alumina in combination with one or two noble metals dispersed on it, can catalyze all the important reactions of reforming. Till now Pt-Re/ Al_2O_3 is well known among the bimetallic catalysts [7-8].

The wet impregnation method has traditionally been used to prepare bimetallic reforming catalysts. However, their final catalytic properties are strongly dependent on the preparation

method employed; therefore, important changes have been observed in the catalytic behavior for the impregnated catalysts, e.g., the order of the metals addition in the case of bimetallic catalysts [8]. It seems necessary to do studies to improve the catalysts performance through employing different methods of synthesis. In this sense, the sol-gel method and the microemulsion technique have been reported as an alternative to produce better catalysts [8-10].

It is well documented that the metal particle size of the catalyst is a parameter of importance for some reactions. Microemulsion, a novel technique for catalyst preparation, enables the control of metal particle size with a narrow particle size distribution, regardless of metal content. Briefly, a microemulsion consists of nanosized water droplets surrounded by an oil phase, stabilized by a surfactant. The size of the metal particles formed in water-in-oil (W/O) microemulsion is controlled by changing the micelle size (the water-to-surfactant (W/S) ratio) [9].

Balakrishnan *et al.* [11-12] pointed out that reforming catalyst with higher surface area and metal dispersion using the sol-gel method, which were more resistant to coke deactivation than those conventionally synthesized. They suggested that the large surface area and big pore sizes obtained by the one-step sol-gel method can be responsible for the resistance to deactivation when the catalysts are tested in the n-hexane conversion due to prevention of pore blocking. [13].

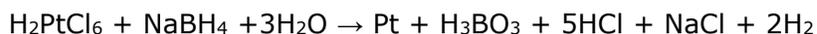
In this study naphtha reforming catalysts were prepared by microemulsion technique with W/S ratios of 0.3, 0.5, 0.66, 0.72 and 1 on gamma alumina and their activity, selectivity and stabilities compared with the catalysts prepared through traditionally impregnation method [9-10]. Fundamental studies in the structural and surface characteristics of impregnated and microemulsion catalysts will certainly contribute to the better understanding of their different catalytic properties. The catalysts were characterized by Brunauer-Emmett-Teller method (BET), temperature program reduction (TPR), ammonia temperature-programmed desorption (NH₃-TPD), CO chemisorptions, transmission electron microscopy (TEM) and at the end were applied to n-heptane reforming reaction for naphtha reforming in the fixed bed microreactor at 500°C and 1 bar during 360 hr test.

2. Experimental

2.1. Catalysts preparation

The support used was a commercial high-purity γ -alumina (Cyanamid Ketjen CK300). Main impurities were Na (5 ppm), Fe (150 ppm) and S (50 ppm). The extruded alumina pellets were sieved, and the 35–80 mesh fractions was separated and dried at 70°C for 8 hr then 120°C overnight, and calcined at 300°C for 3 hr under flow of air (60 cm³/ min.gr). The specific surface area of this support was 212 m²g⁻¹, the pore volume 0.52 cm³ and the average pore radius 10 nm.

The Pt-Re/Al₂O₃ catalysts were synthesized in a reverse microemulsion using a nonionic surfactant Triton X-100 (Aldrich), 1-butanol as the co-surfactant, n-hexane as the continuous oil phase and an aqueous solution as the dispersed phase. The concentration of Pt and Re were adjusted using aqueous solutions of H₂PtCl₆ and HReO₄ (Merck), in order to have a 0.3 wt% of Pt and 0.3 wt% Re on the final catalysts. The W/S molar ratio was varied from 1.0 to 0.3. After vigorous stirring, a microemulsion was obtained (15 min). NaBH₄ was added in excess to improve metal nanoparticle formation in the core of the micelles by reducing the metal oxides [9-10]. The reduction of metals takes place according to the following equation is accompanied by a solution color change from yellow to black [14-15].



Then, the appropriate weight of Al₂O₃-Cl was added under stirring. During the stirring, tetrahydrofurane (THF), an emulsion destabilizing agent, was added drop wise (0.33 ml/min). The mixture was left to stirring overnight and then sample was filtered and washed several times with water and ethanol. Next, the catalyst was dried at 120°C and calcined at 370°C for

3 hr and slowly exposed to an oxygen atmosphere during the cooling step. The catalysts prepared by means of this protocol were denoted as MEC₂-MEC₆.

The Pt-Re/Al₂O₃ control catalyst was prepared by wet impregnation of H₂PtCl₆ and HReO₄ aqueous solutions. The amount and concentration of the solutions were adjusted in order to have a 0.3 wt% of platinum and 0.3 wt% rhenium on the final catalyst. This catalyst was dried, calcined according to above procedure. The catalyst prepared by this method, denoted as IMC₁.

The compositions in all calcined catalysts were verified by ICP-AES. The catalysts nomenclature and properties are listed in Table 1.

Table 1. Chemical composition and chlorine content of the catalysts

| catalyst | Targeted composition, % wt. | | | Measured composition, % wt. | | |
|------------------|-----------------------------|-----|-----|-----------------------------|-------|------|
| | Pt | Re | Cl | Pt | Re | Cl |
| IMC ₁ | 0.3 | 0.3 | 0.8 | 0.290 | 0.290 | 0.78 |
| IMC ₂ | 0.3 | 0.3 | 0.8 | 0.258 | 0.285 | 0.44 |
| IMC ₃ | 0.3 | 0.3 | 0.8 | 0.240 | 0.282 | 0.45 |
| IMC ₄ | 0.3 | 0.3 | 0.8 | 0.255 | 0.272 | 0.58 |
| IMC ₅ | 0.3 | 0.3 | 0.8 | 0.272 | 0.288 | 0.58 |
| IMC ₆ | 0.3 | 0.3 | 0.8 | 0.267 | 0.272 | 0.43 |

2.2. Catalyst characterization

Morphology of all catalysts (IMC₁ and MEC₂-MEC₆) were characterized by Volhard–Charpentier method, BET, TPR, NH₃-TPD, CO chemisorptions, and TEM, according to procedure reported in references 8 and 15.

2.3. Catalyst activity test

One gram of each catalyst (diluted with 4 g quartz) was charged in an inconel fixed bed reactor of 2.54cm internal diameter, forming a bed of 54cm height. The catalyst was reduced in situ with hydrogen (60 ml/min) for 4 h at 500°C and sulphided with 0.2 wt. % dimethyl disulphide (DMDS) at same temperature for 90 min. The reforming of n-heptane was used as a test reaction. In each test run, n-heptane (Merck, 99.9%) was supplied to the reactor and the reaction was carried out for 6 hr at 500°C, 0.1 MPa, and molar ratio of H₂/n-heptane = 7.5. The reaction products were analyzed in a HP 5890 SERIES II Gas Chromatograph equipped with flame ionization and thermal conductivity detectors. Product yields were obtained from the chromatographic data. The yield of product i is the percentage of n-heptane converted into this product and is calculated as [11]:

$$C_i \text{ Yield} = \frac{\%C_i 100X}{\sum \%C_i} \quad (1)$$

where X is the total conversion; C_i the i compound concentration in the reaction products; $\sum \%C_i$ the sum of C_i products of reaction (n-heptane is not included).

For each experiment, the sum of all the C_i yields was in agreement with the n-C₇ conversion, pointing out an adequate carbon balance. Moreover, the repetitiveness of the n-C₇ reforming reaction test was quite good with a variance lower than 4%.

3. Result and discussion

3.1. Characterization

The chlorine content and elemental compositions of the calcined catalysts, measured by Volhard–Charpentier [16] and ICP method, are given in Table 1. The measured metal loadings were found to be slightly lower compared to the targeted values. The discrepancies may be due to poor homogeneity of microemulsion or particles sticking to the walls of the flasks and some mistake due to weighting. As shown, the chlorine content in the catalyst prepared by

microemulsion technique is lower than the targeted value. This can be due to the formation of solution salt and disappearance by washing.

The size of the particles and morphology of the surface of the support were also observed using TEM images. The TEM images of the catalysts made by impregnation and microemulsion techniques are shown in figure 1.

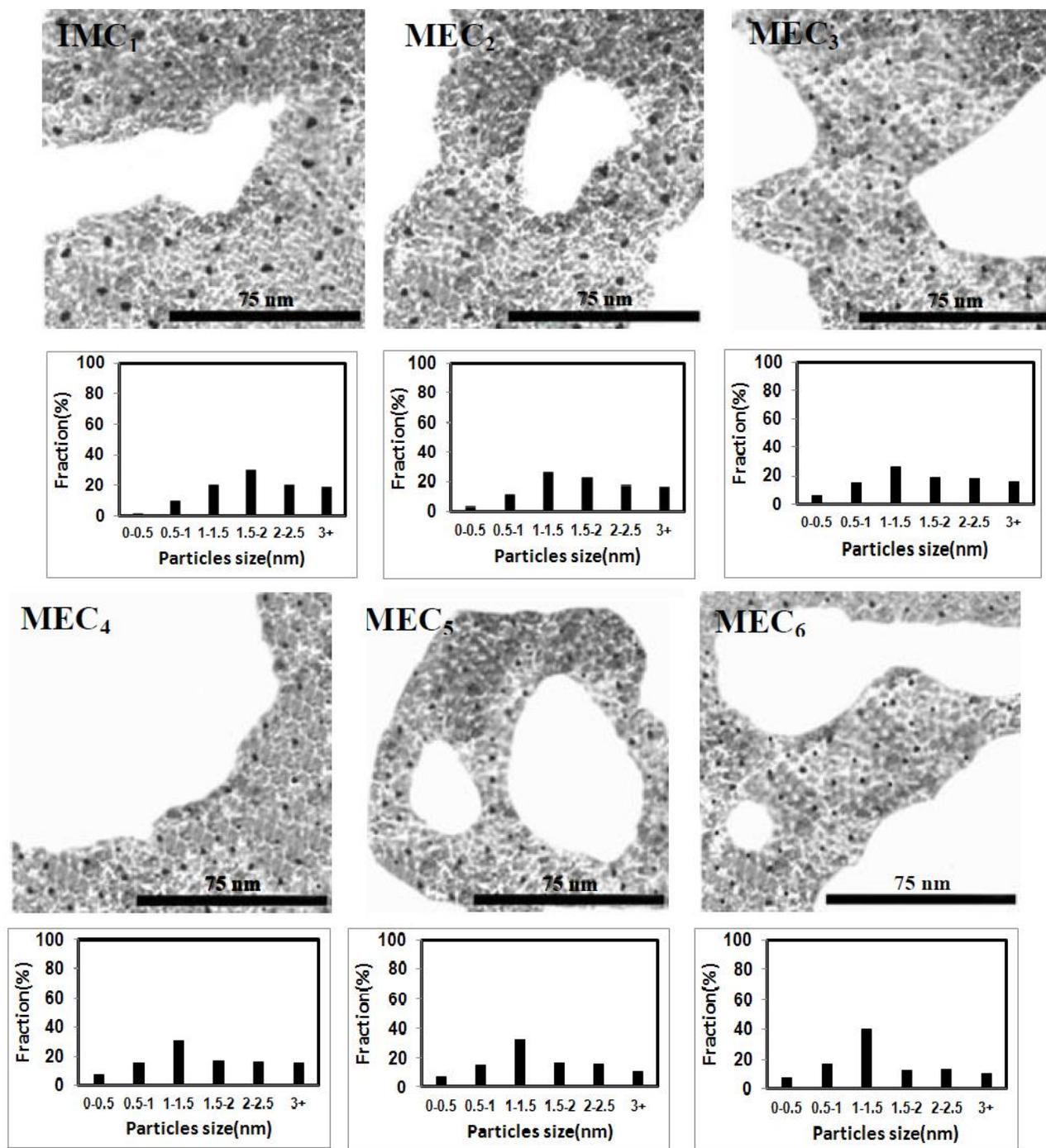


Figure 1. TEM images of IMC₁ and MEC₂- MEC₆ catalysts.

TEM images of these catalysts show some black spots correspond to the platinum-rhenium particles. Figure 1 also depicts the size distribution of the metal particles, which is determined using the population of the total metal particles of each catalyst based on data taken from

different TEM images (six images were presented here). According to TEM images of catalysts, microemulsion technique produced small particles which are uniformly dispersed on the support. This figure shows that metal nanoparticle size distributions for the catalysts prepared with microemulsion method (MEC₂-MEC₆) are better than that of the catalyst prepared with impregnation method (IMC₁). TEM images demonstrate the uniformity of the crystallites in C₆ catalyst and the metal particles size within a narrow range can be observed through this catalyst. According to Figure 1, the average particle sizes for IMC₁ and MEC₂-MEC₆ catalysts are about 2.2, 2.05, 2, 1.96, 1.90 and 1.80 nm, respectively.

Table 2 shows the effect of the synthesis method on the particle size and dispersion of the catalysts. Data of the metal loadings obtained by ICP are also given on this table. As shown small differences between designed and the actual metal loadings can be seen.

Table 2. Metal loading, dispersion, and acidity properties of the catalysts

| sample | particle size (nm) | | Dispersion ^a (%) | | H/Pt ratio ^b | Total acidity mmol NH ₃ /gr ^c |
|------------------|--------------------|------|-----------------------------|-----|-------------------------|---|
| | CO chem. | TEM | CO chem. | TEM | | |
| IMC ₁ | 2.00 | 2.20 | 63 | 54 | 2.40 | 0.34 |
| MEC ₂ | 1.92 | 2.05 | 66 | 57 | 2.73 | 0.36 |
| MEC ₃ | 1.83 | 2.00 | 69 | 58 | 2.99 | 0.38 |
| MEC ₄ | 1.75 | 1.96 | 72 | 60 | 3.04 | 0.41 |
| MEC ₅ | 1.64 | 1.90 | 77 | 62 | 3.05 | 0.46 |
| MEC ₆ | 1.59 | 1.80 | 79 | 66 | 3.22 | 0.48 |

a Determined by CO pulse chemisorption assuming a 1:1 CO:Pt stoichiometry.

b Determined From the H₂ consumption values of TPR profiles. *c* Determined by NH₃-TPD

According to the data obtained from CO chemisorption tests, metal average particle sizes are between 1.44 and 2.60 nm. These data confirms that using microemulsion technique for preparation of Pt-Re bimetallic catalyst especially at low water to surfactant ratios, leads to better dispersion of metal particles on the support. MEC₆ catalyst prepared with microemulsion method (W/S = 0.3) comprise 16% higher dispersion compared to IMC₁ catalyst prepared with impregnation. These results can be compared with those obtained from TEM. As can be seen in Table 2, TEM results show slightly larger particle sizes than those obtained by CO chemisorptions. One possible explanation lies in the experimental errors of both techniques and also to the possibility that CO chemisorption is a more sensitive technique than TEM; therefore, the amount of CO adsorbed is large, giving higher dispersions and smaller particle sizes.

Table 2 also shows the results of NH₃-TPD tests. As shown on this table, acidity of the catalysts prepared with microemulsion method are higher than that of the catalyst prepared by impregnation method in spite of lower chlorine ion levels (Table 1). The acidity of the support and the changes in the coordination spheres of aluminum have important roles in the catalytic behavior. Also, it is possible to observe that existing different aluminum phases which affect the acidity of catalyst supports are dependent to the synthesis method [8]. It seems that microemulsion procedure promotes the presence of these aluminum species which increase the acidity.

Table 3 presents the surface morphological characterization results for the pure and Pt-Re doped Al₂O₃ in both microemulsion and impregnation methods. Results of BET surface area (S_{BET}) in Table 3 show that in all cases the metal incorporation reduced the specific surface area of the catalysts when compared to the bare support. Lower S_{BET} and pore volume of the catalysts indicates some pore blockage due to Pt-Re loading on the support. However, data on this table show that the amount of pore blockage is lower in the case of the catalysts prepared by microemulsion technique especially at low water to surfactant ratios. The decrease

of S_{BET} and the pore volume for the catalysts prepared by microemulsion are lower than IMC_1 catalyst prepared with impregnation method. This is due to the uniform and small metal particles size produced through microemulsion technique. Furthermore the S_{BET} of MEC_2 - MEC_6 gradually increases from 198 to 209 m^2/g because the average particle sizes of these catalysts are linearly depending upon their respective W/S ratio (1-0.3). The MEC_6 catalyst with lower W/S ratio has smaller particle size and consequently less pore blockage, higher dispersion, S_{BET} and pore volume. This is in agreement with the results reported by Abbasi *et al.* [17].

Table 3. Textural properties of the catalysts

| Sample | Preparation procedure | W/S Ratio | S_{BET} (m^2/g) | pore volume (ml/g) | Average pore diameter (Å) |
|----------------|-----------------------|-----------|--|-------------------------------|---------------------------|
| IMC_1 | Impregnation | ----- | 180.23 | 0.37 | 77.0 |
| MEC_2 | Microemulsion | 1.00 | 198.15 | 0.40 | 79.2 |
| MEC_3 | Microemulsion | 0.72 | 199.17 | 0.42 | 82.8 |
| MEC_4 | Microemulsion | 0.66 | 202.61 | 0.43 | 85.3 |
| MEC_5 | Microemulsion | 0.50 | 204.73 | 0.42 | 89.4 |
| MEC_6 | Microemulsion | 0.30 | 209.43 | 0.47 | 91.9 |
| Support | ----- | ----- | 212.40 | 0.52 | 99.8 |

The reducibility of the catalysts in H_2 atmosphere was determined by TPR experiments. The TPR spectra of the calcined catalysts are shown in figure 2. TPR peak temperatures and the TPR area for all samples are presented in Table 4. In the TPR spectra of the catalysts, the low temperature peaks appeared in (220-360°C) are typically assigned to reduction of platinum oxides, weakly interacting with the support. The second peaks (300-470°C) are assigned to reduction of small rhenium oxide species and platinum oxide in its neighborhood. This H_2 -TPR diagram is fairly similar to analogous ones reported in the literature for similar systems [18-21].

According to figure 2, the reduction peaks of MEC_2 - MEC_6 catalysts synthesized by microemulsion technique shifted to higher temperature compared to the catalyst prepared with impregnation method (IMC_1); indicating lower reducibility for small particles. According to the TEM pictures, the deposition of small and uniform metal nanoparticles of these catalysts (especially for the MEC_6 (1.5-2 nm)) led to a higher interaction with γ -alumina, and made the reduction steps of these small particles harder than bigger particles produced through impregnation [22].

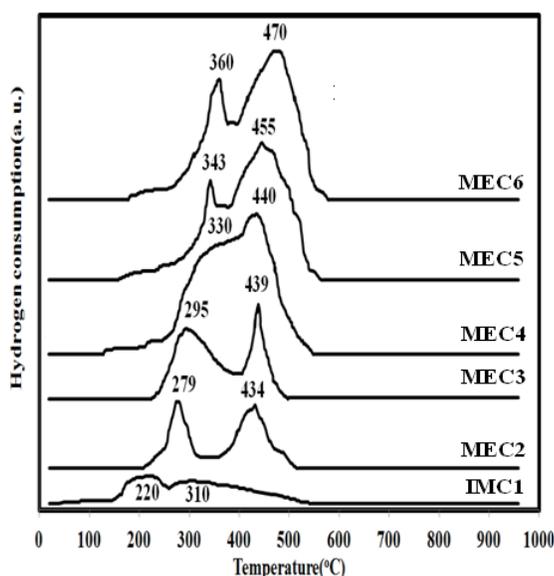


Figure 2. TPR curves for calcined catalysts

In TPR spectra, the peak area is assigned to hydrogen uptake of each catalyst. The results of Table 4 show that for IMC₁ and MEC₂-MEC₆ catalysts, the hydrogen uptake for first and second steps increases by decreasing the metal particle size. This suggests higher reduction degree for small metal nanoparticles synthesized by microemulsion technique [23].

Table 4. Hydrogen consumption and TPR results of catalysts

| Catalysts | First TPR peak (°C) Pt ⁺⁴ →Pt ⁰ | Second TPR peak (°C) Re ⁺⁷ →Re ⁰ | TPR area First peak | TPR area second peak |
|------------------|--|---|------------------------|-------------------------|
| IMC ₁ | 220 | 310 | 107.6 | 88.2 |
| MEC ₂ | 279 | 434 | 198.8 | 147.8 |
| MEC ₃ | 295 | 439 | 218.2 | 150.0 |
| MEC ₄ | 330 | 440 | 228.3 | 180.8 |
| MEC ₅ | 343 | 455 | 233.2 | 188.9 |
| MEC ₆ | 360 | 470 | 238.9 | 198.5 |

3.2. Reaction

Table 5 shows the results of catalysts activity and the different products' yield in n-heptane reforming reaction. The activity (gHC/gcat.hr) of proposed catalyst synthesized by microemulsion technique with minimum water to surfactant ratio (MEC₆) was 50.04 compared to 26.94 for traditionally impregnated catalyst (IMC₁). The MEC₆ catalyst is two times more active, and it is due to small and uniform particles size and consequently the dispersion of metal particles on the support produced through microemulsion technique [14,24].

Table 5. Catalysts' activity and yield of different products in n-Heptane reforming reaction

| Catalyst | Activity (g HC/g cat. h) | Yield (%) | | | | | |
|------------------|-----------------------------|-----------|---------|--------------------------------|---------|---------------------|----------------|
| | | Benzene | Toluene | C ₂ -C ₄ | Methane | Methane/ propane | H ₂ |
| IMC ₁ | 26.94 | 4.36 | 16.92 | 20.70 | 2.65 | 0.39 | 4.66 |
| MEC ₂ | 30.96 | 4.54 | 17.64 | 19.48 | 1.62 | 0.38 | 5.48 |
| MEC ₃ | 37.43 | 4.79 | 18.61 | 17.78 | 1.22 | 0.35 | 5.61 |
| MEC ₄ | 40.54 | 5.10 | 19.82 | 16.32 | 1.18 | 0.28 | 5.87 |
| MEC ₅ | 48.37 | 5.48 | 21.27 | 14.61 | 1.01 | 0.27 | 6.39 |
| MEC ₆ | 50.04 | 5.60 | 21.75 | 10.96 | 0.99 | 0.20 | 6.92 |

Furthermore in case of MEC₂-MEC₆ catalysts prepared by microemulsion technique, the activity of catalysts increased from 30.6 to 50.04 respectively, because the average particle sizes of these catalysts decreased linearly depending upon their respective W/S ratio (W/S decreased from 1 to 0.3). The catalysts with lower W/S ratio, have smaller particle size, less pore blockage, higher S_{BET} and pore volume and higher percentage dispersion which can be responsible for their higher catalyst activity [8,13].

According to Table 5, the MEC₂-MEC₆ catalysts also show an increase in hydrogen yield due to the smaller particle size of platinum oxides which increased the dehydrogenation reaction. Comparing the product yields for IMC₁ and MEC₆ catalysts, it can be seen that, benzene and toluene yields increased from 4.36% and 16.92% to 5.60% and 21.75%. Higher benzene and toluene yields in the case of MEC₆ catalyst may be due to the small and uniform particle sizes of MEC₆ catalyst synthesized through microemulsion technique. In a similar research, Bilone and Helle mentioned that there is a causal relation between the dividing of the platinum surface into small ensembles of contiguous platinum atoms and the enhancement of the selectivity for mild dehydrogenation [25].

On the other hand, the observed increase in benzene production in microemulsion catalysts corresponds to the increase in the amount of surface platinum as corroborated by CO chemisorption (Table 2), which suggests benzene production occurs mainly on Pt [26].

The changes in selectivity and yield of benzene and toluene can be explained if we keep in mind the metal-support strong interaction in microemulsion catalysts occurred. This interaction can be connected with the peculiar activity of the metal-support boundary (adlineation) sites suggested by Hayek *et al.* [27], where the adlineation of the defect of the support and the metal sites at the surface may be an important factor, which is promoted by the acidity of the support surface. Therefore, platinum in the adlineation sites is electron deficient and has a very strong effect in the selectivity and yield of benzene and toluene [26].

In microemulsion catalysts, the acidity is higher than impregnation catalyst. This acidity partly is due to high dispersion of active phase (Pt) as shown by CO chemisorptions in Table 2 [26]. The weak acidity is the main part of the total acidity according to NH₃-TPD spectrums (spectrums are not shown here). The production of toluene and benzene depend on the activity in dehydrocyclization reaction. Dehydrocyclization requires sites of lower acid strength than those needed for cracking [1]. This also causes the production of methane (C₁) and C₂-C₄ are lower in microemulsion catalysts compared to impregnation catalyst [28].

As shown in Table 5, the decrease in the metal particle size is effective in inhibiting the hydrogenolytic activity of the Pt-Re ensembles (a site composed of a large number of contiguous active metal atoms). The MEC₆ catalyst synthesized through microemulsion technique with smaller Pt-Re ensembles has a methane yield of 0.99% compared to the IMC₁ catalyst with methane yield of 2.65%. This is logical, since hydrogenolysis occurs better on a large ensemble [29]. It must be taken into account that methane is produced mainly from a hydrogenolysis reaction catalyzed by the metal sites, while propane is formed by a bifunctional mechanism controlled by the acid function of the catalyst. So for catalysts synthesized by microemulsion technique, the methane production reduced more than the production of propane and methane to propane ratio decreases or remains almost constant. These results confirm our suggestion about the catalysts performance which emphasized by other researchers [1, 26-28].

Figure 3 compares the percentage n-Heptane conversions for all the catalysts during 360 h continues synthesis. According to this figure, the catalysts prepared with microemulsion experience higher n-Heptane conversions as compared to the catalyst prepared with impregnation method. All catalysts suffered a deactivation rate. A 90% initial conversion was observed for MEC₆ catalyst with a residual conversion of 85% after 360 hours continues reaction showing 5% catalyst deactivation. Whereas, for the IMC₁ catalyst an initial conversion of 75% and residual conversion of 45% were obtained, showing a higher catalyst deactivation (30%). Higher resistance to deactivation was found for the catalysts prepared with microemulsion (MEC₂-MEC₆) compared to traditionally impregnated catalyst (IMC₁). Microemulsion catalysts with higher surface area and higher metal dispersion were more resistant to coke formation than that prepared by conventional impregnation method. The large surface area and big average pore size for MEC₆ catalyst can be responsible for its' higher resistance to deactivation and prevention of pore blocking [11-13, 26]. Small particles are less sensitive to coke formation than larger particles also has been previously suggested by Beltramini *et al.* [30].

Figure 4 shows the TPO traces of the carbon deposited on the used catalysts at the end of the reaction of n-Heptane. It can be seen that on the IMC₁ catalyst after the n-Heptane reaction, the coke is mainly burned at about 490°C which can be attributed to the burning of carbon on the support, with a shoulder at about 400°C that could be due to the coke deposited on the support, in the vicinity of the metal. This phenomenon was previously observed by Duprez *et al.* [31]. They reported that this coke results from a continuous slow migration of carbonaceous fragments from the metal to the support. In microemulsion catalysts (MEC₂-MEC₆) were observed a remarkable decrease of the coke content. This is due to the fact that coking is a structure-sensitive reaction and that microemulsion technique decrease the effective size of Pt and Re ensembles thus inhibiting the formation of coke on the metal

function. In the case of the microemulsion catalysts the lower coking rate in comparison to the IMC₁ catalyst is related to a lower formation rate of coke precursors. After dehydrogenation, olefinic compounds undergo dehydrocyclization reaction on weak acid sites of microemulsion catalysts [31].

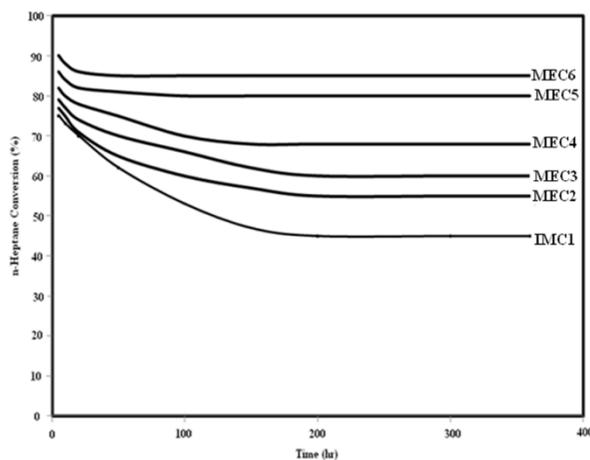


Figure 3. n-Heptane conversion profiles of IMC₁ and MEC₂- MEC₆ catalysts

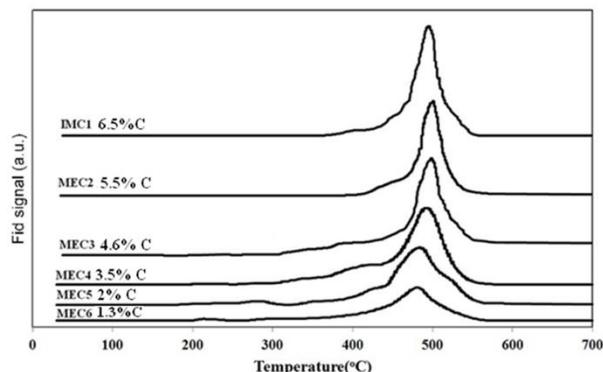


Figure 4. Temperature programmed oxidation of coke deposited after n-heptane reaction (360 h on stream)

Table 6 reports the variations of pore size and BET surface area and CO chemisorption of IMC₁ and MEC₆ catalysts after the n-Heptane reforming reaction within a time period of 360 h. According to this table the particle size, pore size, and BET surface area of MEC₆ catalyst didn't show a sensible change. The stability of the catalyst may be attributed to extent of increasing the metal-support interaction due to decreasing the particle size, which prevented metal site agglomeration or sintering. This matter has been mentioned by other researchers [22].

Table 2. Textural properties, and cluster sizes of IMC₁ and MEC₆ catalysts after 360 h n-Heptan reforming reaction

| Catalyst | | BET surface area (m ² /g) | Total pore volume (ml/g) | Average pore diameter (Å) | Particle size (nm) CO chem. |
|------------------|--------------------|--------------------------------------|--------------------------|---------------------------|-----------------------------|
| IMC ₁ | Before reaction | 180.00 | 0.37 | 77.0 | 2.00 |
| | After reaction (a) | 170.50 | 0.33 | 73.8 | 2.2 |
| MEC ₆ | Before reaction | 209.43 | 0.47 | 91.9 | 1.59 |
| | After reaction (a) | 206.50 | 0.46 | 91.5 | 1.62 |

^a after coke removal

4. Conclusion

The bimetallic Pt-Re/Al₂O₃ nanocatalysts were synthesized by impregnation and microemulsion methods with W/S molar ratio of 0.3, 0.5, 0.66, 0.72 and 1. According to S_{BET}, the nano particle synthesized by microemulsion has more active sites for reaction. CO chemisorptions results and TEM images showed that the microemulsion technique at lower W/S molar ratio produce small and uniform nanoparticles and consequently increase the dispersion of nanoparticles on the alumina supports. According to TPR profile, these Pt-Re nanoparticles were reduced at higher temperatures due to increasing metal-support interactions. It was also found that activity and selectivity of the catalysts are dependent to the synthesise method. The proposed Pt-Re nanocatalyst synthesized by microemulsion technique increased the catalyst activity, the yield of benzene, toluene. Also the yields of undesirable products like methane decreased. In addition the catalyst deactivation rate decreased significantly.

References

- [1] d'Ippolito SA, Vera CR, Epron F, Samoila P, Especel C, Marecot P, Gutierrez LB, Pieck CL. *App. Catal. A: Gen.* 370, (2009) 34–41.
- [2] Gates BC, Katzer JR, Schuit GCA. *Chemistry of the Catalytic Processes*; McGraw-Hill Chemical Engineering Series: New York, 1979.
- [3] Satterfield CN. *Heterogeneous Catalysis in Industrial Practice*; McGraw-Hill: New York, 1991.
- [4] Regalbuto JR, Antos GJ. *Preparation of Reforming Catalysis*, Marcel Dekker: New York, 2004; pp 141-198.
- [5] Hansel V. U.S. Patent 2,479,101, 1949.
- [6] Hansel V. U.S. Patent 2,479,110, 1949.
- [7] Klusksdahl HE. U.S. Patent 3,415,737, 1968.
- [8] Ignacio CA, Zavala AV, Viveros T. *Energy & Fuels* 2009, 23, 3835–3841.
- [9] M. Trepanier, A. Tavasoli, A. K. Dalai, N. Abatzoglou, *Appl. Catal. A*, 353, 193 (2009).
- [10] Karimi A, Nasernejad B, Rashidi AM, Tavassoli A, Pourkhalil M. *Fuel* 117 (2014) 1045–1051.
- [11] Balakrishnan K, Gonzalez RD. *J. Catal.* 1993, 144, 395–413.
- [12] Balakrishnan K, Gonzalez RD. *Langmuir* 10(7), 1994, 10, 2487–2490.
- [13] Cho IH, Bark PS, Cho SJ, Ryoo R. *J. Catal.* 1998, 173, 295–303.
- [14] Siné G, Smida D, Limat M, Foti G, Comninellis C. *J. of The Electrochem. Soci.* 154, (2007) B170-B174.
- [15] Karimi A, Rashidi AM, Nasernejad B. *J. Energy Chem.* 2013; 22:582–590
- [16] Carvalho LS, Conceição KCS, Mazzieri VA, Reyes P, Pieck CL, Rangel MdC. *Appl. Catal. A: General* 419–420, (2012) 156-163.
- [17] Abbasi Z, Haghghi M, Fatehifar E, Saedy S. *J. of hazardous materials* 186, (2011) 1445-1454.
- [18] Carvalho LS, Conceição KCS, Mazzieri VA, Reyes P, Pieck CL, Range MdC. *Appl. Catal. A: General* 419–420, (2012) 156-163.
- [19] Mazzieri VA, Grau JM, Vera CR, Yori JC, Parera JM, Pieck CL. *Catalysis Today* 107–108, (2005) 643-650.
- [20] Benitez V, Pieck C. *Catalysis Letters* 136, (2010) 45-51.
- [21] Mazzieri VA, Grau JM, Yori JC, Vera CR, Pieck CL. *Appl. Catal. A: General* 354, (2009) 161-168.
- [22] Ojeda M, Rojas S, Boutonnet M, Pérez-Alonso FJ, Garcia-Garcia FJ, Fierro JLG. *Appl. Catal. A: General* 274, (2004) 33–41.
- [23] Sánchez MA, Mazzieri VA, Grau JM, Yori JC, Pieck CL. *J. of Chem. Tech. & Biotec.* 86, (2011) 1198-1204.
- [24] Baranova EA, Tavasoli A, Amir T. *Electrocatalysis* 2, (2011) 89-95.
- [25] Biloen P, Helle JN, Verbeek H, Dautzenberg FM, Sachtler WMH. *Journal of Catalysis* 63, (1980) 112-118.
- [26] Contreras-Andrade I, Vazquez-Zavala A, Viveros T. *Energy & Fuels*, 23, (2009) 3835–3841.
- [27] Hakey K, Kramer R, Pál Z. *Appl. Catal. A: Gen.* 162, (1997) 1–15.
- [28] Epron F, Carnevillier C, Marecot P. *Appl. Catal. A: Gen.* 295, (2005) 157–169.
- [29] Augustine SM, Sachtler WMH. *The Journal of Physical Chemistry* 91, (1987) 5953-5956.
- [30] Beltramini J, Trimm DL. *Appl. Catal.* 31, (1987) 113–118.
- [31] Duprez D, Hadj-Aissa M, Barbier J. *Appl. Catal.* 49, (1989) 67–74.

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