Al-Khwarizmi Engineering Journal, Vol. 5, No. 3, PP 77–86 (2009)

Al-Khwarizmi
Engineering
Journal

Characterization of Metal Dispersion of Some Naphtha Reforming Catalysts by Methylcyclohexane Dehydrogenation Reaction

Ahmed J. Ali ***Ameel Mohammed Rahman**

**Department of Biochemical Engineering/ Al-Khwarizmi College of Engineering/ University of Baghdad*

(Received 29 July 2008 :accepted 2 June 2009)

Abstract

The dispersion of supported Pt and Pt–Ir reforming catalysts have been studied, after treatment with oxidative and reducing atmosphere. Methylcyclohexane dehydrogenation reaction in the absence of hydrogen was used as a test reaction. An attempt was made to relate the behavior of the catalysts upon subject to reaction, to the dispersion of the same type of catalysts upon treatment with similar atmosphere and temperatures which appeared in literature. The total conversion of reaction can be explained by a change in metal dispersion. Thus, methylcyclohexane dehydrogenation reaction appears to be a really “structure sensitive” reaction.

The toluene yield increases as the oxidation temperature increases over the studied catalyst RG-402, RG-412, RG-422 and RG-432 respectively and reached a maximum value at 550°C. Above 550 the conversion decreases due to the effect of catalyst sintering.

No significant change were observed for reduction temperature range 400-600°C for the above studied catalysts.

The selectivity order for the studied catalysts and for reduction treatment experiments arranged as follows:
RG-422> RG-432> RG-412> RG-402

Keywords: Platinum catalyst, dehydrogenation, metal dispersion

1. Introduction

Naphtha reforming is usually called “platforming” due to the use of catalysts based on platinum supported on alumina. Pt/Al_2O_3 catalysts have been widely used as catalysts.

During the naphtha reforming a complex reaction network takes place which includes both desired and undesired reactions. The desired transformations are dehydrogenation of naphthenes, isomerization and dehydrocyclization of paraffins. Undesired reactions are the hydrogenolysis and the cracking of paraffins that produce light gases of negligible value and decrease the overall liquid C^{5+} yield. Coking is another secondary reaction which rate needs to be decreased to prevent the premature deactivation of the catalyst by the accumulation of carbon deposits on the active sites.

In bifunctional reforming catalysts used for catalytic reforming of naphtha to produce higher octane number gasoline or aromatics, a careful balance has to be maintained between the hydrogenation–dehydrogenation function of the metal part (Pt, and or Ir, Re, In, etc.) and the acidic function (eg. Al_2O_3 and chlorine). Many papers had been published concerning $Pt\text{-}Re/Al_2O_3$ [1,2] and $Pt\text{-}Sn/Al_2O_3$ [3] catalysts. Addition of the Iridum component is known to lead to an improvement in the octane number (more branched alkanes, cycloalkanes, and aromatics) and lowers the rate of coke deposition, resulting in an increased stability[4]. The behavior of an Ir-Pt reforming catalysts was found to be Pt-catalyst like under n-heptane reforming experiments. Relatively, little has been appeared in literature concerning Pt-Ir loaded catalysts. In reforming processes, addition of tin to monometallic Pt/Al_2O_3 catalysts provides better stability, mitigates the sintering effect, improves selectivity by inhibition of hydrogenolytic effect of platinum, and decrease isomerisation and coke deposition, while aromatization is increased [5-10].

Two different effects caused by addition of a second metal are suggested in the literature: one geometrical, in which a physical dilution of platinum by a second metal takes place, and one electronic, where the formation of alloys causes a change in bond strength between the chemisorbed hydrocarbon and the active metal [11-15].

Acquiring high metal dispersion of active phases on the surface of reaction is the key point in preparing a high active catalyst. Researchers, found that the surface area and porosity alone cannot explain the metal dispersion on the catalyst [16].

Methylcyclohexane (MCH) dehydrogenation has long been used as a model reaction to probe catalytic performance of catalysts [16]. As one of the most effective catalysts for this reaction, Pt/Al_2O_3 has been extensively studied [17]. This reaction has gained a renaissance because it is considered an efficient method to store and supply H_2 through a reversible hydrogenation-dehydrogenation cycle [18].

In the previous work, the study of methylcyclohexane dehydrogenation reforming reactions showed that the former can be used to estimate platinum dispersion in the catalysts, whereas the distribution of products in the latter gives indications on the degree of deactivation of a catalyst and how it will perform in the industrial process [5, 19-22].

In the present study, four types of reforming catalysts with different Pt dispersion were used. Dehydrogenation of methylcyclohexane in the absence of hydrogen at 450°C was chosen as a model reaction for the comparison of the state of metal function upon oxidation and reduction at different temperatures.

2. Experimental Work

2.1. Methods and Materials

(i) Catalysts

Four types of catalysts were supplied from IFP (Institut Français du Pétrole) had been used in this work, with platinum varying around the industrial metallic loading (0.35-0.6wt.%). The properties of these cylindrical extrudates catalysts are shown in Table 1.

The spectroscopy grade methylcyclohexane (Fluka) used in this investigation was more than 99% in purity and was passed over a bed of molecular sieve (BDH, type 5A) to remove impurities, notably, water and sulfur containing species.

High grade quality hydrogen and Nitrogen and oxygen gases with a purity of 99.99% were used in this work. The nitrogen was further purified by passing over a Cu bed at 400°C, to remove traces of H2 and O2. Then passed over molecular sieve to remove traces of water. Traces of O2 and H2O in H2 gas were removed by a Matheson deoxe unit and a silica gel column respectively. Traces of water in the process gases were removed by a Matheson model 450 drier.

Table 1,
Catalysts Specifications

Catalyst	Pt content wt.%	Promoter (Ir) PPM	Metal Dispersion	Surface Area m^2/g	Chlorine Content wt.%
RG-402	0.6	None	64	158	1.02
RG-412	0.35	None	65	162	1.00
RG-422	0.6	500	74	182	1.11
RG-432	0.35	500	80	196	1.09

(ii) Catalyst Activity Test

The catalyst activity test experiments were performed in a laboratory fixed bed type reactor with a continuous flow system at atmospheric pressure. The flow diagram of the laboratory reaction unit is shown in Fig. 1.

The flows of gases were measured by calibrated rotameter and controlled by a needle valve. The flows of gases used were: oxygen-free nitrogen (90 ml/min), nitrogen (114 ml/min) and hydrogen (88 ml/min). Nitrogen was used for heating the reactor bed from room temperature to reaction temperature. Then the treatment gases were introduced to the reactor according to the conditions of experiments.

Methylcyclohexane was fed by the calibrated syringe pump at a rate of 6ml/h into the preheater section then to the evaporator section of the reaction zone. Methylcyclohexane vapor was then fed to the reactor containing the catalyst bed by incoming hydrogen as well as the diluent nitrogen gas.

The reactor was a vertical mounted pyrex tube of 2 cm inside diameter and 35 cm long surrounded by a well insulated jacket heater. The temperature was measured by using Ni/Cr thermocouple and controlled by a temperature controller. Reaction period of 30 min were employed in all experiments to ensure the attainment of steady state conditions. A fresh catalyst was used in each experiment. 1.5 g of each catalyst was charged between two layers of inert materials (quartz chips-to serve as a preheating section). The average size of the extruded shape catalyst granules was 1.5 mm in diameter by 4 mm in length.

The effluent gases from the reactor were passed through the condenser, which was maintained at about 0°C by ice cubes.

The collected liquid products were analyzed by gas-liquid chromatography (INTERSMAT INSTRUMENTS) equipped with stainless steel column of 3.2mm diameter and 2 m long filled with 10% SE-30 on Chromosorb W and using a flame-ionization detector.

Methylcyclohexane dehydrogenation reaction yields toluene, benzene, methylcyclohexenes, metylhexadiens and cracked product in the collected liquid phase. It was found that the major products from the dehydrogenation of MCH were hydrogen and Toluene.

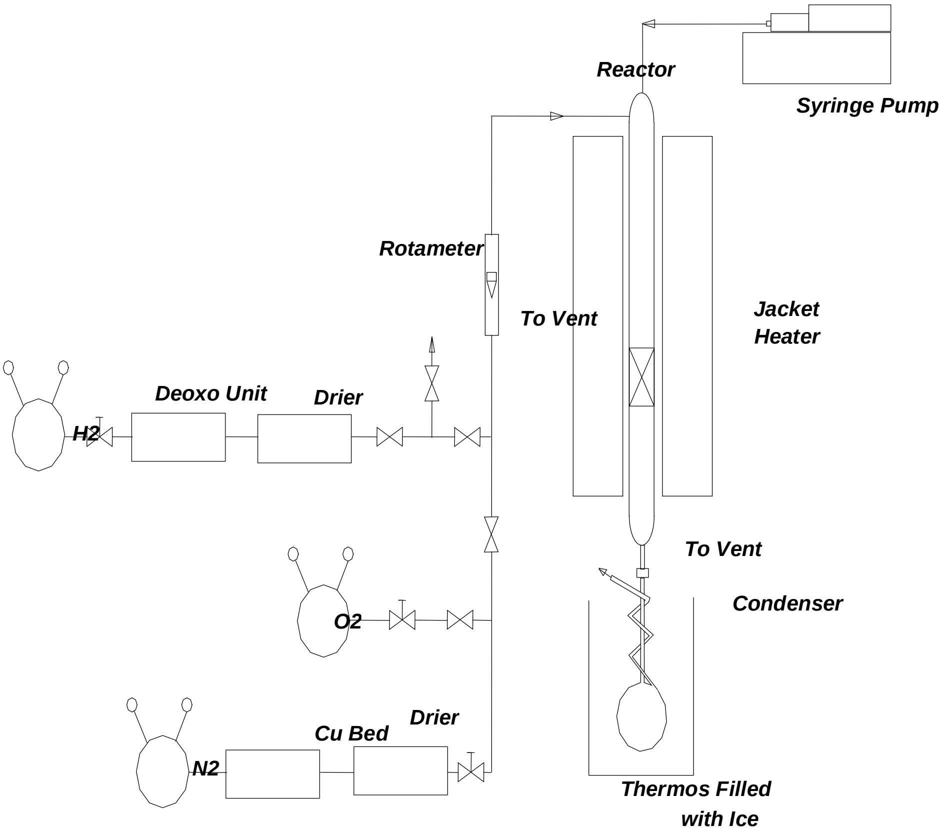

Fig. 1. Catalyst Test Apparatus.

3. Results and Discussion

The conversion of MCH to toluene was used as an indication of the extent of dehydrogenation reaction. This reaction was known to be a highly endothermic reaction [8]. Inspection of effluent gases from condenser was carried out periodically and only traces amount of benzene were detected.

The effect of different oxidizing and or reducing atmosphere on MCH dehydrogenation reaction for catalysts listed in Table 1 was investigated in this study to see whether this reaction represent the metal dispersion state of the catalysts investigated.

3.1. The Effect of Oxidizing Atmosphere

The effect of oxidation treatment on the conversion of MCH to toluene at 450°C was studied over the temperature range 400-600°C and over the four catalysts are shown in Fig.2.

As shown in Fig.2, the catalytic activity increases and toluene yield increases as the temperature increases and reach a maximum value at 550°C. Then toluene yield dropped severely at 600°C for both Pt and Pt-Ir catalysts. This behavior was observed for supported Pt catalysts, where at temperatures ≥ 600°C the catalysts can be sintered in a short time up to a value never obtained in hydrogen atmosphere [21].

Various investigators have reported increases in platinum dispersion upon treatment of Pt/Al_2O_3 in oxygen containing atmosphere at temperatures 400–580°C, whereas at higher temperatures sintering occurs. Most of these studies indicates a maximum dispersion at temperatures 500–580°C [17-22] except the work of Hassan et al. [23] who observed a decrease in metal dispersion on increasing oxidation temperature.

Increases in Pt dispersion predicted by most of the investigators was achieved wherever the catalysts containing chlorine or not. Lietz et al. [24] had related the increase in metal dispersion to the state of platinum in the catalyst (soluble or crystalline form) as suggested by McHenry et al. [25] for chlorine containing catalysts.

The observed relation between metal dispersion and catalytic activity had also been proved by Aben et al. [26] for benzene dehydrogenation, Dautzenberg and Platteeuw [27] for n-Hexane dehydrocyclization and isomerization, and Lee and Kim [28] for cyclohexane hydrogenation. It is clearly appeared from above discussion that the Pt–Ir catalysts behave like Pt catalysts as found by Ramaswamy et al. [29] on working with catalysts of low Ir content (Pt/Ir=10:1). The Pt–Ir catalysts used in this investigation are within this ratio (Pt/Ir=14:1 to 8:1). Granam and Wank [19] had approached to a quite different behavior on working with higher Ir content catalysts (Pt/Ir=1:1) after relating metal dispersion to oxidation temperature.

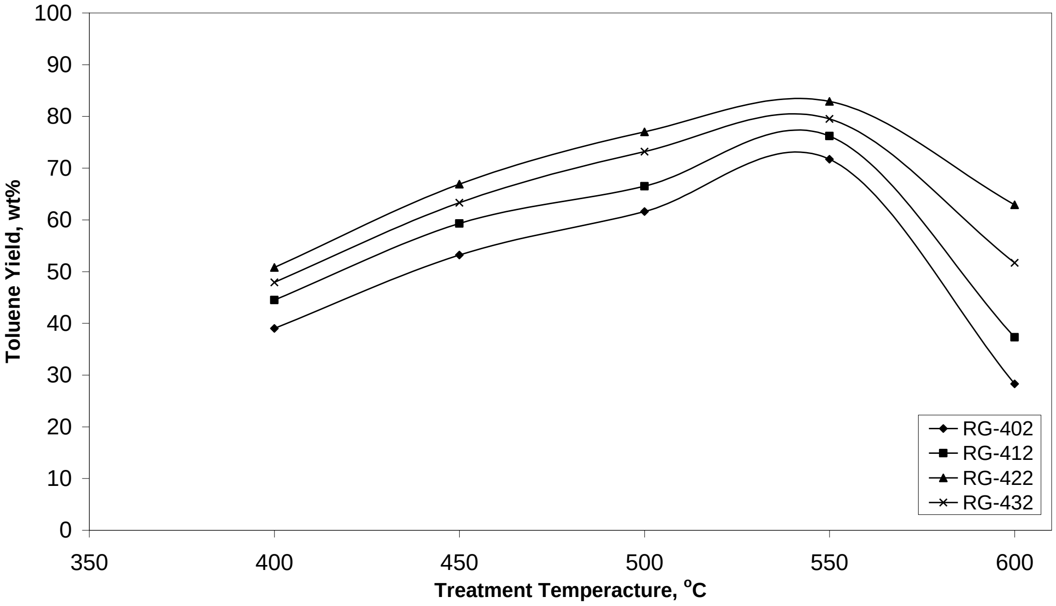

Fig.2, Effect of 1h Oxidation Treatment on MCH Dehydrogenation Reaction at 450°C.

3.2. The Effect of Reducing Atmosphere

As shown in Fig.3, the supported Pt and Pt–Ir catalysts are reduced with pure hydrogen at different temperatures followed by MCH dehydrogenation reaction at 450°C. A constant MCH conversion was observed for both supported 0.6%Pt RG-402 and 0.6%Pt/Ir RG-432 catalysts at different reduction temperatures and as shown in Fig.3. This indicates that, reduction at temperatures 400–600°C have somewhat no effect on metal dispersion as indicated by Smith et al. [30] and Dautzenberg and Wolters [17].

Reduction of reforming catalysts at different temperatures characterized by hydrogen–chemisorption as an indication of metal dispersion had been the subject of many published works. Graham and Wank [19] observed a monotonic decrease in dispersion upon increasing of reduction temperature for 1% Pt and 1%Pt–1%Ir catalysts. While, Dautzenberg and Wolters [17] found that crystalline growth does not occur to any extent on reduction at different temperatures for supported 0.4–2%Pt catalysts. Smith et al. [23] also claimed that, increasing of temperature of reduction (from 500 to 600°C) did not seems to influence the amount of sintering on working with light metal loading, and that particle rounding appeared to be the major change.

Increasing of Pt content from 0.35-0.6 wt.% was appeared to have a slight effect on catalytic activity as shown in Fig. 3.

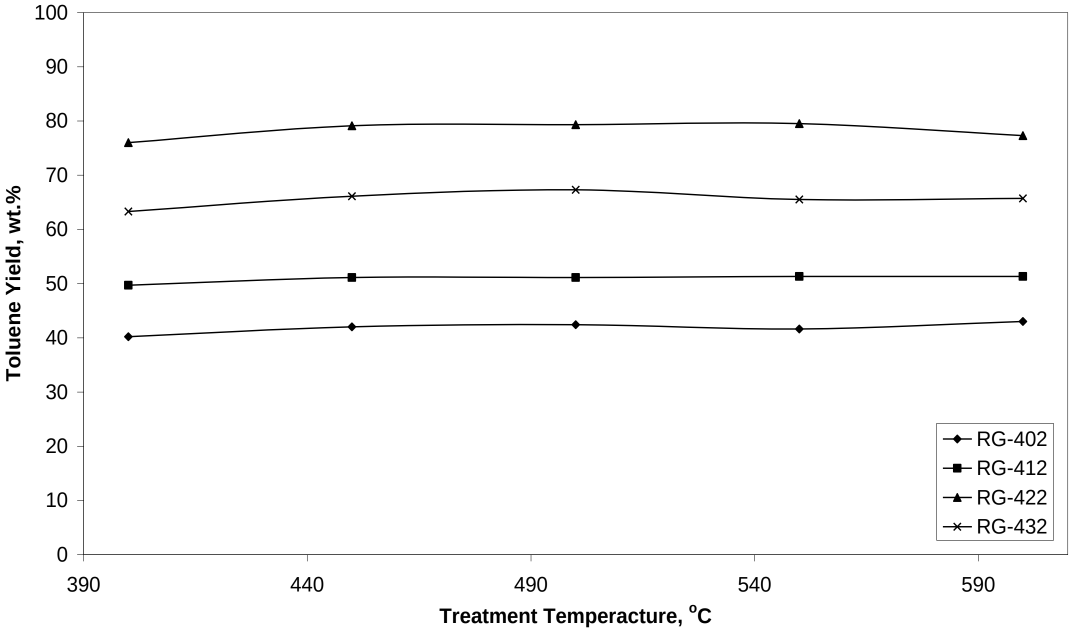

Fig.3, Effect of 1h Reduction Treatment on MCH Dehydrogenation Reaction.

3.3. Selectivity and Product Distribution

In this study, only the product distribution over the studied reduction temperature was presented here. Product distribution shows that the main reaction is dehydrogenation. Concerning dehydrogenation, the selectivity order for the four commercial catalysts is, RG-422> RG-432> RG-412> RG-402 and as shown in Figs.4 to 8. In this case the evaluation of selectivity with temperature is more interesting; as it was observed that the reaction rate is not controlled by the Pt dispersion [17, 20, 22].

Liquid product selectivity is shown in Figs. 4 to 8, where both catalysts give somewhat similar product distribution. A different behavior was observed for supported 0.35%Pt RG-422 and 0.35%Pt–Ir RG-412 catalysts as shown in Fig.6. Minimum MCH conversions were observed at a reduction temperature of 500°C. Hassan et al. [23] had obtained a somewhat similar trend for metal dispersion (indicated by H_2- chemisorption) upon reduction at different temperatures (300-800°C) for 0.2–2%Pt catalysts. The authors had no data observation at a reduction temperature of 500°C, and a minimum dispersion was obtained at 400°C.

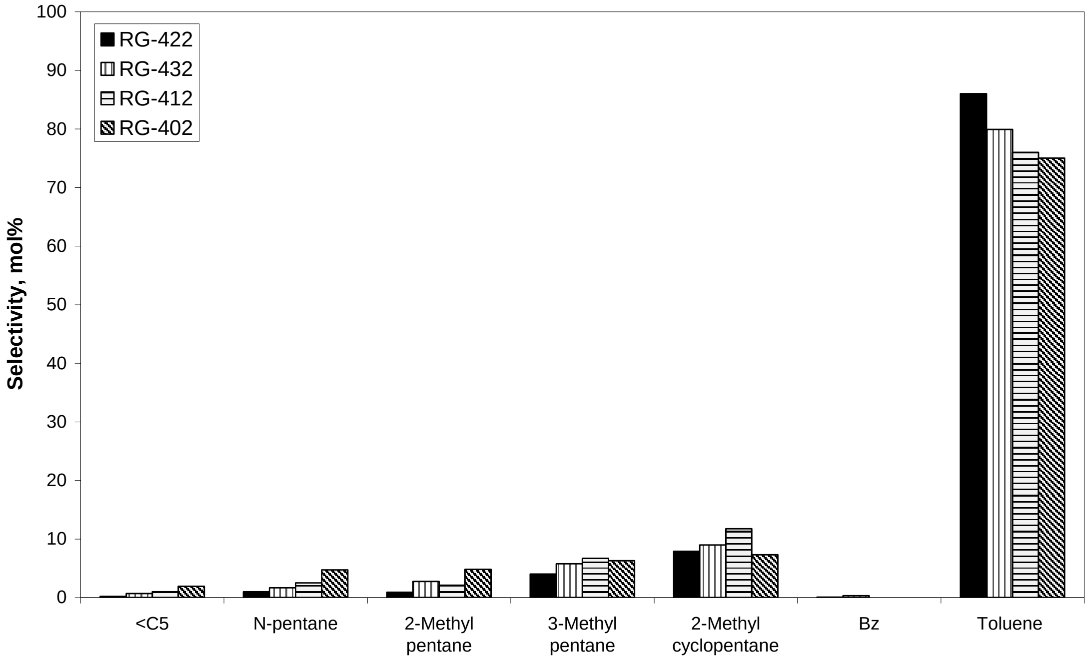

Fig.4, Selectivity of Products after 1h Reduction at 400°C Temperature and of MCH Dehydrogenation Reaction at 450°C.

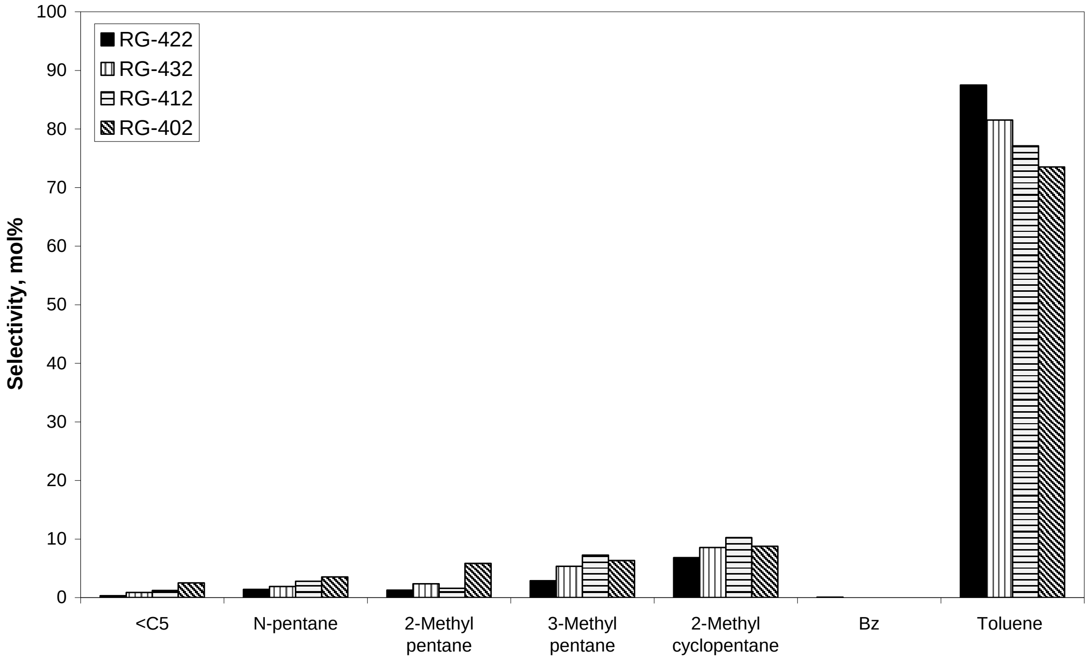

Fig.5, Selectivity of Products after 1h Reduction at 450°C Temperature and of MCH Dehydrogenation Reaction at 450°C.

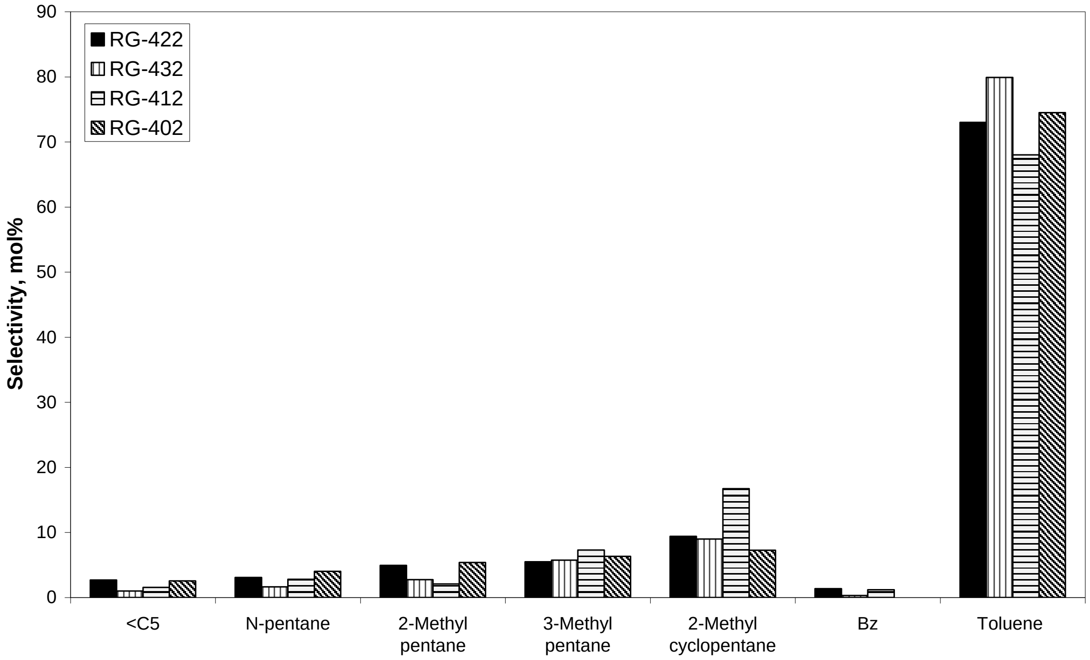

Fig.6, Selectivity of Products after 1h Reduction at 500°C Temperature and of MCH Dehydrogenation Reaction at 450°C.

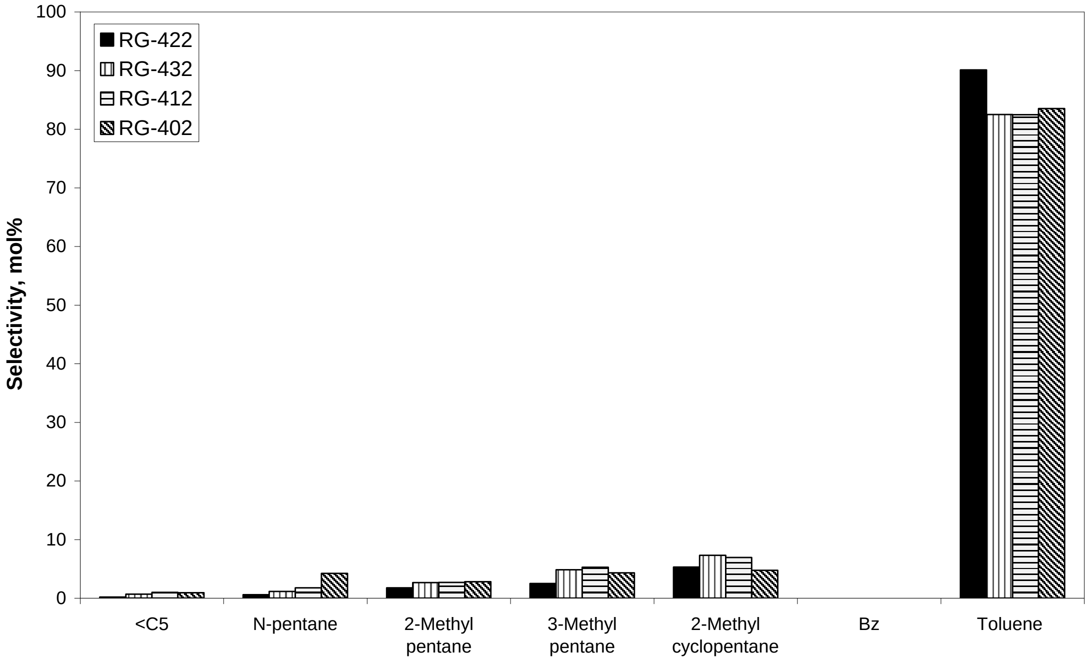

Fig.7, Selectivity of Products after 1h Reduction at 550°C Temperature and of MCH Dehydrogenation Reaction at 450°C.

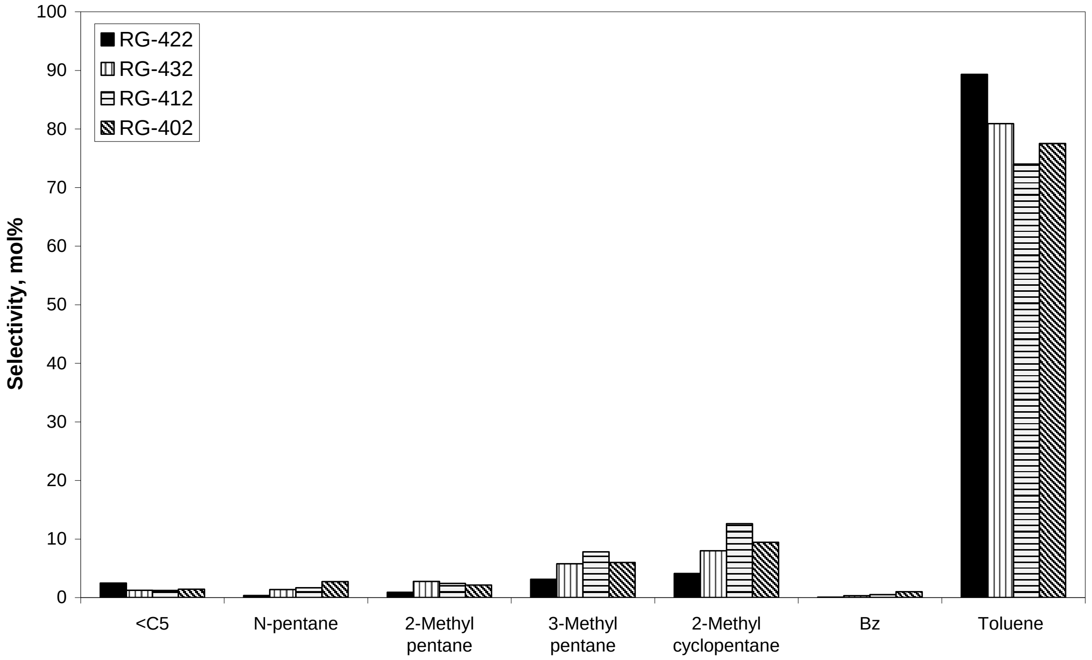

Fig.8, Selectivity of Products after 1h Reduction at 600°C Temperature and of MCH Dehydrogenation Reaction at 450°C.

4. Conclusions

- Methylcyclohexane conversion increases as the oxidation temperature increases and reached 71.7, 76.2 79.5 and 82.9 wt.% for RG-402, RG-412, RG-422 and RG-432 catalysts respectively at 550°C. Above 550 ^{0}C the conversion decreases due to the effect of catalyst sintering.
- Increasing Pt content from 0.35 to 0.6 wt.% was appeared to have a little effect on catalytic activity for both Pt and Pt/Ir catalysts.
- No significant change where observed for reduction temperature range 400-600°C for the above studied catalysts.
- The product distribution of the reduction treatment experiment shows that the main reaction is dehydrogenation. The selectivity order for the studied catalysts is as follows:

RG-422> RG-432> RG-412> RG-402

From these experimental observations, it appears that, such reforming catalysts as subjected to MCH reaction are structure sensitive and this reaction can characterize metal dispersion.

5. References

[1] Fung, A.S., Kelley, M.J., Koningsberger and Gates, B.C., "γ-Al_2O_3-Supported Re-Pt Cluster Catalyst Prepared from $[Re_2Pt(CO)_{12}]$: Characterization by Externded X-Ray Absorption Fine Structure Spectroscopy and Catalysis of Methylcyclohexane Dehydrogenation", J. Am. Chem. Soc., 119, 5877 (1997).

[2] Parera, J. M., "Deactivation and Regeneration of Pt-Re/Al_2O_3 Catalysts", *Stud. Surf. Sci. Catal.*, 68, 103-10 (1991).

[3] Rajeshwer, D.; Basrur, A. G.; Gokak, D. T.; Krishnamurthy, K. R., "Method for Metal Dispersion Measurements in Bimetallic Pt-Sn/Al_2O_3 Catalysts", *J. Catal.*, 150, 135-42, (1994).

[4] Duprez, D.; Hadj-Aissa, M.; Barbier, J., "Effect of Steam on the Coking and on the Regeneration of Metal Catalysts: A Comparative Study of Alumina-Supported Platinum, Rhenium, Iridium and Rhodium Catalysts", *Stud. Surf. Sci. Catal.*, 68, 111-8 (1991).

[5] Gonzalez-Marcos M.P., Guil J.M. Inarra B., Gutierrez-Ortiz, "Development of an Industrial Characterization Method for

Naphtha Reforming Bimetallic Pt-Sn/Al_2O_3 Catalyst Through n-Heptane Reforming Test Reactions", Catal. Today 107-108, 685-692, (2005).

[6] Anderson, J. R. and Avery, N.R., *J. Catal.*, 5, 446 (1966).

[7] Fujikawa T., F.H. Ribeiro, G.A. G.A. Somorjai, J. Catal., 178, 58, (1998).

[8] Palazov A., Ch. Bonev, D. Shopov, G. Lietz, A. Sarkang, J. Volter, J. Catal., 103, 249, (1987).

[9] Burch, R., L. C. Garla, J. Catal., 71, 360, (1981).

[10] Che, M., C.O. Bennett, Adv. Catal., 36, 55, (1986).

[11] Xiaoyun Li., Ding Ma. And Xinhe Bao, "Dispersion of Pt Catalysts Supported on Activated carbon and Their catalytic Performance in Methylcyclohexane Dehydrogenation", J. Catal., 29, 3, 259-263, (2008).

[12] Okada Y., Sasaki E., Watanabe E., Hodo S., Nishijima H. Int. J. Hydrogen Energy, 31, 10, 1348, (2006).

[13] Gonzalez-Marcos, M.P., B. Inarra, J. M. Guil, M.A. Gutierrez- Ortiz, Appl. Catal., A273, 259, (2004).

[14] Ritchie, A.W., Nixon, A.C., "Dehydrogenation of Methylcyclohexane Over a Platinum-Alumina Catalyst in Absence of Added Hydrogen", Ind. Eng. Chem. Prod. Res. Dev. 5, 59-64 (1966).

[15] Parmaliana, A., Frusteri, F., Mezzapica, A., Giordano, N., "The Role of Chlorine in the Regeneration of Hydrogen of Coked Reforming Catalysts", J. Catal. 111, 235-242 (1988).

[16] Straguzzi, G.I., Aduriz, H.R., Gigola, C.E., "Redispersion of Platinum on Alumina Support", J. Catal. 66, 171-183 (1980).

[17] Dautzenberg, F. M., and H.B.M. Wolters, "State of Dispersion of Platinum in Alumina Supported Catalysts", J. Catal. 51, 26 (1978).

[18] Fiedorow, R.M.J.; Chahar, B. S.; and S. E. Wanke, "The Sintering of Supported Metal Catalysts. 2. Comparison of Sintering Rates of Supported Pt, Ir, and Rh Catalysts in Hydrogen and Oxygen", J. Catal. 51, 193–202 (1978).

[19] Graham, A.J. and S. E. Wank, "The sintering of Supported Metal Catalysts. 3. The Thermal Stability of Bimetallic Pt–Ir Catalysts Supported on Alumina", J. Catal. 68, 1–8 (1981).

[20] Lieske, H., Lietz, G., Spindler, H., Volter, J., "Reactions of Platinum in Oxygen-and Hydrogen-Treated Pt/g-Al_2O_3 Catalysts. 1-Temperature Programmed Reduction, Adsorption, and Redispersion of Platinum", J. Catal. 81, 8-16 (1983).

[21] Straguzzi, G.I., Aduriz, H.R., Gigola, C.E., "Redispersion of Platinum on Alumina Support", J. Catal. 66, 171-183(1980).

[22] Lee, T. J., Kim, Y.G., "Dispersion of Supported Platinum Catalysts in Oxygen. 1-Experimental Evidences of Redispersion. KJChE 2, 55-61 (1985).

[23] Hassan, S.A., Khalil, F.H., El-Gamal, F.G., "The Effect of Different Atmospheres on The Sintering of Pt/Al_2O_3 Catalysts", J. Catal. 44, 5-14 (1976).

[24] Lietz, G., Lieske, H., Spindler, H., Hanke, W., Volter, J., "Reactions of Platinum in Oxygen-and Hydrogen-Treated Pt/g-Al_2O_3 Catalysts. 2-Ultaviolet-Visible Studies, Sintering of Platinum, and Soluble Platinum", J. Catal. 81, 17-25 (1983).

[25] McHenry, K.W; R.J. Bertolacini; H.M. Brennan; Wilson, J. L. and H.S. Seeling, "The Nature of Platinum Dehydrocyclization Catalyst", in Proc. 2nd Int. Cong. Catal. (Paris), 2295-2311(1961).

[26] Aben, P.C., Platteeuw, J.C., Stouthamer, B., in Proc. 4th Int. Cong. Catal. (Moscow) 1, 395 (1971).

[27] Dautzenberg, F.M., Platteuw, J.C., J. Catal. 24, 364- (1972).

[28] Lee, T.J., Kim, Y.G., "Dispersion of Supported Platinum Catalysts in Oxygen. 1-Experimental Evidences of Redispersion. KJChE 2, 55-61(1985).

[29] Ramaswamy, A.V., Ratnasamy, P., Sivasanker, S., Leonard, A.J., "Structure, and Catalytic Properties of Bimetallic Reforming Catalysts", in Proc. 6th Int. Cong. Catal. (London), 855-862 (1977).

[30] Smith, D.J., White, D., Bird, T., Fryer, J.R., "The Characterization of a model Platinum/Alumina Catalyst by High Resolution Electron Microscopy", J. Catal., 81, 107-118 (1983).

تشخيص تشتت المعدن لبعض العوامل المساعدة المستخدمة في تهذيب النافثا بتفاعل إزالة الهيدروجين لمثيل سيكلو هكسان

احمد جواد علي   *اميل محمد رحمن

*قسم الهندسة الكيميائية الإحيائية/ كلية الهندسة الخوارزمي/ جامعة بغداد

الخلاصة

تم دراسة انتشار المعدن Pt وPt-Ir المحملة على العوامل مساعدة RG-402، RG-412، RG-422 و RG-432 التي تستخدم لتهذيب النافثا بعد إجراء عمليات الأكسدة و الاختزال بضغط جوي اعتيادي. استخدم تفاعل إزالة الهيدروجين لمثيل سيكلو هكسان بغياب الهيدروجين كتفاعل اختبار لهذه الدراسة.

جرت محاولة ربط تصرف العوامل المساعدة المستخدمة لهذا التفاعل لتوضيح تأثير تشتت المعدن جراء معاملته بعمليات الأكسدة والاختزال الموضحة في الأدبيات. يمكن التعبير عن التحول الكلي بالتغير الذي يحدث لتشتت المعدن. وبهذا يمكن القول بان تفاعل تحول Methylcyclohexane هو تفاعل حساس بتغير بنية العامل المساعد.

لوحظ ان نسبة إنتاج التلوين تزداد بزيادة درجة حرارة الأكسدة للعوامل المساعدة المستخدمة لتصل الى أعلى معدلاتها عند درجة حرارة 550°م. وبارتفاع درجة الحرارة لوحظ ان نسبة الإنتاج يتناقص إشارة الى ظاهرة تلبد العامل المساعد.

لم يلاحظ أي تغير في نسب إنتاج التلوين عند اختزال العوامل المساعدة بدرجات حرارية تراوحت من400-600°م.

يمكن التعبير عن انتقائية العوامل المساعدة المستخدمة بالترتيب التالي: RG-422> RG-432> RG-412> RG-402
