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Effect of platinum doping of partially reduced Mo-SiO$_2$ catalysts on hydrogen storage in liquid hydrocarbons

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Abstract— **Mesoporous Mo-SiO$_2$ and SiO$_2$ synthetized by sol-gel method were impregnated with Pt precursor in order to obtain Pt/Mo-SiO$_2$ and Pt/SiO$_2$ catalysts. The catalysts were tested in cyclohexane (CH) and methylcyclohexane (MCH) dehydrogenation reaction and characterized using different techniques. For MCH dehydrogenation, the catalysts' specific initial activity followed the trend: Pt/Mo-SiO$_2$ > Mo-SiO$_2$ > Pt/SiO$_2$. The synergy effect between Pt and Mo did not occur due to the large contribution of acidity of partially reduced Mo-SiO$_2$ sample to its catalytic response and to the absence of H$_2$ spillover for Pt/Mo-SiO$_2$. Unlike MCH dehydrogenation, the synergy between Pt and Mo was observed for CH dehydrogenation over Pt/Mo-SiO$_2$ catalyst. For both Pt/SiO$_2$ and Pt/Mo-SiO$_2$, the catalyst bifunctionality (metal and acid functions) and the H$_2$ spillover effect were more important for catalyst behavior in CH dehydrogenation than in MCH dehydrogenation.**

Keywords— **Mo-SiO$_2$ catalyst; Pt/Mo-SiO$_2$ catalyst; characterization, dehydrogenation; methylycyclohexane; cyclohexane.**

I. INTRODUCTION

The concept of storing hydrogen in organic liquids is based on the reversible catalytic reactions of hydrogenation and dehydrogenation of cycloalkanes/aromatic hydrocarbons: the hydrogenation of aromatics allows storing hydrogen while the dehydrogenation of cycloalkanes to aromatics is used to extract it [1-3]. The alternative method for reversible hydrogen storage is based on physisorption of hydrogen on the suitable adsorbents. However, both adsorption and desorption of hydrogen are diffusion controlled [4]. Microporous adsorbents, e.g. zeolites and activated carbons, demonstrated appreciable sorption capacities whereas the mesoporous silicas exhibited a low H$_2$ storage capacity [5]. Thus, the most adequate for the industrial application is dehydrogenation of liquid organic hydrocarbons such as methylcyclohexane (MCH) or cyclohexane (CH), thanks to their relatively high H$_2$ content, the good reversibility of both reactions and easy liquids transportation [1-3]. Moreover, both reactions are strongly endothermic and limited by the thermodynamic equilibrium [3]. Hence, a shift of the reaction towards the direction of dehydrogenation is necessary to improve the conversion while trying to work at low temperatures. For this purpose, the use of a catalyst having well-selected criteria is essential to optimize the performances of dehydrogenation. Several types of catalysts have been proposed for the MCH dehydrogenation reaction with aiming at reducing the high temperatures (573-673 K) required for this type of this endothermic reaction. The first catalysts used were based on monometallic platinum supported on Al$_2$O$_3$ [5]. It was reported that the qualities of platinum as dehydrogenation catalyst are its ability to very quickly eliminate the hydrogen from the reaction medium thanks to its intrinsic capacities of hydrogenation/dehydrogenation, which promotes the displacement of the reaction in the dehydrogenation direction [6,7]. In addition, it was reported that a dehydrogenation catalyst giving good catalytic results in MCH dehydrogenation should combine a metallic function with a moderate acidity to avoid undesirable by-products [6]. In this sense, more researches were devoted to deposit platinum on a suitable carrier to promote its dispersion and increase the contact surface between the reactant and the catalytic sites. Meanwhile, adding a second metal to Pt, known to usually improve the catalytic performances of the monometallic catalysts, was suggested in order to enhance the catalytic performances in the MCH dehydrogenation reaction [8]. The nature of the second metal can generally be classified in two categories: (i) noble metals and those of the next columns in the periodic table (mainly Ir and Re) and (ii) non-noble metals (Sn, Pb, Mo ...) [8].

In our previous work, Mo-SiO$_2$ catalysts prepared by sol-gel method have been demonstrated to have good catalytic responses in the reaction of methylcyclohexane dehydrogenation [9].Thus, the promotion of Mo-based catalysts with platinum seemed to be a good alternative to enhance the activity of monometallic Mo-SiO$_2$ catalysts, and better catalytic results were effectively obtained for the bimetallic Pt/Mo-SiO$_2$ catalysts [10]. However, it was hard to know how the electronic and chemical properties of the

bimetallic Pt/Mo-SiO$_2$ catalysts have been modified compared to their parent metals.

For this reason, and in order to elucidate the factors that influenced the activity of the monometallic Mo-SiO$_2$ by the addition of platinum, we have studied Pt(X)Mo(Y) catalysts supported on SiO$_2$ with X= 0 or 5 wt.% and Y= Mo/Si*100 molar ratio = 10 in addition to the monometallic Pt/SiO$_2$ and SiO$_2$ catalysts. The physicochemical properties of the monometallic Mo-SiO$_2$ and bimetallic Pt/Mo-SiO$_2$ catalysts were determined by a variety of physico-chemical techniques in order to find the origin of the difference in the catalytic performances between them.

II. EXPERIMENTAL

A. Catalysts Preparation

Three catalysts were synthesized in the present work, a monometallic one referred to as Mo-SiO$_2$ and another bimetallic one referred to as Pt/Mo-SiO$_2$, in addition to Pt/SiO$_2$ sample used for comparison. The pure SiO$_2$ sample used as support was prepared through a one-step sol-gel method by mixing the convenient amounts of HNO$_3$ and EtOH. The silica source used was tetra-ethoxy-silane (TEOS) while nitric acid (HNO$_3$) was employed as a hydrolysis catalyst for TEOS and ethanol (EtOH) as a solvent. Briefly, TEOS was added dropwise to the mixture of acid and solvent. The whole preparation was stirred until gelation at a temperature of 333 K. After gelation, the obtained gel was dried in an autoclave under ethanol supercritical conditions, and then calcined at 773 K under a flow of oxygen.

As for the preparation of Pt/SiO$_2$ catalyst (5 wt.% of nominal Pt loading), the pure SiO$_2$ material was impregnated with an aqueous solution of Pt[(NH$_2$)$_6$NO$_3$]$_2$. After sample drying overnight at 373 K, the sample was calcined at 773 K. Otherwise, the Mo-SiO$_2$ sample was prepared using the sol-gel method. The same preparation procedure of pure SiO$_2$ was used, with the addition of the appropriate quantity of molybdenum acetylacetonate (Mo(Acac)) to TEOS solution in order to obtain [Mo/Si]*100 of 10 molar ratio. The obtained gel was also dried in an autoclave under ethanol supercritical conditions, and then calcined at 773 K under a flow of oxygen. Finally, the bimetallic Pt/Mo-SiO$_2$ solid was prepared by wet impregnation of the Mo-SiO$_2$ sample with an aqueous solution of Pt [(NH$_2$)$_6$NO$_3$]$_2$ which volume was selected to obtain a final Pt content of 5 wt.%. After sample drying overnight at 373 K, the sample was calcined at 773 K.

B. Catalytic Test

The gas phase dehydrogenation of two different reactants (pure methylcylohexane or pure cyclohexane) was performed in a high-pressure laboratory-scale set-up equipped with down-flow fixed bed catalytic reactor. The reaction was carried out at 673 K and 2.2 MPa of total hydrogen pressure. First, the catalyst was reduced in-situ at 673 K for 3 h with a mixture of H$_2$ and N$_2$. The reactor effluents were condensed and liquid samples were analyzed using a gas chromatograph.

III. RESULTS AND DISCUSSION

A. Calcined Catalysts Characterization

The Pt and Mo contents of the synthesized samples are reported in Table 1. It can be noticed that a non significant decrease of the molybdenum content occurred after Pt incorporation to the Mo-SiO$_2$ sample. This slight decrease was explained by a little loss of molybdenum during the impregnation of monometallic Mo-SiO$_2$ with the aqueous solution of platinum precursor [11].

Otherwise, for the bimetallic Pt/Mo-SiO$_2$ and Pt/SiO$_2$ samples, the platinum content per mass unit is approximately equal the nominal one (5 wt.%).

Table I
Physico-chemical properties of the oxide catalyst precursors and HRTEM data of freshly partially reduced samples.

Sample	Mo^a (wt.%)	Pt^a (wt.%)	S$_{BET}$^{b} (m^2 g^{-1})	d ^{b} (nm)	MoO$_2$ particle diameter^c (nm)
SiO$_2$	-	-	984	13 ; 21	-
Pt/SiO$_2$	-	4.3	635	5.2	-
Mo-SiO$_2$	8.4	-	776	3.8 ; 15.1	11
Pt/Mo- SiO$_2$	8.0	3.8	546	3.6	6.8

^{a} as determined by ICP-AES;
^{b} as determined from N$_2$ physisorption analysis: S$_{BET}$: BET surface area;
^{c} as determined from HRTEM micrographs.

The effect of the platinum addition on the textural properties of the synthesized samples was studied using N$_2$ physisorption technique. All the isotherms are of type IV corresponding to mesoporous materials according to IUPAC nomenclature [12]. The textural properties of the samples obtained from the N$_2$ physisorption method are given in Table I. The specific surface areas calculated according to the Brauner-Emmett-Teller (BET) model [13], decrease when incorporating the molybdenum or platinum to the silica gel and then decrease again when adding the platinum to the monometallic Mo-SiO$_2$ sample. The bimetallic Pt/Mo-SiO$_2$ catalyst shows the lowest surface probably due to the coexistence of platinum and molybdenum which would diminish the division state of the silica inducing a decrease in the BET surface. This same trend in surface areas was also recorded for the porous volume and diameter.

To explain the developed surface of SiO$_2$, it can be suggested that thanks to the nitric acid acting as a hydrolysis catalyst, a slow condensation type oxolation has occurred taking place between silanol groups (Si-OH), which would then contribute to the formation of small particles.

When adding the molybdenum, the acetylacetonate ligand of the molybdenum precursor (Mo(Acac)) would contribute

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to the gelation process [14,15] as it acted as a chelating agent. Thus, due to the relatively high amount of molybdenum, more rapid and incomplete hydrolysis and condensation reactions would occur, leading to large clusters. This would also result in blocking the bigger mesopores of silica with the creation of new mesopores existing probably on the molybdenum particles formed on the top of the small silica mesopores (Table 1).

In the other hand, the decrease in the surface area and the disappearance of the large silica pores after the addition of platinum to SiO_2 and to $Mo\text{-}SiO_2$ samples could be explained by the pore mouth blocking by the large amount of platinum deposited on the surface which induced a decrease in the division state.

The increase in the particle size after impregnation by the platinum precursor and calcination at 500 °C was confirmed by SEM-EDS micrographs given in Fig. 1. Thus, it can be concluded that the aggregation sequence during the impregnation of calcined $Mo\text{-}SiO_2$ by platinum precursor and its consecutive calcination would increase the size of molybdenum particles already formed during the sol-gel process.
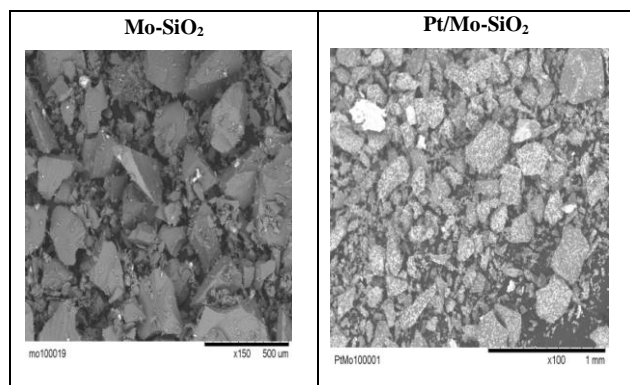

Fig. 2 SEM-EDS micrographs of the calcind $Mo\text{-}SiO_2$ and $Pt/Mo\text{-}SiO_2$ samples.

B. Partially-reduced Catalysts Characterization

The effect of $Mo\text{-}SiO_2$ catalyst modification with Pt on the hydrogen adsorption was investigated by temperature-programmed desorption of H_2 (TPD-H_2). Noticeably, $Pt/Mo\text{-}SiO_2$ sample exhibit a larger H_2-TPD peak area than monometallic $Mo\text{-}SiO_2$ counterpart and the addition of Pt to SiO_2-supported Mo catalyst led to a shift of hydrogen desorption peaks to lower temperature. Since the peaks' maxima for $Pt\text{-}SiO_2$ and $Pt/Mo\text{-}SiO_2$ are different, a possible electron-donating effect of Pt cannot be excluded. Indeed, from the viewpoint of valence-bond theory, it is known that hydrogen is easy to dissociate and can easily be adsorbed on the electron-deficient Pt. The irreversibly desorbed H_2 observed at higher temperatures and assigned to spillover hydrogen was observed only for Pt/SiO_2 catalyst. It was suggested that the irreversibility of the spillover hydrogen

might result from dihydroxylation of the support at high temperature.

Otherwise, the acidic properties of the partially-reduced $Mo\text{-}SiO_2$ and $Pt/Mo\text{-}SiO_2$ samples were analyzed by temperature programmed desorption of NH_3. A noticeable difference in the acidic properties is observed between the monometallic and the bimetallic samples. In fact, a diminution of weak and medium strength acid sites amount for $Pt/Mo\text{-}SiO_2$ compared to the monometallic $Mo\text{-}SiO_2$ sample suggests a strong decrease of Lewis acidity after Pt incorporation. This is linked to a reduction in the number of Mo^{6+} species in the bimetallic catalyst compared to the monometallic one.

HRTEM technique revealed MoO_2 particles on $Mo\text{-}SiO_2$ sample while the $Pt/Mo\text{-}SiO_2$ sample exhibit Pt crystallites in addition to MoO_2 crystals. However, the MoO_2 are smaller in the bimetallic catalyst compared to the monometallic one, contrary to what was suggested for the calcined samples through the EDS analysis. This is explained by the effect of the reduction under a flux of H_2.

C. Spent Catalysts Characterization

XPS analysis of partially-reduced and spent catalysts showed that the silicon atom is affected neither by the pretreatment conditions nor by the addition of the platinum to the monometallic sample. As for the Binding Energy (BE) of the platinum of the reduced $Pt/Mo\text{-}SiO_2$ sample, the $Pt4f_{7/2}$ core level spectra exhibit only one component corresponding to metallic Pt. However, after MCH dehydrogenation, the $Pt4f_{7/2}$ core level spectra of this catalyst has two components corresponding to metallic Pt and to PtO_x oxide species probably formed after the oxidation of the platinum under the catalytic test conditions [16].

A large difference is also noticed in the molybdenum BE between the monometallic and the bimetallic samples. Noticeably, the partially-reduced $Mo\text{-}SiO_2$ sample shows BE of Mo $3d_{5/2}$ component shifted to higher values compared to the partially reduced $Pt/Mo\text{-}SiO_2$ suggesting a stronger interaction between the oxo-molybdenum species and the hydroxyl groups of the silica support in the former sample.

After partial reduction at 673 K and MCH dehydrogenation, the $Mo\text{-}SiO_2$ and $Pt/Mo\text{-}SiO_2$ samples show a component corresponding to Mo^{6+} species. The partially reduced and spent $Mo\text{-}SiO_2$ show the Mo $3d_{5/2}$ lines reported for Mo^{5+} species, fitting the findings reported previously for the MoP/SiO_2 system [17]. On the contrary to $Mo\text{-}SiO_2$, after partial reduction and MCH dehydrogenation the $Pt/Mo\text{-}SiO_2$ catalyst exhibit a component ascribed to the formation of a molybdenum bronze H_xMoO_3 by hydrogen spill over among the MoO_3 lattice [16].

Otherwise, in good agreement with the N_2 physisorption data, the Mo/Si surface ratio of spent $Mo\text{-}SiO_2$ is lower than the surface Mo/Si atomic ratio of spent $Pt/Mo\text{-}SiO_2$ catalyst. Thus, during on stream conditions, the catalyst surface underwent enrichment with molybdenum species. Similar

phenomenon probably occurs during reaction of CH dehydrogenation.

X-Ray diffraction analysis was performed to investigate the crystalline phases formed during CH and MCH dehydrogenation reaction. The spent Mo-SiO$_2$ sample displayed peaks related to the MoO$_2$, MoO$_3$ and Mo$_3$Si phases with the persistence of the large curve centered at $2\theta \approx 23°$ corresponding to the amorphous silica. Remarkably, the Mo$_3$Si phase was also detected suggesting the incorporation of Mo into inner silica structure of the Mo-SiO$_2$. In the other hand, the monometallic Pt/SiO$_2$ catalyst exhibits 2 diffraction peaks at 2θ of 39.7º and 47.38° corresponding to (111) and (200) reflections, respectively, of the fcc Pt metal phase (JCPDS card 00-004-0802) [20]. Additionally, this sample shows 2 diffraction peaks at 2θ of 54.7º and 60.1° corresponding to PtO phase (JCPDS card 00-027-1331). As for Pt/Mo-SiO$_2$ sample, it also exhibits both Pt^0 and PtO phases. The presence of an additional diffraction peak at 2θ of 40.26º strongly suggests the formation of intermetallic phase between Pt and Mo (Pt$_2$Mo; JCPDS card 00-017-0720). Finally, the presence of Mo^0 crystals (JCPDS card 00-042-1120) on the surface of Pt/Mo-SiO$_2$ might indicate that, upon reaction conditions employed, the Mo^{4+} ions were reduced to Mo^0.

In order to reveal the origin of catalyst deactivation during CH dehydrogenation, the spent catalysts were characterized by TG/DTA in oxidative atmosphere (O$_2$/N$_2$ mixture). Concerning the type of coke species, there are two types of coke formed on the catalyst surface: "soft-type" which suffers oxidation in temperature region 500 - 700 K and "refractory-type" which is eliminated at much higher temperature (> 800 K). It was revealed from thisTG/DTA analysis that, most likely, inert carbon or graphitic carbon was formed on the surface of all catalysts [19]. In addition, at least two kinds of carbon species were found to be formed on the active sites: inert carbon or graphitic carbon and filamentos or graphitic carbon deposited on the SiO$_2$ support. The coke formation on the catalyst surface follows the trend: Mo-SiO$_2$ > Pt/Mo-SiO$_2$ >> Pt/SiO$_2$. This trend is in good agreement with information obtained from TPD-H$_2$ and TPD-NH$_3$ techniques. The weight loss due to the removal of carbon was largest for Mo-SiO$_2$ than for both Pt-containing catalysts indicating that the Pt is an effective promoter for sustainability against coke formation. Taking into account that coke is preferently formed on acid sites, especially on strong acid sites [20], the largest coke formation during CH dehydrogenation over Mo-SiO$_2$ is due to its largest acidity among the catalysts studied.

Additional information on the coke carbon structure formed during CH dehydrogenation was obtained from Raman spectroscopy. The Raman spectra of the spent Pt/SiO$_2$, Mo-SiO$_2$ and Pt/Mo-SiO$_2$ catalysts are given in Fig. 2.
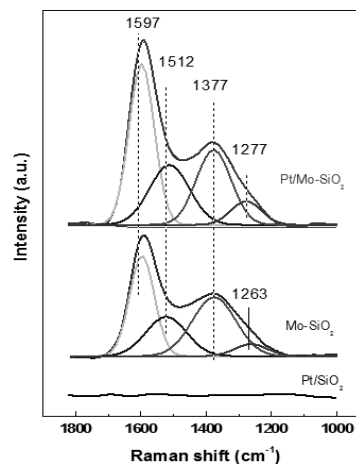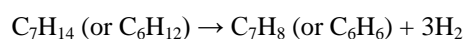

Fig. 2 Raman spectra of the spent catalysts tested in CH dehydrogenation.

In good agreement with the activity trend and TPO/TG characterization, two characterics coke bands near 1600 cm^{-1} and 1360 cm^{-1} were observed only for Mo-SiO$_2$ and Pt/Mo-SiO$_2$ samples. Noticeably, the spent Pt/SiO$_2$ sample did not exhibit bands in the 1850 - 1000 cm^{-1} region, which agrees with the high stability of this sample during time on stream of 4 h. Since both bands were broad, following the work by Kawakami et al. [21], the Raman spectra in Fig. 2 were fitted with four peaks. After Gaussian deconvolution, both Mo-SiO$_2$ and Pt/Mo-SiO$_2$ samples exhibits peaks ascribed to graphitic structure (1597 cm^{-1}), graphitic defect (1377 cm^{-1}) and random carbon fractions of coke (1512 cm^{-1} and around 1263-1277 cm^{-1}) [21]. The peak intensity ratio ($R=I_{1377}/I_{1597}$) of the band ascribed to graphitic defect to the band of graphite was calculated to evaluate perfection degree of graphite structure. The peak intensities ratio was larger for Mo-SiO$_2$ than for Pt/Mo-SiO$_2$ indicating that larger graphitic defects were formed on the former sample. For both catalysts, the formation of graphite was two times larger than formation of graphitic effects.

D. Catalytic Activity

The effectivity of partially reduced Mo-based catalysts toward H$_2$ generation was evaluated in the individual MCH and CH dehydrogenation reactions carried out at the same reaction conditions. For all catalysts, the major products resulting from the MCH dehydrogenation were toluene and cyclohexane whereas from the CH dehydrogenation it was benzene (selectivity in range 96-100%). For the MCH dehydrogenation, other minor reaction products were isomerization and hydrocracking products.

During both MCH and CH dehydrogenation reactions, there is generation of 3 moles of H$_2$ per mole of reactant according to the following equations:

$$C_7H_{14} \text{ (or } C_6H_{12}) \rightarrow C_7H_8 \text{ (or } C_6H_6) + 3H_2$$

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The catalyst effectivity toward hydrogen production was estimated by comparison of the yields of toluene in the MCH dehydrogenation and the yields of benzene in the CH dehydrogenation.

Both Pt-containing catalysts exhibited larger effectivities toward hydrogen production in the CH dehydrogenation than in the MCH dehydrogenation reaction. Considering initial yield of benzene (at *TOS*=0), the catalyst effectivity toward hydrogen production follows the trend: $Pt/Mo-SiO_2$ > Pt/SiO_2 >> $Mo-SiO_2$. However, this trend is changed after reaction time of 3 h: Pt/SiO_2 > $Pt/Mo-SiO_2$ >> $Mo-SiO_2$. Noticeably, for both MCH and CH dehydrogenation reactions, the $Pt/Mo-SiO_2$ demonstrated to be more effective toward hydrogen production than both monometallic Pt/SiO_2 and $Mo-SiO_2$ catalysts.

The effectivities of hydrogen production in the absence of the catalyst deactivation (at *TOS*=0) could be explained by the comparison of the initial catalyst's activities for the MCH and CH dehydrogenation**.** Thus, it was noticed that for the MCH dehydrogenation, the specific activity of bimetallic $Pt/Mo-SiO_2$ sample was not larger than the sum of individual activities of Pt/SiO_2 and $Mo-SiO_2$ indicating that the synergy effect between Pt and Mo did not occur. As regard to the MCH dehydrogenation, the lager initial reaction rate of $Mo-SiO_2$ with respect to Pt/SiO_2 could be explained considering the larger acidity of partially-reduced $Mo-SiO_2$ with respect to $Pt/Mo-SiO_2$ sample, as deduced from $TPD-NH_3$ of the partially-reduced samples. In other words, for $Mo-SiO_2$ a larger contribution of acidic sites on the catalytic activity probably occurred while for bimetallic $Pt/Mo-SiO_2$ it is the metallic function which took the advantage. Interestingly, the new catalytic sites were created upon on-stream reaction conditions: the Pt_2Mo crystal phase was detected by XRD on the surface of spent $Pt/Mo-SiO_2$ catalyst after the CH dehydrogenation.

The formation of this phase (Pt_2Mo) together with the presence of metallic Pt^0 might explain the reason why the $Pt/Mo-SiO_2$ exhibits larger amount of H_2 chemisorbed hydrogen than its monometallic $Mo-SiO_2$ catalyst base, as demonstrated by $TPD-H_2$. Additionally, the presence of Pt in the proximity of MoO_2 species led to easier H_2 desorption from metal phases, as deduced from the shift of temperature. It can be suggested then that the higher activity of $Pt/Mo-SiO_2$ with respect to the $Mo-SiO_2$ counterpart is likely associated to the hydrogen-recombination abilities of Pt which facilitates the fast elimination of hydrogen atoms from the reaction favoring, thus, the dehydrogenation [22].

The larger specific activities of both Pt-containing catalysts in the CH dehydrogenation than in the MCH dehydrogenation strongly suggest that the adsorption of CH molecule on the active sites is favored, probably due to the absence of methyl group. In the case of MCH dehydrogenation, the other reaction products, i.e. toluene, might remain adsorbed on the active phase of the Pt-containing samples, thus inhibiting the adsorption of MCH. These suggestions could be confirmed referring to the selectivity of the catalysts toward the reaction

products. Indeed, it was reported that the by-products, i.e. isomerization products, are formed on acidic sites while toluene is formed on metallic sites of the catalysts after direct dehydrogenation of MCH molecules [23]. In the same context, Belatel et al. [24] correlated the appearance of the by-products in MCH dehydrogenation through an isomerization pathway in which a ring shortening takes place on acidic function. Finally, the lowest coke formation on the $Pt/Mo-SiO_2$ catalyst with respect to $Mo-SiO_2$ was confirmed by both TPO/TG and Raman spectroscopy. This could be tentatively explained by the enhancement of hydrogen dissociation on the well dispersed active sites of the former sample. The dilution effect of MoO_2 might also prevent excessive deactivation of the Pt sites of this catalyst [25].

IV. CONCLUSIONS

In this work, partially reduced silica-supported monometallic Mo and bimetallic Pt/Mo catalysts were characterized and then tested in two reactions: The dehydrogenation reaction of MCH and of CH, in the context of the hydrogen storage. The surface properties were modified by the addition of platinum. The impregnation of calcined $Mo-SiO_2$ by platinum precursor and its consecutive calcination increased the size of molybdenum particles already formed during the sol-gel and modified the porous distribution. After partial-reduction, the molybdenum particles became smaller on bimetallic catalyst. It was also revealed that H_2 is more easily desorbed from $Pt/Mo-SiO_2$ than $Mo-SiO_2$ thanks to the co-presence of Pt in the proximity of molybdenum. Otherwise, the number of weak and medium strength acid sites was also decreased after adding the platinum. This led to the formation of less coke on the monometallic $Pt/Mo-SiO_2$ than on $Mo-SiO_2$.

As for the catalytic activity, the bimetallic $Pt/Mo-SiO_2$ catalyst showed higher activity than monometallic $Mo-SiO_2$ in the two reactions. This was related to the hydrogen-recombination abilities of Pt which facilitates the fast elimination of hydrogen atoms from the reaction favoring, thus, the dehydrogenation direction. In addition, for $Mo-SiO_2$, a larger contribution of acidic sites on the catalytic activity probably occurred, while for bimetallic $Pt/Mo-SiO_2$, it is the metallic function which took the advantage

Concerning this latter sample, a synergy effect between Pt and Mo occurred only during the CH dehydrogenation and the bifunctionnal character (metal and acid functions) was more important in CH dehydrogenation than in MCH dehydrogenation.

REFERENCES

[1] M. Roumanie, « Microréacteur pour la catalyse hétérogène Application : Stockage de l'hydrogène dans les hydrocarbures Filtre pour cpteur gaz », PhD Thesis, Ecole Supérieure Nationale des Mines de Saint-Etienne, Saint-Etienne, France, Oct. 2005.

[2] F. Alhumaidan, D. Cresswell, and A. Garforth, "Hydrogen Storage in Liquid Organic Hydride: Producing Hydrogen Catalytically from Methylcyclohexane", *Ener. Fuels*, vol. 25, pp.4217-4234, Sept. 2011.

[3] Gy. Onyestyák, G. Pál-Borbély, H.K. Beyer, "Cyclohexane conversion over H-zeolite supported platinum" *Appl. Catal. A: Gen.*, vol. 229, pp. 65-74, Apr. 2002.

[4] P. Pascal, *Nouveau Traité de Chimie Minérale*, Vol. VIII, Masson and Cie, Ed. Paris, France, 1965.

[5] M.G. Nijkamp, J.E.M.J. Raaymakers, A.J. van Rillen, and K.P. de Jong, "Hydrogen storage using physisorption – materials demands", *Appl. Phys. A.*, vol. 72, pp. 619-623, May 2001.

[6] D.K. Cromwell, P.T. Vasudevan, B. Pawelec, and J.L.G. Fierro, "Enhanced methylcyclohexane dehydrogenation to toluene over Ir/USY catalyst", Catal. Today, vol. 259, pp. 119-129, Jan. 2016.

[7] N. Kariya, A. Fukuoka, and M. Ichikawa, "Efficient evolution of hydrogen from liquid cycloalkanes over Pt-containing catalysts supported on active carbons under "wet–dry multiphase conditions"", *Appl. Catal. A: Gen.* vol. 233, pp. 91-102, July 2002.

[8] G. Leclercq, S. Pietrzyk, T. Romero, A. El Gharbi, L. Gengembre, J. Grimblot, F. Aïssi, M. Guelton, A. Latef, and L. Leclercq, "Investigation on Active Sites in Pt−Mo on Silica Catalysts for Reactions of Hydrocarbons with Hydrogen", *Ind. Eng. Chem. Res.*, vol. 36, pp. 4015-4027, Oct. 1997.

[9] N. Boufaden, R. Akkari, B. Pawelec, J.L.G. Fierro, M. Zina, and A. Ghorbel, "Dehydrogenation of methylcyclohexane to toluene over partially-reduced Mo-SiO₂ catalysts", *Appl. Catal. A: Gen.*, vol. 502, pp. 329-339, Aug. 2015.

[10] N. Boufaden, R. Akkari, B. Pawelec, J.L.G. Fierro, M. Zina, and A. Ghorbel, "Dehydrogenation of methylcyclohexane to toluene ovr partially-reduced silca supported Pt-Mo catalysts", *J. Molec. Catal: Chem.*, vol. 420, pp. 96-106, Aug. 2016.

[11] J.L.G. Fierro, *"Metal oxides and applications"*, J.L.G. Fierro, Ed., Taylor and Francis Group, Boca Raton, USA, 2006.

[12] K.S.W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, "Reporting physisorption data for Gas/solid systems with special reference to the determination of surface area and porosity" *Pure & Appl. Chem.,* Vol. 57, pp. 603-619, 1985.

[13] S. Brunauer, P.H. Emmett, E. Teller, « Adsorption of gazes in multimolecular layers », *J. Am. Chem. Soc.,* Vol. 60, pp. 309-319, Feb. 1938.

[14] R. Akkari, « Elaboration par voie sol-gel et caractérisation de catalyseurs acides à base de zircone sulfatée supportéé par la silice », Thèse de doctorat, Université Tunis El Manar, Faculté des Sciences de Tunis, Tunis, Tunisie, Juin 2006.

[15] C. Sanchez, J. Livage, M. Henry, and F. Babonneau, « Chemical modification of alcoxide precursors », *J.Non-Cryst. Solids*, vol. 100, pp. 65-67, Mar. 1988.

[16] G. Leclercq, T. Romero, S. Pietrzyk, J. Grimblot, and L. Leclercq, « properties of platinum molybdenum bimatallic catalysts deposited on silica », *J. Mol. Catal.*, vol. 25, pp. 67-86, July 1984.

[17] D.C. Phillips, S.J. Sawhill, R. Self, and M.E. Bussell, "Synthesis, characterization and hydrdesulfirization properties of silica-supported molybdenum phosphide catalysts", *J. Catal.,* vol. 207, pp. 266-273, Apr. 2002.

[18] B. Gurau, R. Viswanathan, R.X. Liu, T.J. Lafrenz, K.L. Ley, E.S. Smotkin, E. Reddington, A. Sapienza, B.C. Chan, T.E. Mallouk, S.J. Sarangapani, "Structural and elechtrochemical characterization of binary, ternary and quaternary platinum alloy catalysts for methanol elecrto-oxidation", *Phys. Chem. B*, vol. 102, pp. 9997-10003, Dec.1998.

[19] W.D. Zhang, B.S. Liu, C. Zhu and Y.L. Tian, "Preparation of La₂NiO₄/ZSM-5 catalyst and catalytic performance in CO₂/CH₄ reforming to syngas", *Appl. Catal. A: Gen.,* vol. 292, pp. 138-143, Sep. 2005.

[20] M. Guisnet, and P. Magnoux, "Coking and deactivation of zeolites: Influence of the pore structure" *Appl. Catal.,* vol. 54, pp. 1-27, Sep. 1989.

[21] M. Kawakami, H. Kanba, K. Sato, T. Takenaka, S. Gupta, R. Chandratilleke, and V. Sahajwalla, "Characterization of thermal annealing effects on the evolution of the coke carbon structure using Raman spectroscopy and X-Ray diffraction", *ISIJ Int.,* vol. 46, pp.1165-1170, Aug. 2006.

[22] B.J. Wood, and H. Wise, "Diffusion and heterogeneous reaction. II. Catalytic activities of solids for hydrogen –atom recombination", *J. Chem. Phys.* Vol. 29, pp. 1416-1417, Dec. 1958.

[23] F. Alhumaidan, D. Tsakiris, D. Cresswell, and A. Garforth, "Hydrogen storage in liquid organic hybrids: selectivity of MCH dehydrogenation over monometallic and bimetallic Pt catalysts", *Int. J. Hydrogen Energy,* vol. 38, pp. 14010-14026, Oct. 2013.

[24] H. Belatel, H. Al-Kandari, F. Al-Khorafi, A. Katrib, and F. Garin, "catalytic reactions of methylcyclohexane (MCH) on partially reduced MoO₃", *Appl. Catal. A: Gen.*, vol. 275, pp. 141-147, Nov. 2004.

[25] J.K.A. Clarke, "Selectivity in catalysis by alloys", *Chem. Rev.,* vol. 75, pp. 291-305, Juin 1975.