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Research Article
MoO_3/TiO_2 Hydroisomerization Performance Using n-hexane in Comparison with a Platinum Commercial Catalyst; Pilot Scale

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Abstract

Background and Objective: Isomerisation is one of the main processes in the refinery to convert light naphtha such as n-hexane into their respective isoparaffins with high octane number. In this paper the performance of locally prepared light-naphtha isomerization catalyst MoO_3/TiO_2 was evaluated in a pilot-scale and compared to Platinum on Zeolite (Pt/Z) commercial catalyst under different operating conditions such as temperature, pressure, hydrogen to oil ratio and liquid speed velocity, using normal hexane (nC6). **Materials and Method:** BothMo_2O_3/TiO_2 and Pt/Z catalysts were tested in the pilot plant designed by the Petroleum Research Center (PRC), The performance of the catalyst was tested under the selected conditions then compared to the performance of a commercial Pt/Zin the same pilot plant under the same conditions. **Results:** The MoO_3/TiO_2 showed acceptable performance for converting the nC6 to six carbon atom paraffin isomers (SCA P-isomer) the 2-methyl pentane and the 2,3-dimethylbutane (23DMB). The MoO_3/TiO_2 operates steadily within the pressure range 5 to 10 bar, but at higher pressures, its cracking function dominates to unacceptable levels. Pt/Z, unlike the $MoO_3/TiO_{2,}$ did not show a tendency to form the formation of the benzene and heptane and its cracking function reached 3.1% only at 290°C, which is the catalyst maximum operating temperature. **Conclusion:** The stability test showed that the Pt/Z is stable with time on stream and change in reaction temperature, whereas the MoO_3/TiO_2 performance was considered sensitive to temperature change.

Key words: Hydroisomerization, n-hexane, isoparaffins, titania support, molybdenum catalyst, zeolite

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Gasoline that is sold in the market is a blend of several light naphthas, hydrotreated straight run naphtha, the reformer naphtha, alkylated naphtha, isomerized light naphtha and light naphtha from hydrocrackers and fluid catalytic cracking[1-4]. The selection of light-naphtha isomerization processes depends on many parameters; for example, the refinery processing configuration and the availability and quality of the straight run light-naphtha[5-8]. The general direction in the recent years has shown a noticeable shift toward the processes that employ platinum dispersed on zeolite catalysts and enhanced with membrane chambers for the separation of the iso-paraffins from the normal ones for recycling[9]. Historically, light naphtha isomerization catalysts developed over four generations. The Friedel Crafts catalyst ($AlCl_3$) generation, the metal-acid bifunctional catalyst generation, the bifunctional catalyst enhanced with a halogen generation and the bifunctional zeolitic catalyst generation. Among the four generations, only the bifunctional enhanced with a halogen and the zeolitic catalysts are still in use[9,10]. Nowadays, three types of light-naphtha isomerization catalysts are available commercially; the zeolitic catalyst, the amorphous chloride catalyst and the sulfated zirconia catalyst. Each of the three types includes platinum in its chemical formulation. Platinum is a rare and expensive metal and its recovery after usage from the bulk catalyst is also expensive[11,12]. For this reason, many research centers have been trying to replace the platinum with a cheap metal that has properties similar or closer to platinum in terms of the performance.

Recently, developed trioxide molybdenum (MoO_3) deposited on titania (TiO_2) (MoO_3/TiO_2) has gained considerable attention among researchers as a new arrival and a potential candidate to replace the platinum. In comparison to a platinum supported catalyst such as the platinum on zeolite or the platinum/on amorphous chloride alumina, the reduced form of the MoO_3 (MoO_2) is responsible for the dehydrogenation and hydrogenation reactions (metallic function) and the TiO_2 is responsible for the carbocation and olefin isomerization reactions (acidic function). Several works have investigated the physical and chemical characteristics of the reduced surface of the MoO_3/TiO_2 and the catalytic activity for converting different classes of hydrocarbons of five, six and seven carbon atoms[13-20]. Almost all the studies cited above have agreed that the optimum temperature at which the catalyst operates optimally is 350°C. However, for the normal hexane, the same studies did not agree on the conversion levels, selectivity and yield of the individual isomers and cracking even when the catalyst was tested under the same operating conditions. This is due to many factors, of which, preparation of the catalyst sample at different laboratories and by different individuals, different characterization equipment, tools and protocols, different testing reactors of varying sizes and different testing protocols.

This paper compares the MoO_3/TiO_2 performance to a commercial platinum on the zeolite (Pt/Z)catalyst.

MATERIAL AND METHODS

Study area: This work was carried out over two phases completed in 2018 and all related data revision and analysis were completed in late 2019.

Catalyst and feed: The $MoO_3/TiO_2$was prepared at the chemistry department of the Kuwait University and under the supervision of the catalyst developer. An incipient wetness impregnation method was used for the preparation of the TiO_2 (Degussa) supported MoO_3 catalyst. The requisite amount of Mo (19.6 wt.%) was achieved by adding the stoichiometric amount of ammonium hepta molybdate-tetrahydrate (AHM) solution over TiO_2. In this process, the required stoichiometric amount of AHM salt was dissolved in de-ionized water at room temperature close to a neutral pH, the catalyst was dried under vacuum at 70°C. The impregnated solid was then dried in an air oven at 110°C overnight and calcined at 550°C for 5 hrs. The solid catalyst contained nano dispersed MoO_3 along with the substitutional doping of Mo in the TiO_2 and the expected supported catalyst has an effective substitution of Mo^{6+} at the Ti^{4+} sites in TiO_2 support. Preparation method and technique of the MoO_3/TiO_2 can be found in more detail at Al-Kanadari *et al.*[20]. The textural properties of the supported catalyst were measurements using an N_2 adsorption-desorption experiment at -160°C and reported in Table 1 with a pore volume of 0.3 mL g^{-1} and the BET surface area of 65 m^2/g. The average pore size distribution of the supported catalyst has about 75% of the pore size within the range of 100-300 Å while lower than this range contains about 15%. The other catalyst used in this study is a platinum on zeolite (Pt/Z) commercial catalyst and was acquired from an international catalyst manufacturer and supplier. As requested by the catalyst supplier, specific information of the Pt/Z catalyst will not be revealed in this paper, whereas Table 1 presents selected physical properties of the MoO_3/TiO_2. Normal hexane of 99+ purity was used to evaluate the performance of both catalysts.

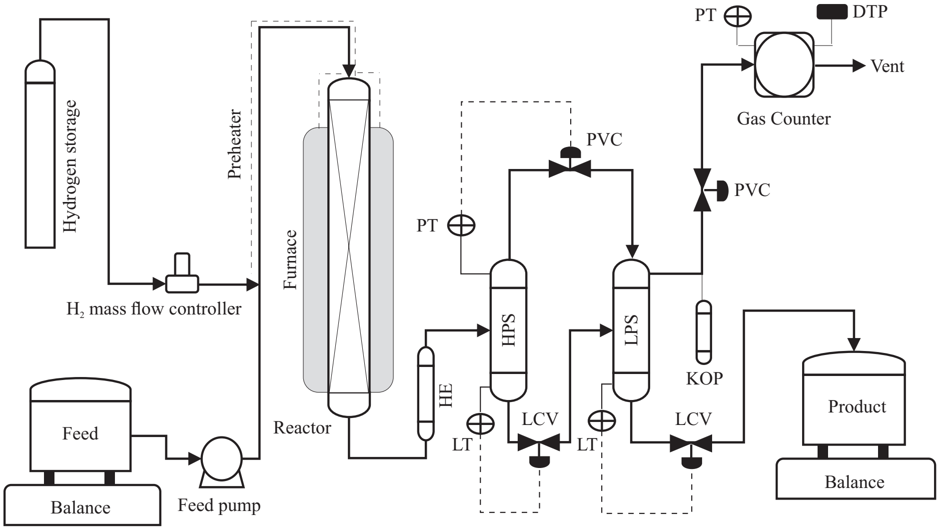

Fig. 1: Pilot plant used in the study
Source: KISR

Table 1: Physicochemical properties of MoO_3/TiO_2

Properties	Value
Compact bulk density (g mL^{-1})	1.02
Surface area (m^2/g)	65.02
Pore volume (mL g^{-1})	0.3046
Average pore diameter, Å	136.6
Pore volume distribution (mL g^{-1})	
10-100	0.034
100-300	0.23
300-450	0.03
450-650	0.0048
> 600 Å	0.0046

*g: Gram, mL: Milliliter, Å: Median pore diameter

Pilot plant: A pilot plant designed by the Petroleum Research Center (PRC) of Kuwait Institute for Scientific Research (KISR) and fabricated by Xytle limited of India was used in this study. A simplified process flow diagram of the pilot plant is shown in Fig. 1. A positive displacement pump was used to deliver the feed to the stainless-steel cylindrical tube reactor of 52 cm in length (from the liquid distributor to bottom support) with a total volume of 75.2 mL. The electrical heating blocks cover 46 cm of the reactor length as shown in Fig. 2. Each heating block is equipped with two skin thermocouples, one is used to signal the controller during actual operation to provide the heat needed to maintain the desired reaction temperature and the other one is used as a Temperature Safety Switch (TSS) to shut down the heater in case of overshooting. The top zone of the reactor that is covered by the top heating block was packed with a carborundum of the same size used in catalyst dilution. To confirm the reactant temperature thermocouples were positioned inside the thermowell at three points, 1.0 cm before the catalyst bed and midpoint and endpoint of the catalyst bed. The reactor is surrounded by an electrical furnace consisting of three independent heating blocks, each of 15.3 cm in length. The reactor area within the top heating block is filled with an inert material to maintain the temperature of the reactants at the desired value. Reaction products are separated using high/low-pressure separator (HPS/LPS), the effluent from the reactor passes through a heat exchanger to reduce its temperature before it enters the High-Pressure Separator (HPS). Liquid from the HPS is displaced to the LPS throughout a pneumatic Level Control Valve (LCV). The pressure inside the LPS is controlled by a manual back-pressure control valve set at 2.5 bar-gauge. The volume of the gases that leave the LPS are metered by a Gas Counter (GC) under ambient pressure and temperature, considering that the GC itself is equipped with a Digital Temperature Probe (DTP) (thermocouple) and an absolute pressure transmitter. Liquid from the LPS leaves to the product tank throughout an LCV. The product tank is placed on a balance to measure the product mass flow and to compare it with the feed mass flow rate. Because of the volatile nature of the products at normal temperature, all tubes and vessels that come the heat exchanger are properly cooled to 5°C to ensure efficient condensation of the condensable liquids and to prevent liquid carryover in the gas line that connects the LPS to the GC. The pilot plant is fully automated by the Honeywell-C900 stand-alone Programmable Logic Control (PLC).

Testing: Both catalysts required activation by hydrogen. The MoO_3/TiO_2 performance was tested at 350°C and under varying pressure, liquid hourly space velocity and hydrogen to

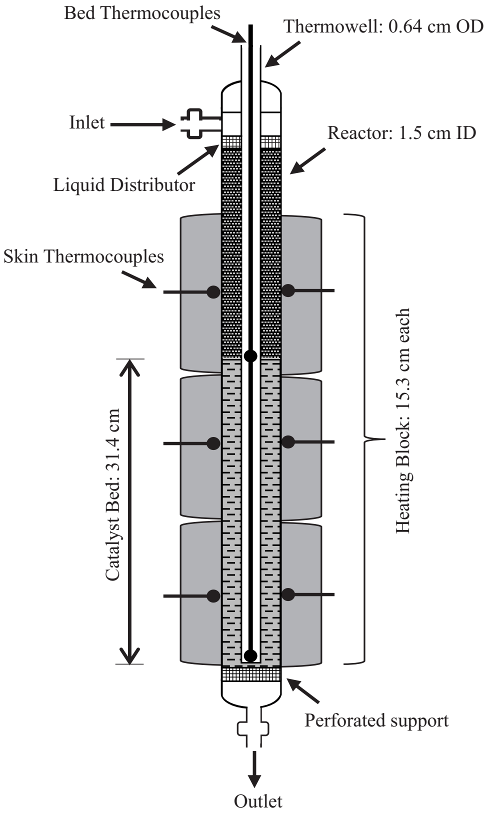

Fig. 2: Reactor's main features and catalyst loading profile
Source: KISR

Table 2: Operating conditions for catalysts testing MoO3/TiO$_2$ and Pt/Z

Effect study	P (barg)	H2/Oil (L/L)	LHSV (h^{-1})	T (°C)	No of test
Mo_2O_3/TiO_2					
Pressure	5, 7.5 10 12.5 15	1000	1.0	350	5
H2/Oil	5	500 750 1250 1500 1750 2000	1.0	350	6
LHSV	5	1000	0.5 0.75 1.0 1.25 1.5 2	350	6
Pt/Z					
Temperature	17.5	367	1.62	240 250 260 270 280 290	1

*LHSV: Liquid hourly space velocity, 1/hour = h^{-1}, barg: Gauge pressure, L: Liter

oil ratio. The Pt/Z performance was assessed at different temperatures with the other operating conditions kept constant. In all experiments carried out in this study, 22.7 mL of the tested catalyst was diluted with an equal volume of proper size carborundum and packed inside the reactor within the area covered by the middle and the bottom heating blocks. The feed flow rate was maintained at the desired value by the pump built-in control logic and verified by the feed tank balance. Hydrogen mass flow rate was controlled by a thermal mass flow meter calibrated to feed hydrogen under standard conditions (21°C and 1 atm), regardless of the operating pressure. Hydrogen and liquid feed meet at a point before the reactor and heated to the reactor temperature before entry as described in Table 2.

Table 2 summarizes the operating conditions for catalysts testing MoO_3/TiO_2 and Pt/Z.

RESULTS AND DISCUSSION

MoO_3/TiO_2 performance

Pressure effect: The catalyst under different operating conditions that are close to industrial practices and thus likely to improve the understanding of the isomerization reaction chemistry and its product selectivity. For the tested operating pressures, the results showed that most of the nC6 converts to paraffinic isomers of Six Carbon Atoms (SCA) (Fig. 3). As it the case in almost all alkane isomerization catalysts, the mass ratios in the liquid product of the produced isomers over the MoO_3/TiO_2 are in the following order: 2-methylpentane> (2MP)>3-methyl pentane (3MP)>2,3-dimethyl butane (23DMB)>2,2-dimethyl butane (22DMB)[14,20]. In addition, iso-pentane (iC5), normal pentane (nC5), methyl cyclopentane (MCP), benzene (Bnz) cyclohexane (CH) and heptane were found in the liquid product, however in small quantities. Isomerization reactions of alkanes that take place over solid catalysts are thermodynamically equilibrated and occur without a variation in the number of moles and therefore they are not influenced by pressure variation[1]. In this study, it was observed that operating the MoO_3/TiO_2 at different total pressure leads to different conversion levels. At 5, 7.5 and 10 barg, the conversion was almost constant at about the 52.5% (average), but at 12.5 and 15 barg, the conversion increased to 57.2 and 59.5%, respectively and the selectivity of the SCA isomers dropped from 89% at 5 barg to 64.9% at 15 barg (Fig. 3). This behavior can be regarded mainly to the cracking reactions. As seen in Fig. 3, the hydrocarbon gas recovery is 2.6 and 12.9% at 5barg and 15 barg, respectively. Cracking, in this case, is probably due to; at certain pressure and above, the acidic function of the support (TiO_2) becomes more active than needed and consequently it imbalances the delicate balance with the metallic function represented by the MoO_2. On the other hand, although the liquid yield of the SCA isomers decreases with the increase in pressure, it was noticed that their ratios in the liquid product to one another are constant, which lead to conclude that the rate by which each individual isomer forms, was thermodynamically limited and in agreement with the ratios reported in literature[21,22,14]. This observation leads us to conclude that the formed isomers in their thermodynamic equilibrium did not contribute significantly to the cracking reactions and the cracked products were formed either by direct cracking of the nC6 over the support or of incomplete isomerization reactions.

Hydrogen to oil ratio effect: As per the results from the pressure effect study, 5 barg was selected as the optimum pressure under which the MoO_3/TiO_2 performs optimally. The results showed that converting the nC6 to isomers over the MoO_3/TiO_2 is noticeably sensitive to hydrogen to oil ratio (H_2/Oil) as shown in Fig. 4. This behavior can be attributed mainly to the kinetic effect particularly, the reactant's contact time with the catalyst. The reaction takes place in the gas phase. The bulk gas moves throughout the catalyst bed with certain linear velocity and doubling the hydrogen flow rate at constant pressure causes the bulk gas linear velocity to redouble[23,24]. This shortens the reactant's residence time and consequently lowers the conversion level. Based on the results, however, this reasoning seems valid when the H_2/Oil ratio is higher than 1000 L/L. Between the H_2/Oil ratios 500-1000 L/L, nC6 conversion (yield) to SCA P-isomers is constant, which means that cracking is the reason behind the high conversion levels that were observed at low H_2/Oil ratios (Fig. 4) and this can be confirmed by the absence of the iC5, nC5, Benzene, CH and the C7 in the liquid product obtained at H_2/Oil ratio of 1500 L/L and higher, considering that these compounds form as a result of the hexane cracking. As it was expected, the mono-branched SCA P-isomers such as the 2 MP and 3 MP was found in high quantities in comparison with the 22 DMB and the 23 DMB. In addition, regardless of the H_2/Oil ratio, conversion level and yields of the SCA P-isomers, they were found in their thermodynamic equilibrium values at 1.5 for the 2 MP/3 MP and 0.3 for the 2 DMB/23 DMB and in total agreement with results obtained in the pressure effect study.

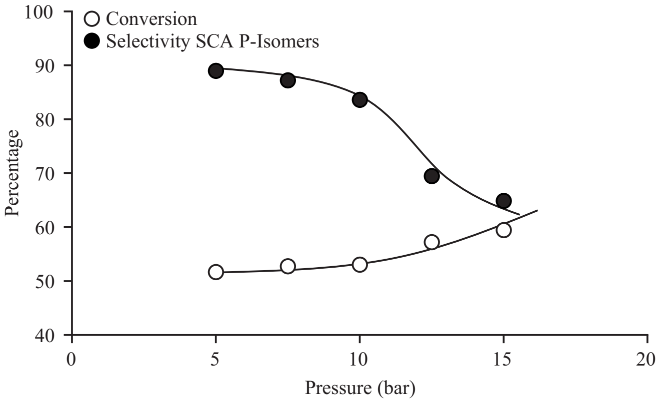

Fig. 3: nC6 conversion over the Mo_2O_3/TiO_2 and selectivity of the SCA paraffinic isomers at different pressures

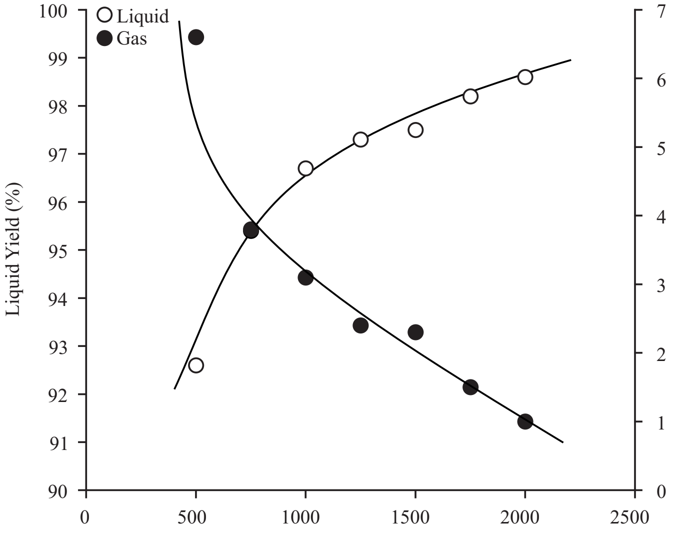

Fig. 4: Mo_2O_3/TiO_2 yield of liquid and Gas at different H_2/Oil Ratios

LHSV effect: Based on the results from the previous studies, the operating pressure and the H_2/Oil ratio were fixed at 5 barg and 1000 L/L, respectively. In this part of the study, it was observed that conversion decreases with the increase in feed flow, whereas selectivity of the SCA P-isomers increases with the increase in feed flow (Fig. 5) For the conversion, the decrease can be regarded mainly to the availability of catalytic sites and their ratios to the number of molecules. At high feed flow rate, not all molecules will have the chance to diffuse into the catalyst interior surfaces where the active sites are located, but, a significant proportion of them will by-pass the catalyst bed through the voids to the product section and thus, the lower conversion levels observed at high LHSV[13,14]. The catalyst behavior with respect to cracking in this part of the study is comparable to its behavior when it was operated at high H_2/Oil ratios; except that at low feed flow, more undesirable side reactions have taken place particularly, the formation of the benzene, cyclohexane and the heptane, as they appear in relatively high quantity in the liquid product (Fig. 5). Also, it is important to note that the maximum yield of the SCA P-isomers could be obtained at LHSV of 0.75 and 1.0 and other values than those will cause the yield to drop sharply. Changing the feed flow did not affect the SCA P-isomers distribution and thermodynamic ratios; the 2MP and the 3MP present in relatively high quantities in comparison with 22DMB and the 23DMB.

The Pt/Z performance: The catalyst was tested under the conditions listed in Table 2 and at different temperatures. As seen in Fig. 6, nC6 conversion increases noticeably with the increase in reaction temperature. However, from the conversion plot, the catalyst response to reaction temperature varies with the temperature region. In the temperature region 240-260°C, conversion increases 1.68 unit/°C and it drops to 1.24 unit/°C between the 260-270°C and finally, it drops sharply to 0.47 unit/°C between the 270-290°C. This is typical behavior of a solid catalyst catalyzing thermodynamically limited reactions such as the isomerization of normal paraffins[25]. Remarkably, the selectivity of the SCA P-isomers was not influenced by the reaction temperature and remained constant at nearly 91.5%. Unlike the Mo_2O_3/TiO_2, the Pt/Z exhibited no tendency for the formation of benzene, cyclohexane, methylcyclohexane and heptane, which implies that the catalyst physical and chemical properties were perfectly tailored to selectively converts the nC6 to SCA P-isomers, mainly (Fig. 6). Also, it appears that the catalyst cracking function does not respond greatly to the reaction temperature, as 3.1% cracking yield was obtained at the catalyst maximum operating temperature (290°C). The total yield of the SCA P-isomers in liquid products reached 72.8% at 290°C with an increase of 49 units in comparison with the yield at 240°C. Fig 7 shows the increase in the individual SCA

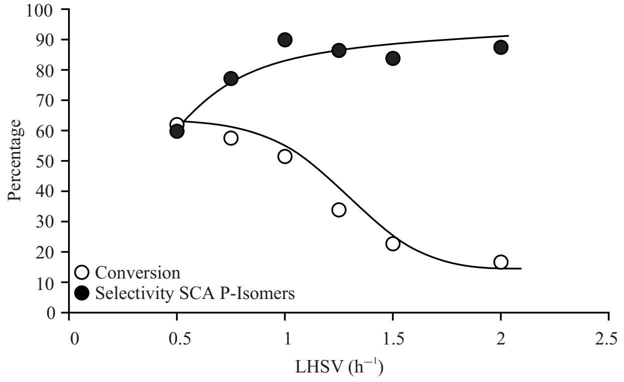

Fig. 5: Conversion of nC6 over the Mo_2O_3/TiO_2 and selectivity of the SCA P-isomers at different LHSV

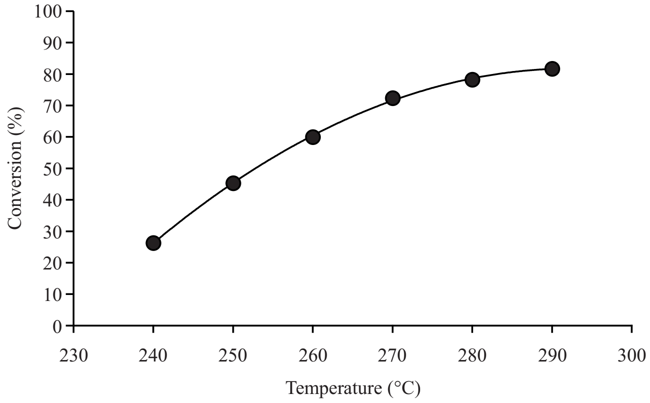

Fig. 6: Conversion of nC6 over the Pt/Z at different temperatures

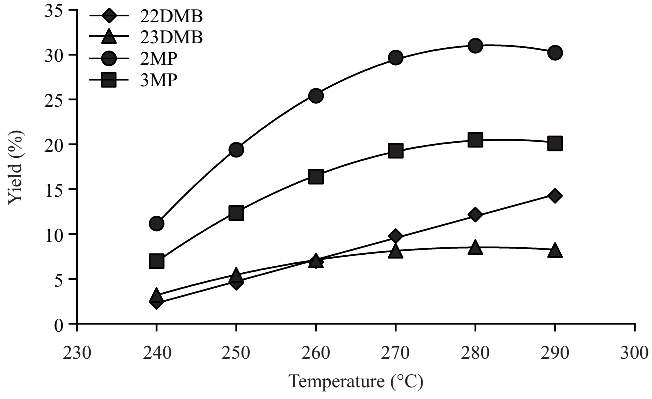

Fig. 7: Yields of the SCA P-isomers formed over the Pt/Z at different temperatures

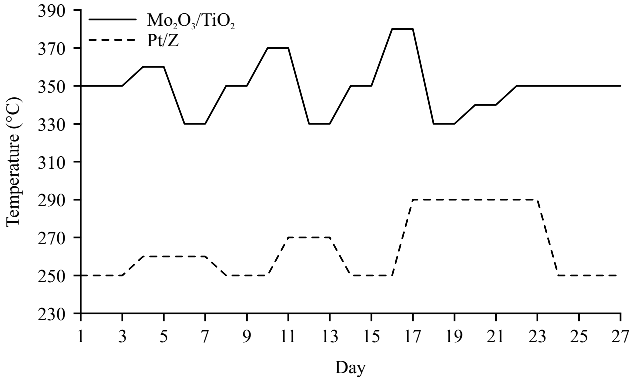

Fig. 8: Temperature changing scenario applied during catalyst stability test

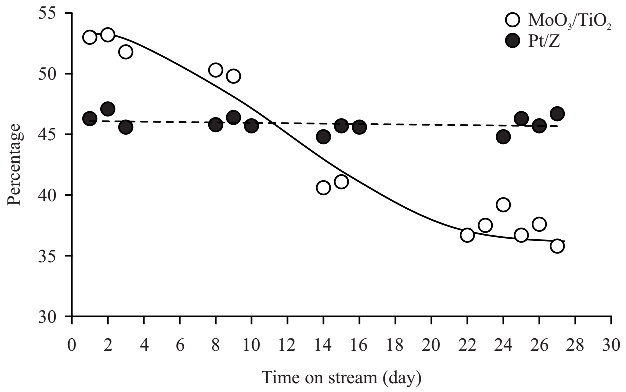

Fig. 9: Conversion with time on stream at 350°C for the Mo_2O_3/TiO_2 and 250°C for the Pt/Z

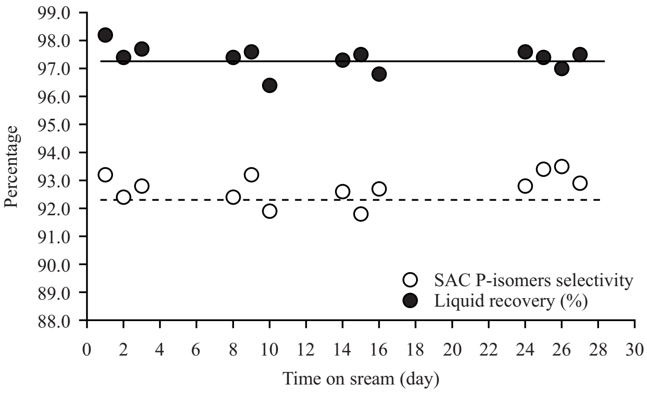

Fig. 10: SCA P-Isomers selectivity and liquid yield with time on stream for the Pt/Z operated at 250°C

Table 3: Results of the Pt/Z tested at different temperatures

Parameters	240	250	260	270	280	290
Conversion (%)	26.3	45.3	60.0	72.3	78.2	81.7
Selectivity to C6 isomers (%)	90.5	92.2	93.1	92.5	92.3	89.2
C6 isomers in liquid (wt%)						
22 DMB	2.5	4.7	7.2	10.2	12.7	15.0
23 DMB	3.3	5.6	7.4	8.5	8.9	8.7
2 MP	11.5	20.1	26.4	31.1	32.4	31.8
3 MP	7.2	12.8	17.0	20.2	21.5	21.1
Total	24.4	43.2	58.0	70.1	75.5	76.6
Recovery (%)						
Liquid	97.8	97.1	96.7	96.2	96.1	95.7
Gas (C1-C4)	1.9	2.4	2.8	3.0	3.5	3.7
Yield (%)						
i-Pentane	0.0	0.2	0.3	0.7	1.3	2.9
n-Pentane	0.0	0.0	0.1	0.2	0.4	1.1
22 DMB	2.4	4.6	6.9	9.8	12.2	14.3
23 DMB	3.2	5.4	7.1	8.1	8.6	8.2
2 MP	11.2	19.4	25.4	29.7	31.0	30.2
3 MP	7.0	12.4	16.4	19.3	20.5	20.1
Total	23.8	41.8	55.8	66.9	72.3	72.8

*C: Carbon, wt: Weight, DMB: Dimethylbutane, MP: Methylpentane

P-isomers with respect to reaction temperature. The plots in Fig. 7 show that the formation ratio of the 2 MP to the 3 MP is constant at the 1.5 regardless of the reaction temperature and this value agrees with the values reported in the literature and the value found for the same compounds over the Mo_2O_3/TiO_2. It is also important to note that the Pt/Z favors the formation of the 22 DMB at a temperature of 260°C and higher at the expense of the 23 DMB formation.

Stability test: In this part of the study, the stability of the MoO_3/TiO_2 was assessed at 5 barg, H_2/Oil ratio of 1000 L/L and LHSV of 1.0 h^{-1} all at 350°C the optimum operating temperature for the MoO_3/TiO_2. Stability performance assessment was carried out at different operating temperatures as shown in Fig 8. It is important to note that the MoO_3/TiO_2 was tested at 380°C by others and the results were found acceptable. The Pt/Z was tested under the operating conditions (Table 2) and according to the temperature changing scenario shown in Fig 8. For both catalysts, temperature ramping was achieved by 0.16°C/min. The temperatures that were selected for both catalysts to study their stability, were the 350°C and 250°C for the MoO_3/TiO_2 and Pt/Z, respectively. As per the results from the previous sections, the Pt/Z exhibited close performance to the MoO_3/TiO_2 performance at 350°C. Fig. 9 compares the conversion of both catalysts with time on stream. The Pt/Z performance was not affected by the change in temperature. Conversion, selectivity, liquid yield and the SCA P-Isomers selectivity were restored every time the catalyst was put to operate at 250°C after a change in reaction temperature (Fig 10). In addition, isomers distribution in liquid product matches the distribution found for them in the Pt/Z performance test.

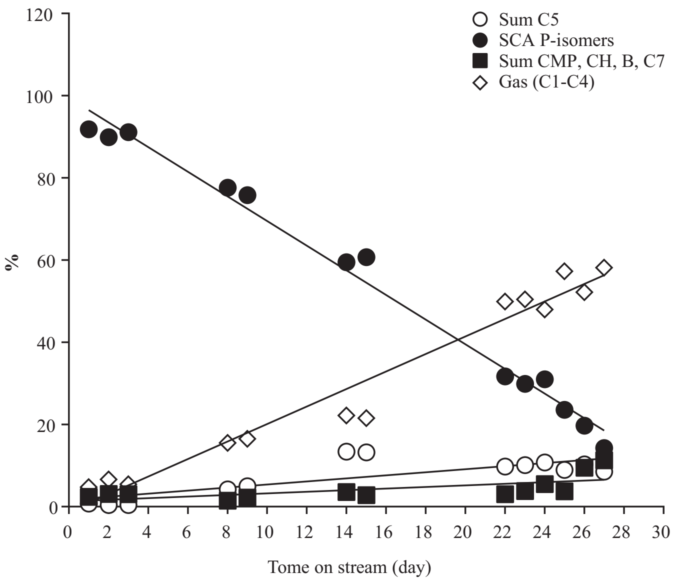

Fig. 11: Selectivity of groups of hydrocarbons at 350°C with time on stream of the Mo_2O_3/TiO_2

Unlike the Pt/Z, the MoO_3/TiO2 performance concerning time on stream and temperature change was far incomparable to the Pt/Z performance (Fig. 10). Conversion could not be restored at the 50-53% level and the SCA P-isomers selectivity dropped sharply due to temperature change and as time progress (Fig. 11). In 27 days on stream, the catalyst activity dropped 17.2 units with respect to conversion and 77.5 units with respect to the selectivity of the SCA P-isomers. In addition, it was observed that the catalyst cracking activity reached its maximum in day 27 at 20.8% in comparison with the 2.5% in day 1. Also, as time progress, it was noticed that the catalyst became selective for the formation of the pentanes, methyl cyclopentane, cyclohexane, benzene and heptane. Table 3 shows that regardless of the reaction temperature and time elapsed, the 2MP and 3MP were the leading isomers in terms of quantity and they were found at their thermodynamic equilibrium value of 1.5. The 22 DMB and 23 DMB distribution was in favor of the 23 DMB, expect that at day 14, the 22 DMB disappeared totally.

CONCLUSION

The Mo_2O_3/TiO_2 is a potential light-naphtha isomerization catalyst; it is made of low-cost metals, it can be synthesized at relatively low cost and the cost of metal recovery after usage is technically simple and cheap. The MoO_3/TiO_2 showed acceptable performance in terms of conversion, selectivity and yield of the SCA P-isomers at the optimum operating conditions. The Pt/Z exhibited close performance to the MoO_3/TiO_2 performance at 350°C. Finally, from the kinetic point of view, it is necessary to consider enhancing the MoO_3/TiO_2 total surface area.

SIGNIFICANCE STATEMENT

This study revealed that the optimum operating conditions for Mo_2O_3/TiO_2at a pilot scale in comparison with refineries operating conditions as well as commercial catalyst performance. Results from a pilot-scale can always reflect a clearer understanding of a catalyst and help to modify any drawbacks that were not observed at a smaller scale. This study will help the researcher to investigate further in the direction of using low-cost catalyst molybdenum (MoO_3) deposited on titania (TiO_2) for hydroisomerization processes.

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