Increased Light Olefin Production by Sequential Dehydrogenation and Cracking Reactions

Xiaoqiao Zhang *, Jianhong Gong, Xiaoli Wei and Lingtao Liu

Research Institute of Petroleum Processing, SINOPEC, 18 Xueyuan Road, Beijing 100083, China
* Correspondence: xqiaozhang@foxmail.com

Abstract: In this study, a sequential reaction using selected metal oxides, followed by ZSM-5-based catalysts, was employed to demonstrate a promising route for enhancing light olefin production in the catalytic cracking of naphtha. The rationale for the reaction is based on the induction of alkenes into hydrocarbon feeds prior to cracking. The optimum olefin induction was achieved by carefully optimizing the dehydrogenation active sites Mo/Al$_2$O$_3$ catalyst. The formed alkenes have a lower activation energy for C-H/C-C bond breaking compared to alkanes. This could accelerate the formation of carbenium ions, thus promoting the conversion of n-octane to produce light olefins. Detailed product distribution and DFT calculation indicated a remarkable increase in ethylene and propylene production in the final product through a modified reaction pathway. Compared with the common metal-promoted zeolite catalysts, the new route could avoid the block of zeolite channels and corresponding decreased catalytic cracking activity. The feasibility of the proposed route was confirmed with different ratios of dehydrogenation catalyst to the reactant. The highest yields of ethylene and propylene reached 13.22% and 33.12% with ratios of Mo/Al$_2$O$_3$ and ZSM-5-based catalyst to n-octane both 10:1 at 600 °C. Stability tests showed that the catalytic activity of the double-bed system was stable over 10 cycles.

Keywords: naphtha; dehydrogenation; cracking; DFT calculation; synergetic effect

1. Introduction

Light olefins, such as ethylene and propylene, are important basic materials in the chemical industry. Because of the increased consumption of their downstream derivatives, the demand for them is growing tremendously each year, especially for propylene [1,2].

Traditionally, steam thermal cracking has been the main source of light olefins; however, this method involves high energy consumption and large CO$_2$ emissions. Moreover, ethylene dominates in cracking products, and propylene is produced as a byproduct, and thus the process is unable to satisfy the demand of the current light olefin market. These limitations have urged substantial interest in the development of alternatives for propylene production. The dehydrogenation of propane has recently gained much attention as an alternative to producing propylene [3]. The CrO$_x$-Al$_2$O$_3$ and platinum-based catalyst systems have been used for industrial dehydrogenation processes. However, major challenges associated with these catalytic systems are the improvement of process economics and olefin selectivity [4].

Catalytic cracking of naphtha has been considered one of the most promising technologies for energy conservation [5–7]. This process should favor the production of propylene rather than ethylene because the transformation proceeds mainly via carbenium ion chemistry. However, the ethylene and propylene productivities achieved using these technologies and catalysts still cannot fulfill the gap between the supply and the demand [8–10]. Continuous effort should be devoted to developing methods of further increasing light olefin production.
Dehydrogenation cracking, which combines catalytic dehydrogenation and cracking reactions, is a promising approach to reducing energy consumption and carbon emission for light olefin production from naphtha [11,12]. The incorporation of transition metals (Zn, Co, Cu, and Ni) into ZSM-5 results in the formation of a bifunctional catalyst in which the metal and acid sites can act simultaneously to improve the yields of light olefins. This is because transition metals are generally used as active components for hydrogenation or dehydrogenation. Metal oxides interact with the hydrogen atoms of alkanes and promote the dissociation of C-H bonds and the subsequent formation of hydrogen and olefins [10,13–15]. The activation energy for C-H/C-C bond breaking is lower for the catalytic cracking of alkenes than that for alkanes [16,17]. However, the improvement is limited because they can only function with little influence on the surface chemistry of the catalyst. Furthermore, the increased amount of metal particles or clusters may cause serious aggregation. Their block of zeolite channels caused a decrease in the catalytic cracking activity.

The influence of the reaction pathways is vital in the catalytic cracking of naphtha. The purpose of this paper is to propose a novel reaction route to increase light olefin production. This sequential reaction was conducted using carefully optimized dehydrogenation metal oxides, followed by ZSM-5-based catalysts in the form of two layers. The introduced metal oxides were expected to induce alkene formation in the hydrocarbon feed after dehydrogenation. Therefore, n-octane could be activated by dehydrogenation sites before further cracking over acidic sites in the ZSM-5-based catalyst. The formation of olefin can accelerate the formation of a carbenium ion and suppress the alkane intermediates, thus promoting the conversion of n-octane to produce light olefins. Catalytic cracking of n-octane was used as the model reaction in this study. A remarkable increase in ethylene and propylene productivity was achieved with the developed reaction route. Stability was also demonstrated in the long-term tests.

2. Results and Discussion

2.1. Characterization of Catalysts

Figure 1 displays the XRD patterns of all the catalysts employed in this study. Peaks corresponding to the cubic crystalline phases of bare \( \gamma-Al_2O_3 \) appeared at \( 2\theta \) values of 37°, 45°, and 67° according to JCPDS card no. 10-0425. The Mo/Al\(_2\)O\(_3\) sample exhibited two weak diffraction peaks at \( 2\theta \) values of 45° and 67°, which were attributed to crystalline \( \gamma-Al_2O_3 \). The small diffraction peaks at \( 2\theta \) values of 23° and 25.7°, assignable to the (110) and (040) planes, respectively, indicate the presence of an orthorhombic phase of MoO\(_3\) (JCPDS card no. 35-0609). The weak diffraction peaks at 23° and 25.7° indicate that molybdenum oxide was well dispersed over the support [3,18]. The XRD pattern of the ZSM-5-based catalyst showed intense peaks corresponding to ZSM-5 in \( 2\theta \) ranges of 7°–9° and 22°–25° [19,20].

Figure 2I,II shows the \( N_2 \) adsorption/desorption isotherms and pore-size distribution of the catalysts. All the synthesized samples showed similar isotherms, consisting of monolayer adsorption, multilayer adsorption, and capillary condensation (Figure 2I). The shape of the adsorption/desorption curves suggested that the synthesized Mo/Al\(_2\)O\(_3\) and Ni-Mo/Al\(_2\)O\(_3\) catalysts exhibited type IV adsorption isotherms, which were unequivocally attributed to mesoporous solids. The H\(_2\)-type hysteresis loop of the isotherms indicated the existence of bottleneck-like mesopores. Pore size analysis (Figure 2II) of the synthesized catalysts indicated a unimodal pore size distribution in the range of 20–100 Å. The calculated average pore diameter of the samples was 10 nm, which was within the standard range of 2–50 nm for mesoporous materials, according to the IUPAC classification. The presence of mesopores and the absence of micropores improved the diffusion (mass transport) of the reactants and products across the active sites.
Figure 1. XRD patterns of Mo/Al$_2$O$_3$, Ni-Mo/Al$_2$O$_3$, and the ZSM-5-based catalyst.

Figure 2. (I) N$_2$ adsorption-desorption isotherms for Mo/Al$_2$O$_3$, Ni-Mo/Al$_2$O$_3$, and ZSM-5-based catalysts. (II) Pore size distribution of the catalysts.

The acid-base characterization of the catalyst demonstrates its essential role in achieving the desired catalyst performance in the dehydrogenation and cracking reactions. NH$_3$-TPD was used to evaluate the strength and availability of the acid sites for adsorption on the catalyst. The complete set of the NH$_3$-TPD traces is presented in Figure 3 to demonstrate the acidic properties of all the employed catalysts. The peak temperature of Mo/Al$_2$O$_3$...
and Ni-Mo/Al₂O₃ was almost the same, centered at 270 °C. This corresponded to the desorption of chemisorbed ammonia on the weak to moderate acidic sites of the catalyst. In the alumina-supported catalysts, the γ-alumina support not only provides the required porosity and surface area for the dispersion of the active catalyst components but also contains acidic sites that take part in some of the reactions.

The total acidity of the catalysts was related to the area under the curve. The desorption peak at a low temperature (T ≤ 300 °C) corresponds to weak acid sites, and the desorption peak at a medium temperature (T = 300–450 °C) corresponds to medium–strong acid sites. The distribution of the amount of acid with different strengths of the catalysts was obtained by integrating the peak area of the catalysts at the corresponding temperatures. From Table 1, it can be seen that the total amount of acid of Ni-Mo/Al₂O₃ was 86.5 μmol/g, which was higher than that of Mo/Al₂O₃. The amounts of weak acid were 33.9 and 35.3, respectively. The trend in the change in the strength of medium–strong acid is almost consistent with that of the total amount of acid. The amount of medium–strong acid was 51.2 μmol/g with Ni-Mo/Al₂O₃ and 22.3 μmol/g with Mo/Al₂O₃. Two desorption peaks were observed in the rich acidic region for the ZSM-5-based catalysts, corresponding to ammonia desorption from the weak and intermediate acid sites. The amounts of weak and medium-strong acids were 90.5 and 45.2 μmol/g, respectively.

![NH₃-TPD of Mo/Al₂O₃, Ni-Mo/Al₂O₃, and ZSM-5-based catalyst.](image)

**Figure 3.** NH₃-TPD of Mo/Al₂O₃, Ni-Mo/Al₂O₃, and ZSM-5-based catalyst.

Table 1. Textural properties and acid distribution of the catalysts.

| Catalyst            | \( S_{\text{BET}} \) (m²/g) | \( V_p \) (cm³/g) | \( V_{\text{micro}} \) (cm³/g) | \( d_p \) (nm) | Weak Acid (μmol/g) | Medium and Strong Acid (μmol/g) | Total Acid (μmol/g) |
|---------------------|-------------------------------|-------------------|-------------------------------|---------------|-------------------|-------------------------------|-------------------|
| Mo/Al₂O₃            | 168.22                        | 0.47              | -                             | 11.14         | 33.9              | 22.3                          | 56.2              |
| Ni-Mo/Al₂O₃         | 163.20                        | 0.44              | 0.08                          | 10.88         | 35.3              | 51.2                          | 86.5              |
| ZSM-5-based Catalyst | 203.00                        | 0.13              | 0.08                          | 2.62          | 90.5              | 45.2                          | 135.7             |

\( S_{\text{BET}} \): total specific surface area; \( V_p \): total pore volume; \( d_p \): average pore diameter.

The textural characteristics of the materials are listed in Table 1. Table 1 indicates that the specific surface area of Mo/Al₂O₃ was 168 m²/g, which decreased slightly to 163 m²/g in Ni-Mo/Al₂O₃. The total pore volume of Ni-Mo/Al₂O₃ was 0.44 cm³/g, which was also slightly smaller than that of Mo/Al₂O₃ (0.47 cm³/g). This was attributed to the pore blockage caused by the addition of nickel oxide. The average pore diameter of the synthesized catalyst decreased after the introduction of nickel oxide, and this is related to the blockage of small pores. The Mo/Al₂O₃ catalyst had a relatively high surface area (168 m²/g), large pore diameter (11 nm), and relatively large pore volume (0.47 cm³/g). All these properties are indicative of a well-formed mesoporous material that can enhance the dispersion of active metals on a support. The micropore volume of the ZSM-5-based catalyst was 0.08 cm³/g and the total pore volume was 0.13 cm³/g. The micropore volume
was not obtained from Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts, which was in excellent agreement with the results acquired by N₂ adsorption.

2.2. Dehydrogenation Performance of Mo/Al₂O₃ and Ni-Mo/Al₂O₃

Identifying an appropriate dehydrogenation catalyst is essential for the on-purpose production of olefins. The dehydrogenation performance of Mo/Al₂O₃ and Ni-Mo/Al₂O₃ was investigated using an ACE equipment to identify a suitable dehydrogenation catalyst. The product distribution at various reaction temperatures is presented in Table 2.

For the n-octane feedstock with a molecular mass of 114, the H₂ yield was predicted to be approximately 1.75% when one hydrogen molecule was abstracted and 5.26% when aromatization occurred. The increase in H₂ concentration suggests successful dehydrogenation of alkanes. The H₂ yield increased with increasing reaction temperature. The H₂ yield of 1.75% at 550 °C for Ni-Mo/Al₂O₃ indicates that one H₂ molecule was abstracted from n-octane. When the reaction temperatures were 600 and 650 °C, the H₂ yields were 6.28% and 10.05%, respectively, indicating aromatization and severe coking. The coke yield was consistent with the trend in H₂ production because of the carbon–hydrogen equilibrium.

| Catalyst       | Mo/Al₂O₃ | Ni-Mo/Al₂O₃ |
|----------------|----------|-------------|
| Reaction Temperature (°C) | 500 | 550 | 600 | 650 | 500 | 550 | 600 | 650 |
| Conversion (%)   | 1.71 | 3.07 | 5.82 | 24.39 | 4.32 | 5.16 | 12.98 | 27.73 |
| Yield (wt%)      |       |       |       |       |       |       |       |       |
| Dry Gas         | 0.54  | 1.75  | 5.08  | 20.75 | 3.45  | 4.67  | 11.39 | 22.44 |
| Hydrogen        | 0.09  | 0.29  | 1.17  | 8.83  | 1.42  | 1.75  | 6.28  | 10.05 |
| Methane         | 0.07  | 0.29  | 1.53  | 5.66  | 0.86  | 1.45  | 2.75  | 5.94  |
| Ethane          | 0.13  | 0.42  | 1.63  | 4.33  | 0.77  | 0.91  | 1.37  | 3.77  |
| Ethylene        | 0.26  | 0.75  | 0.75  | 1.93  | 0.40  | 0.56  | 0.99  | 2.68  |
| LPG             | 3.17  | 6.28  | 14.36 | 7.37  | 4.94  | 5.81  | 5.35  | 6.64  |
| Propane         | 0.39  | 0.64  | 1.40  | 1.90  | 0.83  | 0.75  | 0.70  | 1.00  |
| Propylene       | 1.05  | 2.63  | 6.61  | 2.52  | 1.65  | 2.08  | 1.94  | 2.69  |
| n-Butane        | 0.29  | 0.47  | 0.89  | 0.87  | 0.38  | 0.38  | 0.38  | 0.73  |
| Isobutane       | 0.25  | 0.15  | 0.21  | 0.25  | 0.30  | 0.30  | 0.19  | 0.29  |
| Butylene        | 1.19  | 2.40  | 5.27  | 1.83  | 1.79  | 2.31  | 2.13  | 1.92  |
| Gasoline Product| 95.50 | 90.21 | 73.92 | 52.49 | 85.96 | 82.60 | 68.17 | 45.82 |
| Coke            | 0.80  | 1.43  | 4.71  | 21.38 | 6.17  | 7.96  | 14.58 | 24.12 |
| Olefins (wt%)   | 8.02  | 8.30  | 8.96  | 11.99 | 1.27  | 2.78  | 6.36  | 4.54  |
| Mass balance (%)| 100.01| 99.67 | 98.07 | 101.99| 100.52| 101.04| 99.49 | 99.02 |
| Reaction rate  (mmolₙ-octane⁻¹h⁻¹g⁻¹Cat⁻¹)| 0.59 | 1.06  | 2.01  | -     | 1.49  | 1.77  | -     | -     |

The dehydrogenation reaction in the presence of Mo/Al₂O₃ was much milder than that in the presence of Ni-Mo/Al₂O₃. The H₂ production was very low between 500 and 550 °C, with 0.09% and 0.40% yields, respectively. Between 600 and 650 °C, one H₂ molecule was abstracted from n-octane. To establish the structure–activity relationship, the reaction rates were evaluated with low n-octane conversion (<10%), so as to minimize the effect of mass transport. The reaction rate of Mo/Al₂O₃ at 650 °C was 2.01 mmolₙ-octane⁻¹h⁻¹g⁻¹Cat⁻¹, which was higher than that at 500 and 550 °C. Mass balance of these reactions ranged between 98 and 102%. There are several reports on the use of Mo/Al₂O₃ and Ni-Mo/Al₂O₃ for the dehydrogenation of saturated hydrocarbons [21,22]. When the dehydrogenation activity is weak, the conversion of light hydrocarbon is low; however, when the dehydrogenation activity is strong, an aromatization and severe coking reaction will happen. A high proportion of olefins was found in the liquid product because of the successful dehydrogenation. Metal oxides interact with the hydrogen atoms of alkanes and promote the dissociation of C-H bonds and the formation of hydrogen and olefins [4,23]. It is
worth mentioning that the olefins produced were unstable, often considered intermediate products, and easily cracked into smaller molecules [24].

2.3. Proposed Reaction Pathway and DFT Computations

The proposed reaction pathways of n-octane over a single cracking catalyst (Path I), dehydrogenation, and cracking catalysts (Path II) are shown in Figure 4. The ability of solid acids to protolyze non-activated C-H and C-C bonds was first suggested by Haag and Dessau [16,25]. In the monomolecular mechanism, n-octane first obtains protons from the acid sites of the zeolite, resulting in the formation of carbonium ions [26,27].

As shown in Path I, from the DFT calculation results, the protolysis of the C-C bond results in butane and butyl carbonium, octonium, and H2. The corresponding energy barrier is 240 and 291 kJ/mol, respectively. It indicated that Brønsted active site trend to react with the C-C bond in n-octane, forming the corresponding small molecule alkanes and carbonium ions. The resulting n-butyl carbonium is easily transformed into more stable sec-butyl carbonium. The energy barrier is 60 kJ/mol. The following (classical) bimolecular mechanism involves hydride transfer between an n-octane and an adsorbed sec-butyl carbonium ion, forming butane and sec-octonium. The formed carbenium ions can undergo a number of reactions. The nature and strength of the acid sites of the catalyst influence the extent to which these reactions occur. The dominant reactions of the carbenium ions include β-scission, isomerization, hydrogen transfer, and dehydrogenation. The β-scission of sec-butyl carbonium forms propylene and methyl carbonium. This step has an activation enthalpy of 218 kcal/mol. Hydride transfer between methyl carbonium and n-octane forms methane and octonium. This step has an activation enthalpy of 170 kcal/mol. The associated activation barriers of the initial step are relatively high, and trends to form carbenium and alkane intermediates. It is also difficult for this formed alkane to further crack on the Brønsted active sites. Therefore, the initial step is the rate-determining step.

![Figure 4](image-url)

Figure 4. The schematic diagram for the proposed reaction pathways of n-octane over cracking catalyst (Path I), dehydrogenation, and cracking catalysts (Path II).

Transition metal oxides such as MoO3 are generally used as active components for hydrodenation or dehydrogenation. The activation of n-octane on the (010) surface of MoO3 requires about 140–150 kJ/mol, which is much lower than that required for protolysis [28–30]. The presence of MoO3 was proposed to activate the n-octane molecule and promote the initiation step. After activation, octene is induced in the feed. The octene could further react with active Brønsted sites, forming octonium. DFT calculations indicated that the energy barrier of zeolite to protolyze octene is 110 kJ/mol, which is much lower than that required for the case of n-octane. The octonium can undergo β-scission forming pentene and propyl carbonium. The formed pentene can further react with the Brønsted active sites. The red lines in Path II (Figure 2) indicate that if the reaction pathways could be modulated to convert n-octane to octene via dehydrogenation, the energy barrier would decrease. The formation of olefins can accelerate the formation of a carbennium ion and suppress the alkane intermediates, thus promoting the conversion of n-octane to produce light olefins.
2.4. The Feasibility of Sequential Dehydrogenation and Cracking Reactions

The textural characteristics and detailed product distribution are presented to better understand the catalyst activities. The results indicate that Mo/Al₂O₃ was the optimum catalyst for promoting the production of light olefins under the chosen reaction conditions. We designed a progressive double-bed catalyst system based on a dehydrogenation cracking mechanism (Figure 5). In the first stage, Mo/Al₂O₃ was utilized as the dehydrogenation site. Hydrocarbon feeds containing adequate amounts of olefins proceed to the second bed (containing a ZSM-5-based catalyst), where a cracking reaction occurs. ZSM-5 containing acid sites is a good choice to demonstrate this new route [31,32].

![Proposed reaction path comprising dehydrogenation and cracking reactions in a double-bed catalyst system.](image)

The catalytic performance of the sequential reactions involving Mo/Al₂O₃ and ZSM-5-based catalysts was tested in a fixed-bed reactor. Figure 6 summarizes the catalytic performance after the introduction of the Mo/Al₂O₃ catalyst in the set of reactions. n-Octane conversion and the yields of ethylene, propylene, and H₂ with increasing metal oxide/n-octane ratio are displayed. The reactions catalyzed by a Mo/Al₂O₃ or ZSM-5-based catalyst alone (denoted as MOₓ and Z, respectively, in Figure 6) were tested as reference reactions. A blank test corresponding to thermal cracking was also presented, denoted as Blank in Figure 6.

Due to the great enhancement of conversion level, light olefins had higher yields. The yield of ethylene and propylene is 10.9%, and 19.3% over single ZSM-5 catalysts at WHSV = 360 h⁻¹, which is much higher than that of thermal cracking. The double-bed reaction using the Mo/Al₂O₃ and ZSM-5 catalysts (metal oxide/n-octane ratios of 2:1, denoted as M + Z) gave 12.5% and 20.0% yields of ethylene and propylene at WHSV = 300 h⁻¹, respectively. The conversion increased from 72.8% to 79.0%. The olefin content increases significantly after coupling the Mo/Al₂O₃ and ZSM-5-based catalysts. This result suggests a prominent synergistic effect between the dehydrogenation and cracking of active sites, in contrast to that in the ZSM-5 reference reaction. The feasibility of the proposed route was further confirmed when the amount of dehydrogenation catalysts was increased—the Mo/Al₂O₃ to n-octane ratio was changed to 4:1, 6:1, and 10:1 (denoted as 2M + Z, M + Z and 5M + Z in Figure 6) at space velocities (WHSV) of 257, 225 and 180 h⁻¹. The slower flow velocity caused by lower WHSV results in a longer contact time between n-octane and the catalysts. As a result, a larger portion of n-octane performed the dehydrogenation.
and cracking reactions on the catalyst surface. Because higher amounts of olefins were induced by the Mo/Al\textsubscript{2}O\textsubscript{3} catalyst, the yields of ethylene and propylene increased to 12.78\% and 21.07\% for 2M + Z, 13.01\% and 21.12\% for 3M + Z, 13.22\% and 33.12\% for 5M + Z, respectively, in the product feed. As stated earlier, the influx of adequate amounts of olefins is advantageous for the production of carbenium ions and olefins over the acid sites of zeolites. This was successfully achieved via this route. Substantial increases of ethylene and propylene were obtained by coupling the Mo/Al\textsubscript{2}O\textsubscript{3} and ZSM-5 catalysts.

![Figure 6.](image)

Figure 6. \(n\)-Octane conversion and yields of ethylene, propylene, and H\textsubscript{2} in a sequential reaction using metal oxides and ZSM-5-based catalysts. M + Z, 2M + Z, 3M + Z and 5M + Z indicate increasing metal oxide/\(n\)-octane ratios of 2:1, 4:1, 6:1 and 10:1 and constant ZSM-5-based catalyst/\(n\)-octane ratio of 10:1.

\(n\)-Octane conversion and selectivities of ethylene and propylene in the set of reactions were presented in Table 3. The results demonstrated that both the conversion and selectivity of ethylene and propylene improved after MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} introduction. The results obtained for this double-bed system compare favorably with that of the Chunyi Li group [33]. In their study, the conversion of \(n\)-heptane increased from 51\% to 59\% by replacing 20\% of the HZSM-5 catalyst with V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}. The contacting sequence with the two different catalysts greatly influenced product distribution. \(n\)-heptane could be activated by lattice oxygen provided by oxidized vanadia before further cracking over acidic sites in the HZSM-5 catalyst.

Compared with the transition metal-promoted zeolites, the double bed system facilitated a modified reaction route. The transition metal-promoted zeolites can act as bifunctional catalysts containing the acid sites in zeolite frameworks and the dehydrogenation centers created by metal species. However, the overloading of metal species on zeolite may cause the serious aggregation blocking of zeolite pores, resulting in the decrease of the catalytic activities. For the double-bed system, the distance of dehydrogenation and cracking active site was beneficial for improving the selectivity to the desired product.
Table 3. \(n\)-Octane conversion and selectivities of ethylene and propylene in the sequential reactions and reference reactions.

|                  | Conversion | Ethylene Selectivity | Propylene Selectivity |
|------------------|------------|----------------------|-----------------------|
| Blank test       | 4.18       | 12.44                | 6.46                  |
| MOx              | 5.82       | 11.00                | 8.08                  |
| Z                | 72.81      | 15.03                | 26.51                 |
| M + Z            | 79.02      | 15.77                | 25.37                 |
| 2M + Z           | 85.10      | 15.02                | 24.76                 |
| 3M + Z           | 95.13      | 13.68                | 22.21                 |
| 5M + Z           | 96.72      | 13.67                | 34.25                 |

2.5. Evaluation of Double-Bed Reaction Performance and Stability

Lastly, we demonstrate that the double-bed system is capable of maintaining desirable properties (\(n\)-octane conversion, light olefin selectivity) in long-term tests. The reactions were performed in a pulse injection manner in the fixed-bed reactor. Figure 7 gives key reaction characteristics for multiple \(n\)-octane catalytic dehydrogenation cracking cycles. This route preserves its high selectivity towards light olefins over 10 cycles. The slight decline in light olefin generation over five cycles may be explained by the coke formation. The 10th cycle still shows high light olefin formation. It is thus a stable and very promising route for \(n\)-octane catalytic dehydrogenation cracking reaction.

Figure 7. \(n\)-Octane conversion and yields of ethylene and propylene over 10 cycles.

3. Materials and Methods

3.1. Materials

The commercial ZSM-5-based catalysts were obtained from Sinopec Catalyst Co., Ltd. (Beijing, China), with 30 wt% of HZSM-5 zeolite (Si/Al ratio = 21) as an active component. \(\gamma\)-Al\(_2\)O\(_3\), \((NH_4)_6Mo_7O_{24}·4H_2O\), and Ni(NO\(_3\))\(_2·6H_2O\) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China).
The Mo/Al$_2$O$_3$ and Ni-Mo/Al$_2$O$_3$ catalysts were prepared using an incipient wetness impregnation technique. The Ni and Mo contents were 2.91 and 1.59 wt%, respectively, corresponding to a Ni:Mo mole ratio of 3:1. Typically, desired amounts of ammonium molybdate tetrahydrate and nickel nitrate hexahydrate were dissolved in deionized water to match the total pore volume of the support. Subsequently, support was added to the solution. The mixture was continuously stirred for 3 h to achieve homogeneous mixing. The resultant paste was dried at 120 °C for 6 h and then calcined at 550 °C for 6 h under an air stream.

The catalysts above were pressed, crushed, sieved to 0.4–0.8 mm, and dried at 80 °C overnight before catalytic tests.

3.2. Catalytic Activity Test

The catalytic cracking of n-octane was carried out in the ACE-model unit R$^+$ (Kayser Corporation). ACE tests were conducted at atmospheric pressure with a catalyst mass of 9.0 g and a catalyst-to-oil mass ratio of 10. The feed was introduced by a pump at a rate of 9 mL/min. The cracking temperature ranged from 500 °C to 650 °C and the WHSV was 4 h$^{-1}$. After the reaction, the remaining hydrocarbons were stripped from the catalyst bed, and the reactor was purged with flowing N$_2$ (140 mL/min). During the cracking and stripping modes, the liquid product was collected in a glass receiver that was located at the end of the reactor outlet, and the temperature was maintained at −15 °C. The gas-phase products were collected in a gas receiver using the water displacement method. The dry gases (H$_2$ and C$_1$–C$_2$) and LPG (C$_3$–C$_4$) in the gaseous products were analyzed using an HP 5880A gas chromatograph. The coke content was determined using a CO and CO$_2$ analyzer at the flue gas outlet.

As the evaluation units require different operating conditions, the sequential reaction with the double-bed catalyst system was performed on a microreactor unit with two reaction zones. The performances were evaluated by pulse injection. Typically, the mass of n-octane was 2 µL. The ZSM-5-based catalyst/n-octane ratio was 10:1 and the metal oxides/n-octane ratio was variable from 2:1 to 10:1 to demonstrate the feasibility of the novel approach. Cracking reactions were conducted at 600 °C, and catalysts were filled in the constant temperature zone of the reactor. The residence time is 28 ms. The first bed was separated from the second one using quartz wool. The gas products were analyzed using an online gas chromatograph (GC) equipped with two columns.

The conversion of n-octane and the selectivity of the products were used to determine the activities of the prepared catalysts, calculated as follows:

Conversion = \( \frac{1 - (C_8H_{18})_{\text{out}}}{(C_8H_{18})_{\text{in}}} \times 100\% \)

Selectivity = \( \frac{m}{[(C_8H_{18})_{\text{in}} - (C_8H_{18})_{\text{out}}]} \times 100\% \)

Here, \((C_8H_{18})_{\text{in}}\) is the feed mass, \((C_8H_{18})_{\text{out}}\) is the n-octane mass in the product, and \(m\) is the product mass.

Yield = Conversion × Selectivity

3.3. Characterization

XRD (X-ray diffraction) characterization was carried out on a Philips X’Pert powder diffractometer using Cu Kα radiation (\(\lambda = 154.05\) pm) in the 2θ range from 5° to 70°. It was operated at 40 kV and 40 mA, with a scanning speed of 10°/min. Nitrogen physisorption isotherms were obtained using a Micromeritics ASAP 2400 volumetric adsorption system. The pore size distribution and surface area were calculated from the adsorption isotherms using the Barrett–Joyner–Halenda method and the–Brunauer–Emmett Teller equation. The micropore volume was calculated from the t-plot curve. The total acidity of the different samples was measured by NH$_3$-TPD using a Micromeritics Autochem II (ASAP 2920) chemisorption system. The acquired TPD curve was then deconvoluted by a method developed by C. Costa et al. [34].
3.4. Computational Studies

DFT calculations were performed using the DMol®3 software developed by Accelrys Inc. The geometries of the metal oxide and zeolite cluster models used in this work were obtained from the framework structure obtained from Material Studio 2019. Relativistic effects were taken into account using an all-electron scalar relativistic method. All calculations were performed using the DNP basis set. The convergence criteria (energy, force, and displacement) were set at 0.05 kJ/mol, 10^12 N, and 5 × 10^-13 m, respectively.

4. Conclusions

In summary, we successfully demonstrated a feasible route to increase light olefin production in the catalytic cracking of naphtha, using n-octane as a model compound. This novel route involves sequential dehydrogenation and cracking reactions in a single reactor with two reaction zones. The Mo/Al₂O₃ dehydrogenation catalyst bed placed before the ZSM-5-based catalyst bed induced alkenes into the hydrocarbon feed. The formation of alkenes can accelerate the formation of a carbenium ion and suppress the alkane intermediates, thus promoting the conversion of n-octane to produce light olefins. The yields of ethylene and propylene increased to 12.78% and 21.07% with a Mo/Al₂O₃:n-octane ratio of 4:1 and to 13.22% and 33.12% with a Mo/Al₂O₃:n-octane ratio of 10:1, respectively, in the products. Stability tests showed that the catalytic activity of the double-bed system was stable over 10 cycles. This study opens a new avenue for optimizing catalytic cracking reactions of naphtha. Further investigations to optimize and develop this novel route are currently underway.

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