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Hydrocracking of n-Pentane using Ruthenium Precursor Nanoparticles Loaded over Zeolite

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Abstract

Cracking of n-Pentane was carried out on two type of zeolite catalysts Ru/HZSM-5 and Ru/HMOR. The conversion was high at low temperature and the selective precursor was highly selective to desired product. The selectivity to light olefins decreased with increasing temperature and decreased with increasing hydrogen to hydrocarbon ratio. The results showed that Ru/HMOR catalyst was more active and selective than Ru/HZSM-5 catalyst for the considered temperature range.

الخلاصة

تم اجراء التكسير الحراري للبنتان باستخدام نوعين من العامل المساعد Ru/HZSM-5 و Ru/HMOR. ان عملية التحول تكون عالية في درجات حرارة منخفضة كما ان اختيار المعدن المحمل كان فعال في انتقاء النواتج المرغوبة. ان الانتقائية للمركبات الاوليفينية تتناقص مع ازدياد درجات الحرارة وتتناقص مع زيادة نسبة الهايدروجين الى البنتان. لقد اظهرت النتائج ان العامل المساعد Ru/HMOR اكثر فعالية وانتقائية من العامل المساعد Ru/HZSM-5 لجميع درجات الحرارة.

1. Introduction

Light olefins, such as ethylene, propylene and butene, are produced mainly by the thermal cracking of naphtha to improve octane number and supply these important raw materials for petrochemical industry. In this process, a large amount of energy is consumed because the process is usually operated at high temperatures around 1100 K. Moreover, it is difficult to control the selectivity to obtain propylene in a high yield because the thermal cracking favors the ethylene formation. The catalytic cracking, however, would require less energy and could produce propylene with higher selectivity [1].

The hydroconversion of n-alkenes is achieved over catalysts containing fine dispersed noble metal clusters on a matrix which contains Bronsted acid sites. During the reaction, the noble metal catalysts hydrogen transferred the reactions (hydrogentation-dehydrogentation), while isomerization and hydrocracking reactions occurred on the Bronsted acid site [2]. For the catalysts where the metal function and the acid function are well balanced, isomerization and hydrocracking are consecutive reactions and the rate limiting steps is the skeletal rearrangement of the alkenes obtained via the dehydrogentation over the metal sites, which takes place on the Bronsted acid sites [3].

ZSM-5 is one of the candidates for the production of light olefins through the naphtha cracking. Wang et al. [4] carried out hexane cracking on H-ZSM-5(Si/Al=25) and found that the addition of potassium (2 wt%) or boron (16 wt%) increased the selectivity to C_2-C_4 olefins into >50 C-% though the conversion was significantly decreased. Yoshimura et al.[5] has carried out the cracking of light naphtha and found that the addition of lanthanum (10 wt%) into H-ZSM-5 (100) enhanced the selectivity to ethylene and propylene by 61 C-% and that the further addition of phosphorus (2 wt%) improved the stability in the presence of steam. Other studies on H-ZSM-5 catalysts include the NaOH treatment to form mesopores [6], the addition of gallium [7], the spray-dry preparation with alumina [8], and the preparation of monolith catalyst by Washcoat [9].

Recently, other medium pore zeolites, ZSM-5 and Mordenite have been studied to obtain small olefin molecules. However, the above zeolites do not have enough activity, selectivity and stability for the production of light olefins instead of the commercial thermal cracking process.

In this study, Zeolite ZSM-5 and Mordenite have been used to prepare Ruthenium- incorporated zeolite by the supercritical deposition method using Ru $(\text{acetylacetonate})_2$. Zeolite ZSM-5 and Mordenite were loaded with Ruthenium using super critical carbon dioxide (SC CO_2). After adsorption on to the Zeolite, the

Precursor was reduced, resulting in Zeolite-supported Ru nanoparticles with a very uniform size distribution.

The experiments was included the catalytic cracking of n-Pentane on zeolites prepared with various temperatures to obtain the effective catalyst for the formation of light olefins, especially ethylene, in high selectivity at high conversion levels.

2. Experimental Work

2.1 Material

Two types of zeolite have been used namely ZSM-5 and (Mordenite contains hydrogen cation HZSM-5 and HMOR with Si/Al=90 and 40) respectively were donated from Sud-Chemi company in palletized form (1.5 mm * 2-3 mm), Ru(acac)$_2$ was purchased from Strem Chemical. All of the chemicals were used as received except for zeolite, where it was dried using heat gun under vacuum to remove all moisture from the pores.

2.2 Loading of Ruthenium on Zeolite

The experimental work was done in the Institute of Technical Chemistry and Macromolecular Chemistry (ITMC/ RWTH University/ Aachen/ Germany). The synthesis of Ru containing HZSM-5 and HMOR in SC CO_2 medium was conducted in a 120 mL stainless steel autoclave. In a typical experiment, to produce 0.35 wt% of Ruthenium, 10g of calcined mesoporous support and 100 mg Ru(acac)$_2$ and 10% methanol were filled in to the autoclave under argon. Using of methanol was to increase the polarity of CO_2 because the precursor compounds have low solubility in SC CO_2, solution were loaded in the reactor before it was sealed. The closed reactor was placed in a constant temperature circulating oven of 90 ^{o}C and allowed to equilibrate. After the thermal equilibrium was reached, the reaction vessel was charged with CO_2 to the desired pressure 300 bar using a high pressure syringe pump (JASCO). The vessel contents were mixed mechanically using a magnetic stirrer. The reaction was allowed to proceed for 24hr. During the synthesis, a back-pressure regulator was used to maintain the constant reaction pressure. After the reaction, the reactor was placed in ice cold water and depressurized very slowly and carefully. The samples were recovered from the container, dried at room temperature, the impregnated organometallic precursor was reduced thermally at 350 ^{o}C in presence of hydrogen and nitrogen flow mixture in a 50:50 volumetric ratio at 100 ml/min flow rate and kept at these conditions for 6 hr.

2.3 Reaction Experiments

The Ru over zeolite sample HZSM-5 and HMOR loaded by supercritical carbon dioxide method were tested for cracking of n-Pentane. The setup of the apparatus used for reaction was shown in figure (1).

The samples were originally extruded (1.5 mm * 2-3 mm), charged into the reactor and activated for one hour at temperature 350 ^{o}C just before runs in flow of hydrogen, (100 ml/min). 10g of each catalyst type was used in each run.

N-Pentane feed was pumped from a reservoir using HPLC pump, the feed was passed through one way valve to microstructure evaporator to heat up of n-Pentane to about 180 ^{o}C. The Outlet from the evaporator was mixed with hydrogen before the reactor inlet then passed through the catalyst bed from the top of reactor. The product was connected online to Gas Chromatography.

The catalyst samples were tested under a wide range of operating temperature 250-325 ^{o}C. Hydrogen total pressure was kept constant at 1bar, liquid hour space velocity (LHSV) equal to 1.85hr^{-1} and hydrogen to hydrocarbon ratios (H_2/HC) were taken 3, 6 and 9 moles.

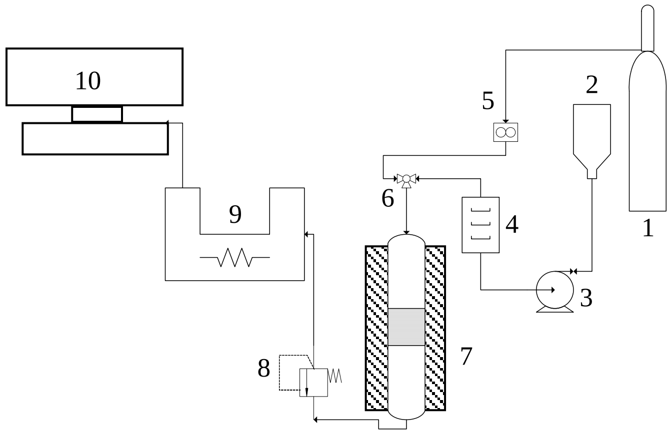

Fig. (1)Shematic flow diagram of catalytic experimant rig
(1) hydrogen Cylinder, (2) n-Pentane container, (3) Dosing Pump,
(4) Microheater, (5) Hydrogen flow meter, (6) Three way one way valve,
(7) Reactor with heat shell, (8) Back Pressure Regulator,
(9) Gas Chromatography, (10) computer

3. Results and Discussion

In this study, Ruthenium was loaded on zeolite for cracking by chance, It is well known that hydrogenation reaction occurs on metal site, but when Ruthenium was used for isomerization of hydrocarbon compounds, the products of the reaction took reverse direction i. e. the reaction was converted from isomerization to cracking, in addition to that, even if Ruthenium was loaded with another metal as bi metal, for isomerization reaction such as platinum, the reaction turns to cracking without affecting the presence of platinum on the reaction.

The results showed that the conversion was begun at low temperature. The selectivity to ethylene and propylene was measured from 250 ^{o}C to 325 ^{o}C, above 325 ^{o}C the conversion of n-Pentane to methane was increased obviously; therefore the experiment was running with these conditions.

The conversions of n-Pentane to cracking product over the Ru/zeloite were shown from figures (2-5). The detailed product distribution upon n-Pentane cracking is shown from figures (6 - 11).

As it is expected that the temperature increase leads to conversion increase gradually, while the selectivity decreases with temperature increase. Temperature increase enhances the methane product; the results show that Ru/HMOR catalyst is more active and selective towards olefins compounds than Ru/HZSM-5 catalyst for the considered temperature range.

Figures (2, 3) illustrate the conversion of n-pentane in presence of Ru/HZSM-5 and Ru/HMOR respectively, the figures show that the increase in temperature leads to increase in conversion significantly as expected, the conversion of n-pentane is much better in presence of Ru/HMOR rather than the presence of Ru/HZSM-5, in addition, the figures show that increasing the proportion of hydrogen to hydrocarbon affect significantly the rate of conversion. The ratio increase as the hydrogen to hydrocarbon of 3 to 9 increases the rate of conversion, as for example at temperature 325 ^{o}C and H/HC=9, the thermal cracking of n-pentane in presence of Ru/HMOR is 99.5%.

The effect of temperature on the selectivity in the presence of Ru/HZSM-5 and Ru/HMOR are shown in figures (4, 5) respectively, where the temperature increase leads to reduce the selectivity of the olefins compounds, in addition to the increase of hydrogen to hydrocarbon ratio leads the transformation to methane and reduction of selectivity, also it was found that Ru/HMOR more effective and selective than RU/HZSM-5 for the olefins compounds.

To illustrate the full analysis of the outputs of thermal cracking of a n-pentane, the data were plotted with selectivity as shown in figures (6-11), where the columns represent the percentages of compounds, and to clarify that we take figure (6), for example. X-axis represents the selectivity in the temperature reaction and the y-axis represents the concentrations, for example, when selectivity 57.912% to be products of the reaction as follows (C_1=20.3, C_2=8.8, C_2=30.9, C_3=11.9, i-C_4=4.9, n-C_4=3.4, i-C_5=8.9 and n-C_5=10.9), that these forms show that olefins compounds high selectivity and compounds of (i-C_4 to i-C_5) are very low due to the Ruthenium very effective for cracking conditions.

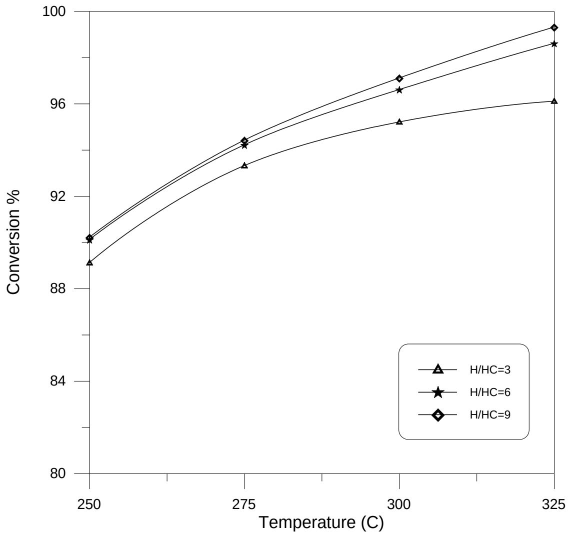

Fig.(2) Conversion v.s. Temperature for Ru/HZSM-5

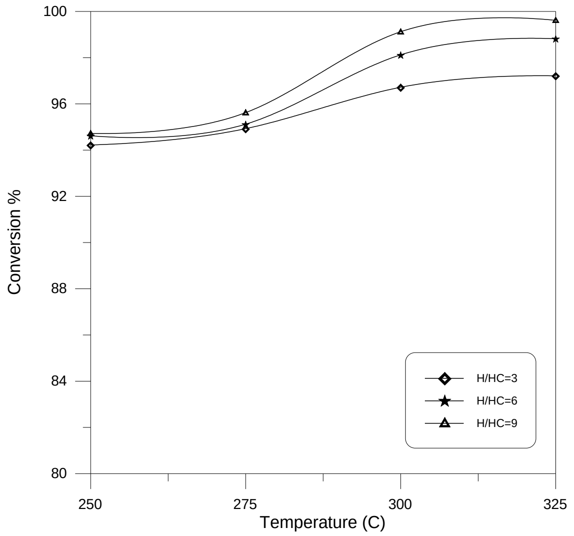

Fig.(3) Conversion v.s. Temperature for Ru/HMOR

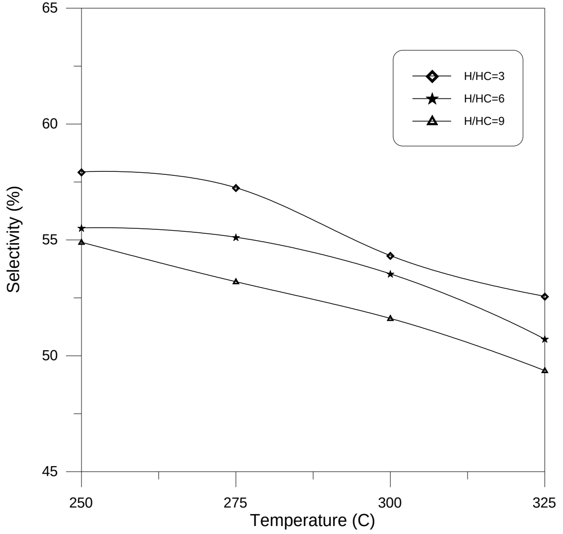

Fig.(4) Selectivity v.s. Temperature for Ru/HZSM-5

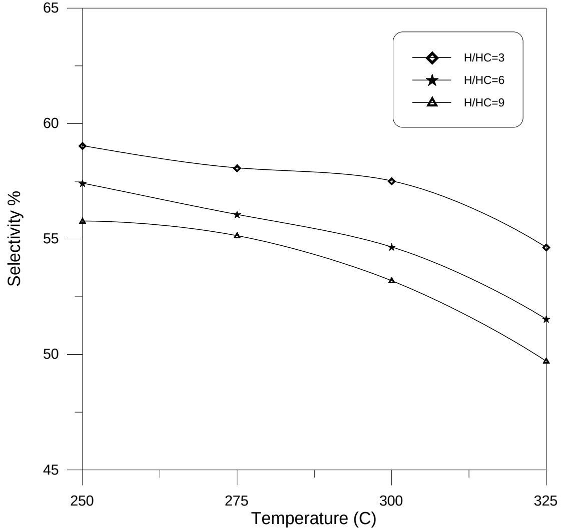

Fig.(5) Selectivity v.s. Temperature for Ru/HMOR

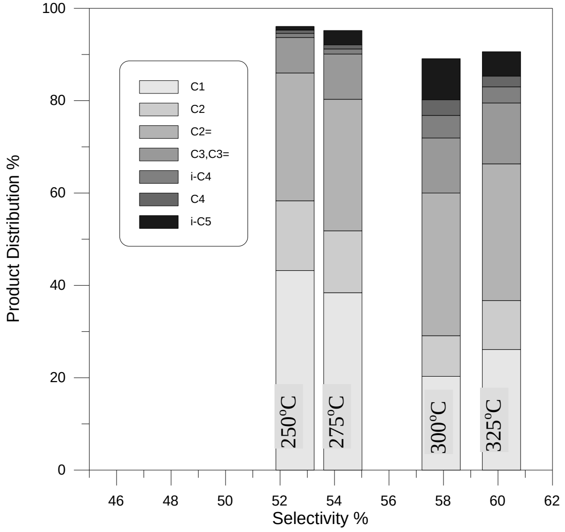

Fig.(6) Product v.s. Selectivity for Ru/HZSM-5 for H/HC=3

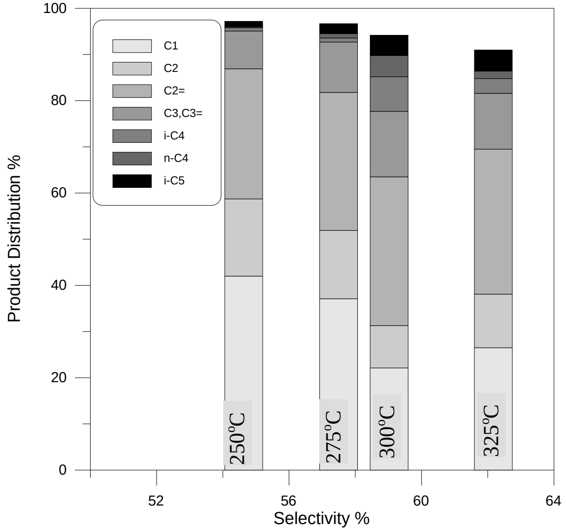

Fig.(7) Product v.s. Selectivity for Ru/HMOR for H/HC=3

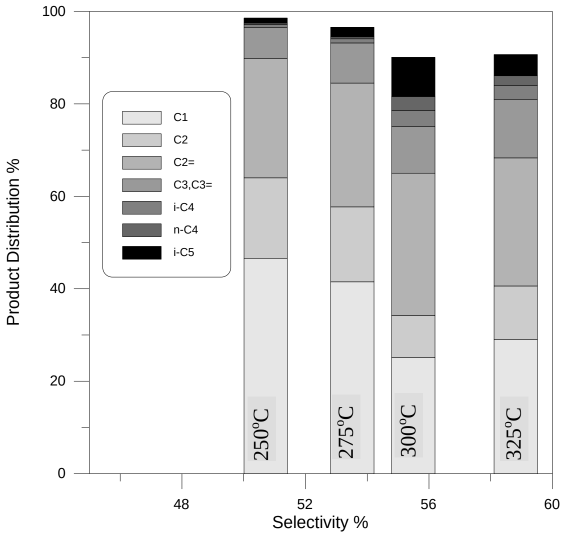

Fig.(8) Product v.s. Selectivity for Ru/HZSM-5 for H/HC=6

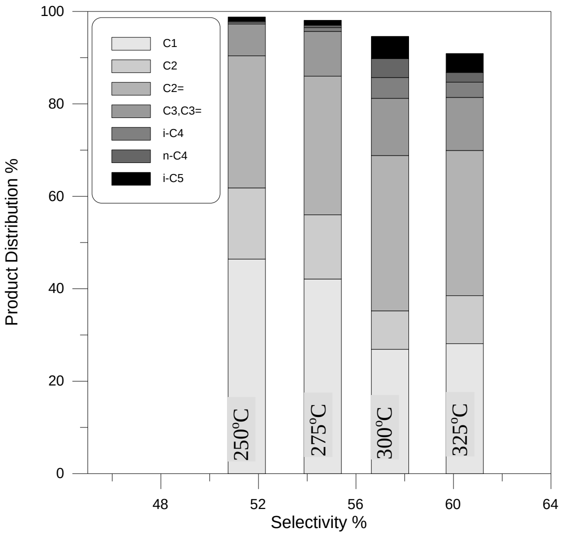

Fig.(9) Product v.s. Selectivity for Ru/HMOR for H/HC=6

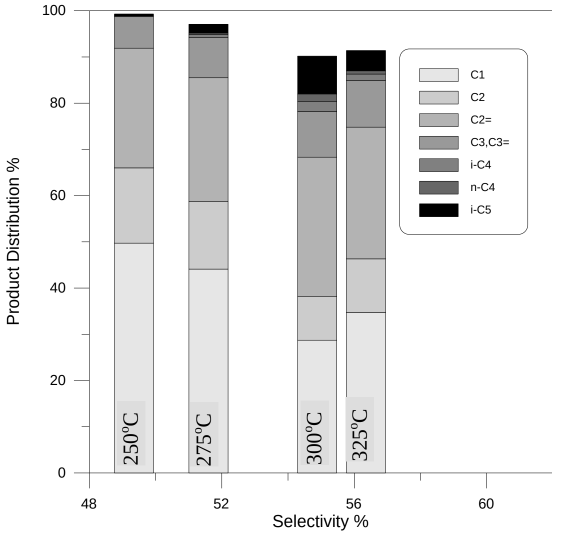

Fig.(10) Product v.s. Selectivity for Ru/HZSM-5 for H/HC=9

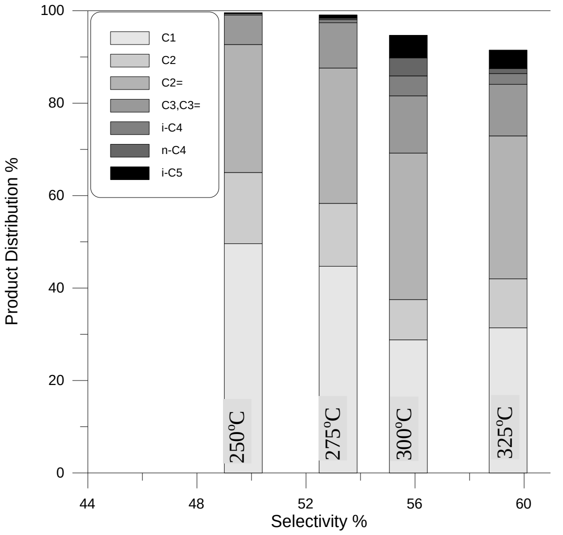

Fig.(11) Product v.s. Selectivity for Ru/HMOR for H/HC=9

4. Conclusion

The cracking reaction is generally very good for these types of catalysts where Ru/HMOR is more active and selective than Ru/HZSM-5. Additionally, the increasing of hydrogen to hydrocarbon ratio gave an increasing of conversion and decreasing of selectivity. In summary, the temperature between 250 ^{o}C to 260 ^{o}C is more active and selective toward olefins.

6. References

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