

Preparation and Characterization of Zeolite-Based Hydrocracking Catalysts

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Abstract: A series of zeolite-based hydrocracking catalysts was prepared using modified Y-zeolite and alumina as support. Nickel, tungsten (NiW) and Nickel, Molybdenum (NiMo) metal pairs were used as active metals. The metals were added using incipient wetness impregnation method. Commercial Y-zeolite was modified by steam treatment at various temperatures and the unit cell size was measured by XRD method. Two sets of catalysts were prepared using modified Y-zeolite and γ -alumina in a ratio of 50:50 and 30:70 respectively. The metal pair loaded on each type of support used was either NiMo or NiW. The objective of the study was to investigate the effect of active metal type and the acidity function on the catalytic activity. The prepared catalysts were characterized by surface area, pore volume, Temperature Programmed-Desorption (TPD) of ammonia and Temperature Programmed-Reduction (TPR). The hydrocracking activity was measured using cumene as a model compound. It was observed that NiW-based catalysts were more active in hydrocracking of cumene than were NiMo-based catalysts. The results of TPD of ammonia are not directly correlated with the conversion of cumene, indicating that the Lewis acid sites from γ -alumina are contributing more to the total acidity measured by TPD of ammonia. The hydrocracking activity of the prepared catalysts was also measured using vacuum gas oil as feed in a batch autoclave reactor. All of the prepared catalysts showed good activity in comparison with a commercial hydrocracking catalyst. However, a clear difference in conversion performance could not be obtained under the conditions the catalysts were tested in the batch reactor.

Key Words: Hydrocracking; Zeolite; TPR; Catalyst Preparation; Characterization

Introduction

Hydrocracking catalysts are bi-functional catalysts. They have hydrogenation-dehydrogenation function as well as acidic function. Proper balancing of these two functions is the deciding factor for the catalyst performance (Marilly and Frank, 1980). The cracking activity is controlled mainly by the support which is acidic in nature, whereas the hydrogenation - dehydrogenation activity is due to the metals loaded on the support. Commonly used supports are (a) amorphous oxides (Sullivan and Scott, 1983) (e.g silica-alumina) (b) crystalline zeolite mixed with a binder, (c) a mixture of crystalline zeolite and amorphous oxides. Hydrocracking catalysts containing fluorinated inorganic oxides as supports have also been reported (Adachi *et al.*, 1990). The metals providing the hydrogenation-dehydrogenation function can be noble metals (Palladium, Platinum) or non-noble metals sulfides from group VIA (molybdenum, tungsten) and group VIIIA (cobalt, nickel). These metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and hetero-atom removal, as well as reducing the coke formation rate. It is however important that there should be a rapid molecular transfer between the acid site and hydrogenation site in order to avoid undesirable secondary reactions. This can be achieved by having the hydrogenation sites located in close proximity to the acid sites.

In catalyst characterization chemical analysis provides the basic information about the chemical composition while surface area and porosity evaluations, X-Ray Diffraction (XRD) sheds light on the catalyst texture. Measurements of gas adsorption isotherms are widely used for determining the surface area and pore size

distribution of various solids (Serwicka and Catalysis Today, 2000).

Temperature Programmed Reduction (TPR) with hydrogen is widely used technique for characterization of hydroprocessing catalysts (Reiche *et al.*, 2000). In TPR experiment, the total amount of hydrogen consumed is determined. This allows the calculation of the degree of reduction and the average oxidation state of the solid after reduction.

Temperature Programmed Desorption method (TPD) is used to determine the acidic properties of solid catalysts. This provides useful information about the concentration and strength of acidic sites. In contrast to other techniques used for acidity measurement like calorimetry (Abello *et al.*, 1997) and FTIR spectroscopy (Barzetti *et al.*, 1996), TPD using ammonia as a probe molecule, appears to be a simpler method. Even though it is non-specific, this technique is still being widely used to measure the total acidity and get a qualitative picture of acid sites and strength (Aren *et al.*, 1998; Narayanan *et al.*, 1998).

In this work a series of NiMo and NiW catalyst were prepared. The metals were loaded on mixed support of γ -alumina with steamed Y-zeolite in different proportions to give the final catalyst. The objective was to study the effect of active metal type and the acid function on the catalytic activity of the hydrocracking catalysts. The prepared catalysts were characterized by different characterization methods. Their activities were tested using cumene hydrocracking in pulse micro reactor. NiW catalysts performed better as compared to NiMo catalysts. The hydrocracking activities of the prepared catalysts were also measured using vacuum gas oil as feed in a batch autoclave reactor. All of the prepared catalysts showed good activity in comparison with a commercial reference hydrocracking catalyst.

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However, a clear difference in conversion performance could not be obtained under the conditions where the catalysts were tested in the batch reactor.

Experimental

Catalyst Preparation: Zeolite-based hydrocracking catalysts were prepared using commercial Y-zeolite CT-417 supplied by CATAL, UK and alumina CP-100 from Aluminum Company of America, USA. Ammonium metatungstate was obtained from Aldrich. Y-zeolite was received in hydrogen form (HY-zeolite). This zeolite was modified by steam treatment at 810 °C for 30 min. The effect of steaming was measured by the variation of the unit cell size determined by XRD analysis. The steam-modified zeolite was also characterized by SEM, TPD, surface area and pore volume measurements.

Two different supports were prepared by mixing the steam modified Y-zeolite with commercial γ -alumina CP-100 in ratios of 50:50 and 30:70 respectively. On these mixtures of zeolite and alumina, first molybdenum and then nickel were impregnated sequentially to give NiMo catalysts HC-1 and HC-2. Calculated amounts of ammonium heptamolybdate and nickel nitrate hexahydrate were used; so that the final catalyst will have 4.25 wt. % NiO and 15.0 wt. % MoO₃. Calcination after each impregnation was carried out at 500 °C for 2 h in a Fisher Scientific programmable Isotemp Muffle Furnace 650 Series.

Two NiW catalysts HC-3 and HC-4 were also prepared by the same procedure as mentioned above using these mixed supports. Calculated amounts of ammonium metatungstate and nickel nitrate hexahydrate were used; so that the final catalyst will have 4.25 wt. % NiO and 24 wt. % WO₃.

Catalyst Characterization: The chemical composition of the catalysts was determined by Perkin Elmer Analyst 100 atomic absorption spectrometer.

The BET surface area, pore volume and pore size distribution were obtained from nitrogen adsorption-desorption isotherms measured at 77 K by a Quantachrome, NOVA 1200 porosimeter, using the BJH method. All samples were pretreated under nitrogen flow at 350 °C for 1h prior to nitrogen adsorption.

The unit cell size of Y-zeolite samples in as-received H-form and hydrothermally treated (steaming) at two temperatures were measured following the ASTM 3942-85 method. X-ray diffraction patterns were determined across the range of 52 to 58° 2 θ . A correction factor was estimated by subtracting the measured 2 θ angle from the calculated angle for CuK α 1. The following conditions were used during the XRD measurements: Step angle 0.010 °, Count time 10.0 sec, Voltage 40.0 kV and Current 30.0 mA.

Scanning Electron Microscopy (SEM) was used to examine the topology of catalyst surfaces and the morphology of particles and crystals. The Y-zeolite samples were mounted on the specimen holder by sprinkling the powder on freshly applied carbon paint. The samples were coated with a thin layer of carbon using a carbon evaporator. The samples were analyzed on a JEOL JSM-5800LV digital scanning electron microscope, fitted with an energy dispersive spectrometer capable of detecting elements in the range of carbon to uranium.

Temperature-Programmed Reduction (TPR) experiments were carried out in a system supplied by Ohkura Riken Co. Ltd., (Model TP-2000). The procedures for pretreatment and subsequent TPR

experiments are as follows. About 150 mg of catalyst sample was placed in quartz tube reactor and was pretreated in flowing dry air (30 cm³/min) at 400 °C for 2 h. The gas mixture used for reduction was 5% H₂ in Ar. The temperature of the reactor was increased linearly from room temperature to 1030 °C at a heating rate of 10 °C/min and then retained isothermally for 15 min. The hydrogen concentration was determined with a Thermal Conductivity Detector (TCD).

The acid properties of hydrocracking catalysts were determined by Temperature-Programmed Desorption (TPD) of ammonia, using TPD instrument ATD 700, supplied by Ohkura Riken Co. Ltd. About 0.5 g of catalyst sample was placed in a quartz tube reactor and was pretreated to 400 °C for 2h. Ammonia (purity 99.99%) was adsorbed at 100 °C (to avoid excessive physical adsorption), for 30 min at 100 torr. Thermal desorption of ammonia was then conducted at 100 torr using He as a carrier gas and raising temperature upto 800 °C at a rate of 10 °C/min. TCD and Quadrupole detector (Massmate 200) was used to monitor the amount of desorbed ammonia.

Catalyst Performance Evaluation: The hydrocracking of cumene was conducted in a pulse-type micro reactor. 1.0 μ l of reactant cumene was injected into the pulse reactor. The reactant vaporizes in the inlet line heaters and then comes into contact with the catalyst inside the micro-reactor. At the same time, the GC was started to record the composition of the reactor outlet. From the corresponding peak areas, the amount of product(s) and remaining reactant was determined and the conversion was calculated.

For batch autoclave reaction studies the prepared catalysts were formed into pellets and then crushed to the size range of 200-600 μ m. All catalyst samples were presulfided ex-situ before the activity tests. For presulfiding, about 1.25 g of catalyst was taken in a small tubular reactor. The reactor was purged with nitrogen at a rate of 60 cm³/min and at atmospheric pressure for 30 minutes. A mixture of 5% hydrogen sulfide and 95% hydrogen was used for sulfiding the catalysts. The temperature of the reactor furnace was increased to 200 °C in about 1 h and maintained at 200 °C for 1 h. The temperature was further increased to 400 °C in about one hour and maintained at 400 °C for 2 h to complete the presulfiding. The reactor was then cooled to room temperature under flowing nitrogen. The catalyst was removed and stored in an airtight bottle. The feedstock used for the batch autoclave reactor experiments was Vacuum Gas Oil (VGO). Since the VGO is solid at room temperature, it is heated to about 80 °C to make it a homogenous liquid. 100g of the VGO was taken into the batch autoclave reactor of a capacity of 300 ml. The reactor vessel containing the feedstock and 1 g of presulfided catalyst was then placed in the furnace along with the appropriate attachments. Nitrogen gas was purged for 30 minutes. The reactor was then pressurized by hydrogen to about one-half of the operating pressure. The temperature of the reactor was closely monitored and adjusted manually as and when necessary. When the inside temperature of the reactor reached the target value, the hydrogen pressure was adjusted to the desired value. From this time onwards, the reaction time was counted.

ASTM method D 2887 was used to determine the boiling range distribution of hydrocracking reaction products by simulated distillation analyzer. The system

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consisted of Hewlett Packard 5880A gas chromatograph equipped with automatic sampler model HP 7673A, a Flame Ionization Detector (FID) and a packed column coated with methyl silicone liquid phase (UCW-982). The gas chromatograph was calibrated by analyzing a mixture of normal paraffins from nC₅ to nC₄₀. Sulfur content in the product was measured by elemental analyzer (Elementar, Vario EL, Germany).

Results and Discussion

The results obtained for the chemical composition of the catalysts by atomic absorption were in agreement with the amount of metals loaded. This confirmed the validity of our synthetic procedure.

X-ray diffraction results of the zeolite samples gave the values of the unit cell size, which are presented in Table 1. A systematic decrease in unit cell size is observed with steaming at a higher temperature. This is due to the progressive de-alumination of Y-zeolite, causing a partial collapse of the zeolite structure, which finally reduces the unit cell size. The unit cell size is found to decrease with decreasing surface area. On the basis of results found Y-zeolite modified at 810 °C was selected for preparation of hydrocracking catalysts.

Table 1: Unit Cell Size for the Y-zeolite Samples

Sample	$d_{(211)}$	Unit Cell Size (a, Å)
Y-zeolite (CT-417) as received	1.673	24.313
Y-zeolite steamed at 710 °C	1.670	24.272
Y-zeolite steamed at 810 °C	1.667	24.230

All the zeolite-based hydrocracking catalysts prepared in the laboratory were characterized for BET surface area and pore volume measurements. The results are given in Table 2. The results showed that the catalysts with 50% zeolite have relatively higher surface area as compared with the catalysts with 30% zeolite used for supporting active metals. The highest surface and pore volume was found for HC-1. On the other

Table 2: Physical Properties of Zeolite-based Catalysts

Catalyst Code	Support Composition		Active Metals	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
	Zeolite	Alumina			
HC-1	50	50	NiMo	267	0.297
HC-2	30	70	NiMo	243	0.224
HC-3	50	50	NiW	232	0.197
HC-4	30	70	NiW	184	0.191

hand lowest surface area and pore volume was observed for HC-4. The reason for low surface area and pore volume for this catalyst could be attributed to the pore blocking by tungsten as the amount was relatively higher for 30% zeolite. It was also observed that catalysts containing molybdenum (HC-1 and HC-2) have higher surface area as compared with those having tungsten as base metal (HC-3, and HC-4). This could be explained on the basis of ionic radii of these metals.

Morphology plays an important role in activity and selectivity of the catalysts. This can be observed by SEM analysis of the catalysts. Fig. 1 and 2 show the SEM micrographs for Y-zeolite (CT-417) before and

after steam modification respectively. Careful examination of the two micrographs at a magnification of 10,000x reveals that steaming caused a little or no effect on the crystal morphology. This indicates high hydrothermal stability of Y-zeolite used in this study. However, surface area measurement showed a decrease in the value from 515 m²/g to 434 m²/g before and after steaming, respectively. This decrease could be attributed to the loss in crystallinity and pore blocking caused by non-frame work aluminum.

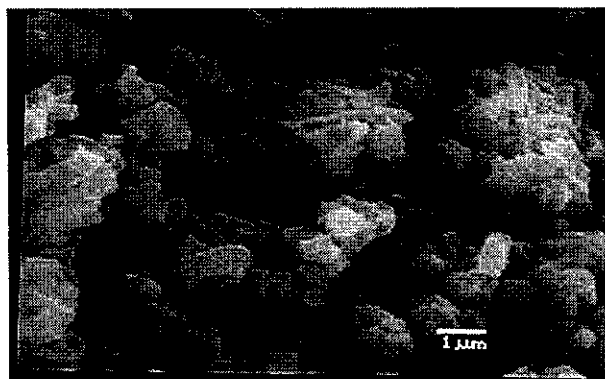


Fig. 1: SEM of Y-zeolite CT-417 (as received) at a Magnification of 10,000x

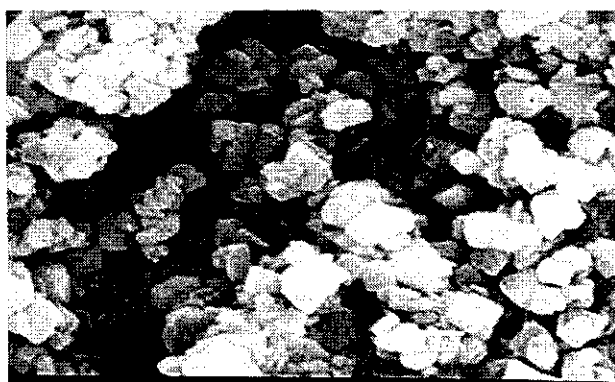


Fig. 2: SEM of Y-zeolite CT-417 (steamed: 810 °C) at a Magnification of 10,000x

Prepared hydrocracking catalysts were characterized by TPR method. Figure 3 shows the results of TPR experiments. All the catalysts showed a double peak reduction pattern except for HC-1. The single peak (413 °C) reduction profile for HC-1 indicates better dispersion of the impregnated metals and all the metal ions are located in one type of position on the support. On the other hand HC-2 which has similar metal composition, gave two peaks (321 and 380 °C) indicating inhomogeneous metal dispersion. Catalysts HC-3 and HC-4 gave two reduction peaks one at 570 °C and the other around 755 °C. This indicates the difficulty in reducing W containing catalysts. It was also observed that the composition of the support did not affect the reduction behavior of these catalysts. On the other hand catalysts HC-1 and HC-2 having different support composition showed marked difference in the reduction patterns.

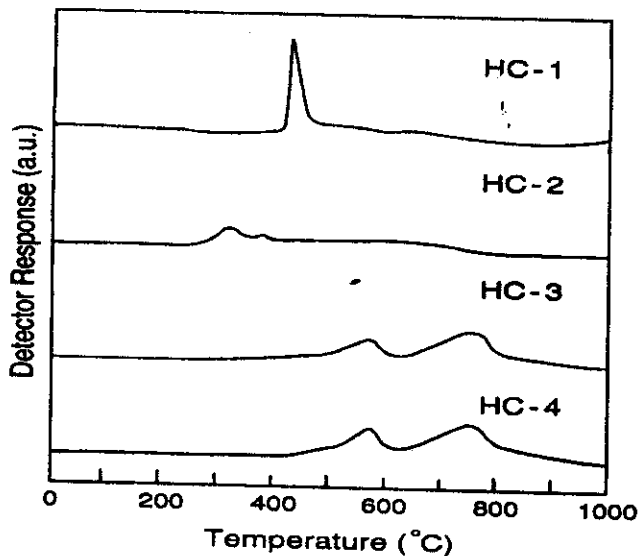


Fig. 3: TPR Profiles of Zeolite-based Catalysts

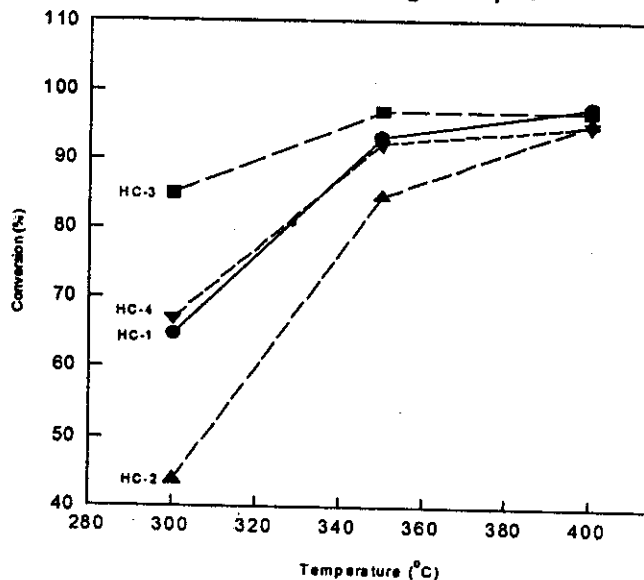


Fig. 5: Cumene Cracking Activity of Prepared Catalysts as a Function of Temperature

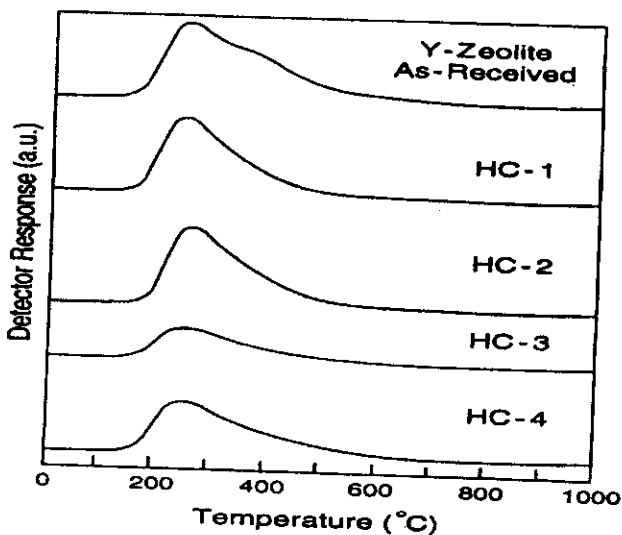


Fig. 4: TPD Profiles of Zeolite-based Catalysts

Catalyst Code	Acidity (mmol/g)	Peak Temperature (°C)
CT-417*	0.535	245
HC-1	0.297	247
HC-2	0.322	257
HC-3	0.145	245
HC-4	0.248	248

* As received HY-zeolite (CT-417, from CATAL, UK)

Temperature-Programmed Desorption (TPD) of NH_3 experiments determined both the number of acid sites (Brønsted and Lewis) and acid strength distribution. Table 3 and Fig. 4 show the results of TPD of ammonia for prepared catalysts.

The acidity of CT-417 was measured as reference point for other catalysts prepared in the laboratory. The highest acidity was observed for HC-2. On the hand minimum acidity was found for HC-3. However for other two catalysts the acidity was comparable. The higher acidity for HC-2 could be attributed to the high amount of alumina in this catalyst. Alumina is known for high Lewis acidity which can not be measured selectively by TPD of ammonia. It was observed that the peak temperatures are similar for all the samples. This indicates that the strength of the acid sites is comparable with one other. CT-417 gave a shoulder around 350 °C indicating some sites of higher acid strength, which is a characteristic of Y-zeolite.

Results of pulse micro reactor study are shown in Fig. 5. Cumene cracking was performed at three different temperatures (300, 350, and 400 °C). As evident from the Figure, thermal cracking dominates the catalyst activity with increase in temperature. For this reason data obtained for cracking activity at 350 °C and 400 °C, does not reflect the true catalytic activity of individual catalysts. Hence a comparison amongst the catalyst at these temperatures becomes very difficult. However results obtained for cumene cracking activity at 300 °C for different catalysts does show some trend. Irrespective of the composition of the mixed support NiW catalysts (HC-3 and HC-4) showed better performance for cracking as compared to NiMo catalysts (HC-1 and HC-2). Higher cracking activity was obtained for catalysts containing higher zeolite content (loaded with similar metals), as expected. A comparison of the results obtained for HC-1 and HC-4 at 300 °C shows that NiW catalyst HC-4 has slightly higher activity than NiMo catalyst HC-1, even though it has less zeolite content. This shows very clearly that the type of metal loaded has an important role to play in determining the cracking activity of the catalyst.

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Table 4: Batch Autoclave Experimental Results

	Catalyst				
	HC-1	HC-2	HC-3	HC-4	Commercial
VGO Conversion (%)	52.5	53.5	49.0	54.5	56.0
Gasoline Fraction (%)	20.4	20.6	18.8	22.4	24.0
Middle distillate (%)	32.1	32.9	30.2	32.1	32.0
Product S (wt. %)	1.21	1.26	1.55	1.56	0.76
HC in Product gas (vol %)	14.5	12.7	20.7	16.3	13.8
C on spent catalyst (wt%)	2.6	2.6	2.4	2.5	10.0

Results obtained for VGO cracking in the batch autoclave reactor are shown in Table 4.

Reaction was carried out at 420 °C, with a pressure of 120 bar for 5 h. The catalytic cracking activity is dominated by thermal effect at 420 °C. For this reason it is difficult to make any comparison among the catalyst activity at this temperature. However, the conversion in all these catalysts was comparable to that of reference commercial hydrocracking catalyst. The prepared catalysts showed lower HDS activity as compared to the reference catalyst. However, it is observed that NiMo catalysts (HC-1 and HC-2) showed relatively better HDS activity as compared to NiW catalysts (HC-3 and H-4). It is also evident from the table that C deposition on the spent catalysts is four times less than that of reference commercial spent catalyst. This indicates that the hydrogenation function of the prepared catalysts prevented carbon deposition to a better extent than the commercial catalyst.

Conclusion

A series of NiMo and NiW based catalyst were prepared; which were characterized by various techniques. The surface acid properties of the catalysts have been evaluated by Temperature Programmed Desorption (TPD) measurements using NH₃ as a probe molecule. TPR results show the comparative ease of reduction of NiMo catalysts. NiW based catalysts reduced at higher temperatures. Cumene cracking activity results show the better performance of NiW catalysts as compared to NiMo catalysts. Batch autoclave

results show that NiMo catalysts performed better HDS activity as compared to NiW catalysts.

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