

CATALYTIC CRACKING OF HEAVY NAPHTHA USING NEW SULPHONATED MICA CATALYST

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ABSTRACT

Sulphonated mica was prepared as catalytic cracking catalyst for heavy naphtha by sulphonation of oxidized mica using sulfuric acid. The oxidized mica was prepared by the treatment of mica with nitric acid to obtain its oxidized form. The raw mica and the prepared catalyst were analyzed by X-ray diffraction and FT-IR spectral analysis. The evaluation of the mica in catalytic cracking reaction of heavy naphtha showed weak activity. Modified mica exhibited high catalytic cracking activity.

Keywords: Heavy Naphtha, Homogenous Catalyst, Oxidation, Catalytic cracking, and Light olefins.

INTRODUCTION

During petroleum fractionation, crude oil is distilled either by thermal distillation for light components, or vacuum distillation for heavy molecular weight components (heavy cuts). Vacuum distillation is performed for the residuals of the thermal distillation. The main component of the vacuum distillation is the heavy naphtha. Naphtha and reformate are complex mixtures of paraffins, naphthenes, and aromatic in the C5–C12 carbon number. Paraffins or alkanes are saturated aliphatic hydrocarbons of either straight-chain (n-paraffins) or branched structures (iso-paraffins). Olefins or

alkenes are unsaturated aliphatic hydrocarbons, and are either straight chains or branched structures, but contain one or more double bonds. Also, in the naphtha range, naphthenes or cycloalkanes are saturated cyclic hydrocarbons that contain at least one ring structure. The most abundant naphthenes found in fossil fuel have ring structures of either five or six carbon atoms. The composition of any naphtha depends on the type of crude oil, boiling range, and whether it is obtained directly from crude oil distillation or produced by catalytic or thermal cracking of heavier oil fractions. Typical straight-run medium naphtha contains 40–70 wt% paraffins, 20–50 wt% naphthenes, 5–20 wt% aromatics, and only 0–2 wt% olefins. Naphtha produced by fluid catalytic cracking, coking, or vis breaking may contain 30–50 wt% olefins (Aitani *et al.*, 2000)

Light olefins such as ethylene and propylene are important building blocks for many end products like polyethylene and polypropylene. Recently, market analysis showed that the demand for propylene is outpacing that of ethylene and the current supply cannot match the demand. A large proportion of propylene, about 65 wt%, is produced by steam cracking and about 30 wt% during the fluid catalytic cracking (FCC) process as a by-product (ShamsiJazeyi., 2010 and Triantafillidis *et al.*,1999). The propylene to ethylene ratio produced by steam cracking of naphtha is about 0.6, whereas the ethylene and propylene yields are about 2 and six wt% from the conventional FCC process. During catalytic cracking, the heavier and more complex hydrocarbon molecules are broken down into simpler and lighter

molecules by the action of heat and catalyst. It is through this way that heavy oils can be upgraded into lighter and more valuable

products (light olefins, gasoline, and middle distillate components). The FCC is one of the most catalytic cracking technologies used widely in a refinery for producing gasoline and diesel. However, the current direction is to maximize olefins such as propylene and butylene by the addition of zeolite (ZSM-5) to the catalyst formulation (Zhu *et al.*, 2013)

Muscovite mica is the substrate of choice for an ever-increasing variety of experiments involving surfaces. Historically, studies of epitaxial crystal growth on mica go back at least to the first half of the nineteenth century (Christenson *et al.*, 2016) and contact angle measurements of liquids on mica were also reported data in very early stage (NEESEN *et al.*, 1884). Naphtha is transformed into reformates through catalytic reforming process which requires the reconstruction of low-octane hydrocarbons in the petroleum naphtha into more valuable high octane gasoline components. In this study, sulphonated mica, a heterogeneous catalyst, was prepared and characterized using infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The prepared catalyst was evaluated in catalytic cracking of heavy naphtha obtained from vacuum distillation of crude oil residues. Parameters influencing the catalytic conversion reaction of the heavy naphtha are investigated. The catalyst activity was correlated to its chemical structure.

EXPERIMENTAL

- 1. Materials:** Mica from Sigma, nitric acid (HNO₃), sulfuric acid (H₂SO₄) and heavy naphtha from Sigma were purchased from Sigma-Aldrich, UK and were used as-received without further purification.
- 2. Preparation of Sulfonated Catalyst:** Two steps were performed to synthesize Mica-SO₃H catalyst: the first step is oxidation of mica by nitric acid. In a typical reaction, 1g of mica was treated with 10 mL of concentrated HNO₃ (13.9 M) at 353 oK until dryness, and the residue was washed with distilled water until all the nitrates were removed (Pradhan *et al.*; 1999) The commercial mica oxidized by nitric acid is referred as Nitric Mica (NM). The second step is acid functionalization of oxidative mica by sulfuric acid (Mica-SO₃H). In a typical reaction, 5 g of oxidized mica was mixed with 100 ml of concentrated H₂SO₄ and heated at 155 oC in a nitrogen atmosphere reflux and stirring for 12 h. The sulfonated mica was filtered and washed several times using deionized water and dried at 100 oC for 24 h to obtain sulfonated mica (NM-SO₃H).
- 3. Characterizations of the prepared Catalyst:** The texture properties of mica and its sub-derived composite material were examined using both HR-transmission electron microscope (HR-TEM) and BET surface area analyzer. Before subjecting to the microscope, all samples were subjected to sonication into ethanol for 10 min to get homogenously dispersed particles. On the other hand, the mica and the functionalized material were subjected to BET analyzer to determine their

Surface area and total pore-volume. Thermal stability of the produced materials was also measured using thermal gravimetric analyzer (TGA-DSC) equipment. The structure and crystallinity nature of the obtained materials during this research work was also confirmed via X-Ray diffraction (XRD) analysis. The functional groups of the mica-based structures were determined using Fourier Transform Infra-red (FT-IR). The surface morphology of the mica and mica/SO₃H were investigated by the scanning electron microscope (SEM).

4.1 X-Ray Diffraction (XRD): X-ray powder diffraction (XRD) patterns had been recorded on a Bruker AXS-D8 Advance (Germany) by using nickel-filtered copper radiation ($\lambda = 1.5405 \text{ \AA}$) at 30 Kev and 40 mA with a scanning speed of 4° min⁻¹ over diffraction angle range.

4.2 Fourier Transform Infra-Red (FT-IR): FT-IR spectra of the freshly-made material recorded on ATI Mattson Genesis series (KBr disc method) apparatus, Model 960 M009 series.

4.3 Catalytic Activity: A high pressure micro fixed bed reactor unit – down flow (cata-test unit) that consists of a stainless steel reactor (internal diameter 19 mm, external diameter 27 mm, and length 50 cm) has been used. It is divided into three zones, each is heated and separately temperature controlled. 50 cc of the catalyst is charged in the middle zone of the reactor. The conversion reactions of the feed stock were carried out at reaction temperature ranges of 300-400 oC .

4.4 Gas chromatography: Representative liquid are samples collected and analyzed by Gas chromatography (GC) model (Agilent 7890) equipped

with (FID) and (TCD) detectors using PIONA and DC-200 columns for liquid and gas samples, respectively.

RESULTS AND DISCUSSION

1) Characterization:

1.1 X-ray Diffraction: The powder X-ray diffraction patterns of raw mica and sulphonated mica catalyst are shown in figure 1. It was noted that the characteristic diffraction peaks showed at $2\theta=8.8^\circ$, 17.7° , 26.7° , 35.9° , 41.5° , 45.4° , 55.1° , 64.4° and they were well indexed to the mica (ICDD Card No. 16-0344) crystallographic planes of monoclinic muscovite-2M1 (JCPDS No. 46-1409), respectively (Ramirez et al.; 2003). The characteristic mica XRD patterns are retained in the XRD patterns of the sulphonated mica framework, which showed the stability of the formed framework compared to mica clay itself.

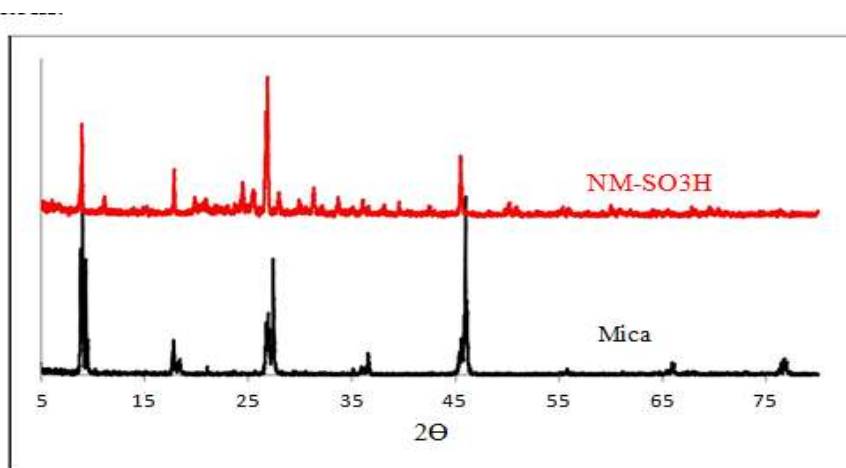


Figure (1): XRD spectra of raw Mica and NM-SO₃H

1.2 Fourier Transform Infra-Red (FT-IR): FT-IR analysis was used to investigate variations in the functional groups of the mica and the functionalized mica structures. FTIR technique is a useful analytical method which can provide sharp tracking for the changes in the structure through the increase and decreases in the intensity of the detected peaks. The FT-IR spectroscopic study of both the raw mica, oxidative mica, and sulphonated mica are presented in Fig 2. The characteristic absorption bands at 3426 and 1629 cm^{-1} represent asymmetrical stretching and bending vibrations of OH group, respectively. The characteristic peak at 1710 cm^{-1} is assigned to the C=O group and the absorption bands at 2984 and 2898 cm^{-1} are assigned for asymmetrical and symmetric stretching vibrations of C-H groups. Si-O-Al bending along with Mg-OH is located at 687 cm^{-1} . The peak at 972 cm^{-1} represents the bending vibration modes due to the Al-AlOH, while the rocking band at 459 cm^{-1} is due to the presence of quartz silica (ShamsiJazeyi *et al.*, 2010). Fig 2 showed a significant difference in FTIR spectra in the range of 1300–1700 cm^{-1} related to the surface functional groups of NM and raw mica. The absorption band at 1620 cm^{-1} represented in the spectrum for raw mica, while it has been weakened in NM. This band represents quinone functional groups (Tukur *et al.*, 2005). Briefly, due to nitric acid treatment, the quinone functional groups were reduced from the raw mica. It was attractive to investigate the possibility of formation of some nitrogen functionalities on the carbon surface during acid treatment with nitric acid.

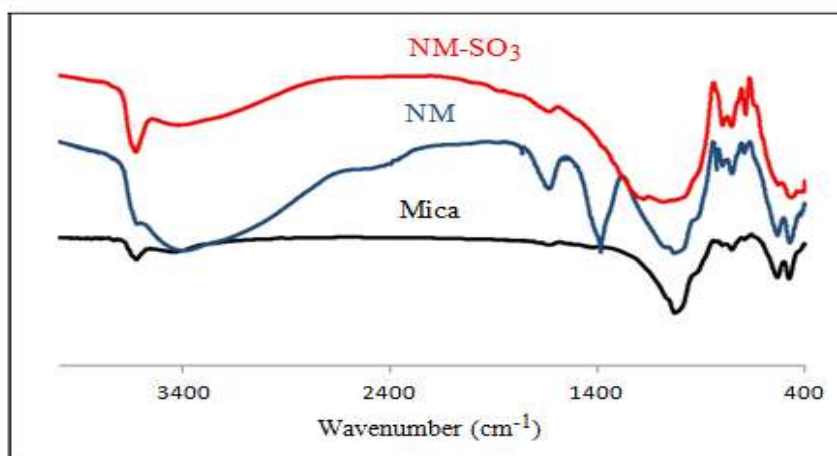


Figure (2): FTIR spectra of raw Mica, NM and NM-SO₃H

1.3 Catalytic Cracking of Heavy Naphtha: The heavy naphtha cracking reaction is used to evaluate the acidity of the prepared samples. The catalytic activity of solid acid catalysts is not only related to the surface concentration of acid sites but also their nature, that is being Lewis or Brønsted sites (Tyagi *et al.*, 2006). The heavy naphtha cracking is a model reaction for identifying the Lewis and Brønsted acid sites present in a catalyst.

2.1 Dodecane cracking: The results of dodecane cracking over mica and NM-SO₃H as a function of temperature are presented in Table 1 and Fig. 3. These results indicate that significant cracking of dodecane occurred over mica and catalyst. As shown in Table 1, the mica shows a very low catalytic activity at all temperatures for dodecane cracking due to a weak of acidity. NM-SO₃H shows high

catalytic activity for dodecane cracking (55.54, 73.18, 80.11, 89.31, and 88.20) at (300, 325, 350, 375 and 400) respectively. This can be attributed to the low critical diameter of dodecane (0.49 nm) which poses no diffusion limitations even in NM-SO₃H. It has been reported that strong acid sites are needed for n-dodecane cracking (Abul-Hamayel *et al.*, 2005).

Table (1): Cracking conversion % of Dodecane over Mica and NM-SO₃H at different temperatures

Temperature, oC	300	325	350		375	400
Materials	Conversion %					
Mica	15.22	18.32	22.10		23.26	23.84
NM-SO ₃ H	55.54	73.18	80.11		89.31	88.20

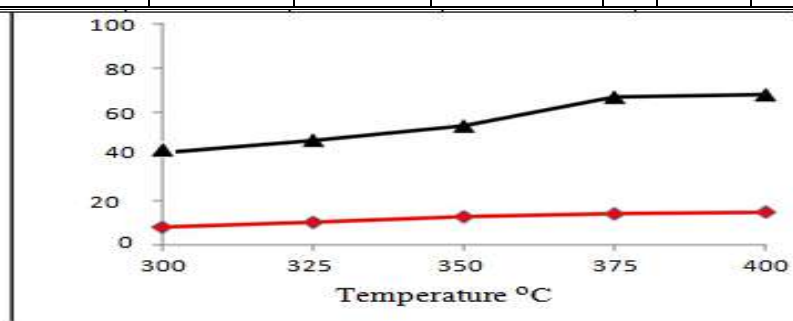


Figure (3): Variation of conversion % of Dodecane over Mica and NM-SO₃H Catalyst.

2.2.Iso-Octane Cracking: The results of iso-octane cracking over both mica and NM-SO₃H as a function of temperature are presented in Fig 4 and Table 2. These results indicate that there was almost very weak cracking of iso-octane at all temperature over mica. This can be attributed to the higher critical diameter of iso-octane which poses severe diffusion limitations (Degnan *et al.*, 2000). The highest conversion of iso-octane was observed

over NM-SO₃H catalyst at all temperatures due to a high acid sites on the catalyst.

Table (2): Cracking conversion % of Iso-Octane over Mica and NM- SO₃H at different temperatures

Temperature, oC	300	325	350	375	400
Materials	Conversion %				
Mica	12.11	14.32	16.43	17.65	17.11
NM-SO ₃ H	60.38	65.12	68.11	74.00	75.23

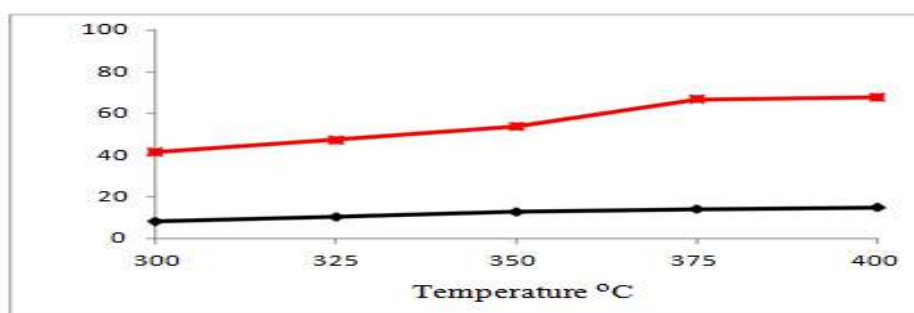


Figure (4): Variation of conversion % of Iso-Octane over Mica and NM-SO₃H Catalyst.

2.3 Ethyl Benzene Cracking: The results of ethyl benzene cracking over mica and NM-SO₃H as a function of temperature are presented in Fig 5 and Table 3. These results indicate that there was almost surely weak cracking of ethyl benzene at all temperatures over mica. This can be attributed to the higher critical diameter of ethyl benzene (0.56 nm) than mica which poses severe diffusion limitations in order to weakly of the acid site on mica (Zhao *et al.*, 1999). The highest conversion of ethyl benzene was observed over NM-SO₃H catalyst possibly due to diffusion limitation in its catalyst component and high acidity.

Table (3): Cracking conversion % of Ethyl Benzene over Mica and NM-SO₃H at different temperatures

Temperature, oC	300	325	350	375	400
Materials	Conversion %				
Mica	8.14	10.35	12.73	14.05	14.91
NM-SO ₃ H	41.57	47.31	53.87	66.85	67.81

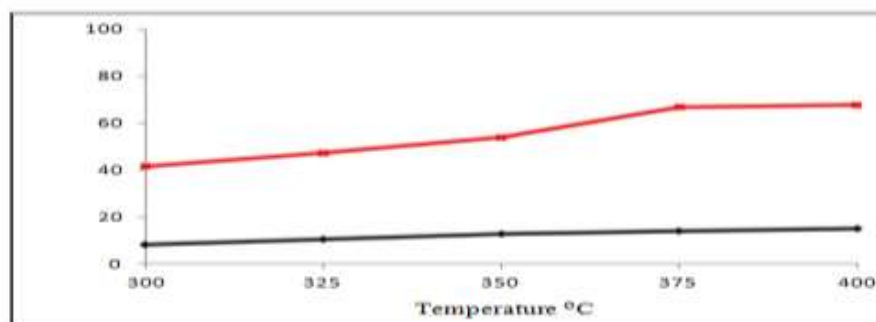


Figure (5): Variation of conversion % of Ethyl Benzene over Mica and NM-SO₃H Catalyst.

CONCLUSION

The present work reports on a heterogeneous catalyst involving both the proper control of the surface chemistry and rigorous control of high acidic functional groups. The oxidation mica is successfully prepared with nitric acid to increasing of a hydroxyl group. The sulfonyl group was grafted on mica with sulfuric acid to acidification of oxidized mica For the Residue of Crude Oil and its treatment. The activity of NM-SO₃H catalyst was higher than pure mica for heavy naphtha cracking at all temperatures. The high-performance catalytic activity of the prepared catalyst is related to high acidity.

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التكسير الحفزي للنافثا الثقيلة باستخدام عامل حفاز جديد من الميكا المعدلة

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المستخلص

في هذا البحث تم تحضير عامل حفاز من الميكا عن طريق تفاعلها في صورتها المتأكسدة مع حمض الكبريتيك المركز، تم تحديد التركيب الكيميائي له باستخدام الأشعة تحت الحمراء والتركيب البلوري، ثم تم استخدام العامل الحفاز المحضر في التكسير الحفزي لمتكاثفات النافثا الثقيلة، وتم مقارنة ناتج التكسير باستخدام الميكا غير المعدلة والميكا المعدلة. أظهرت النتائج كفاءة العامل الحفاز المحضر في عملية تكسير المكونات ذات النسب الأكبر في متكاثفات البترول الثقيلة وهي الدوديكان، والإيثيل بنزين والأيزو أوكتان. الكلمات الدالة: النافثا الثقيلة، الميكا، الدوديكان، والإيثيل بنزين، والأيزو أوكتان