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Optimizing n-heptane isomerization: The role of copper in enhancing the catalytic activity and selectivity of Pt and Cu-Pt/montmorillonite K10 catalysts

M.A. Sayed [a] [1], Muhammad A. Abo El-Khair [a] [1], A.A. Ragab [b], Ahmed O. Abo El Naga [a], Walaa S. Gado [c], Asmaa S. Morshedy [a]

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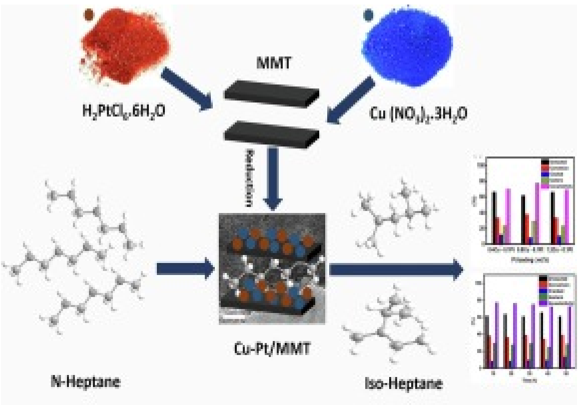
Highlights

- Copper enhances catalytic activity and selectivity in n-heptane isomerization.
- Synergistic effect between Cu and Pt on Montmorillonite K10 improved selectivity for desired isomerized products.
- Montmorillonite K10 support boosts catalyst stability and efficiency.
- Efficient sustainable fuel production through hydrocarbon conversion and isomerization.

Abstract

The development of efficient catalysts for n-heptane isomerization is essential for enhancing gasoline octane numbers. In this study, Pt and Cu-Pt/Montmorillonite K10 (MMT) catalysts were prepared and evaluated to investigate the effect of copper on catalytic performance and selectivity in the isomerization of n-heptane. Comprehensive characterization techniques, including XRD, BET, FTIR, TEM, and TPR, were used to investigate the structural, chemical, and electronic properties of the catalysts. Catalytic performance was tested in a fixed-bed reactor over a temperature range of 200°C–450°C, with a liquid hourly space velocity (LHSV) of $1\,h^{-1}$ and an H_2/n-heptane ratio of $20\,mL^{-1}$. The Pt/MMT catalyst exhibited an isomerization yield of 23.5% and a selectivity of 66.8% at 350°C. In contrast, the incorporation of Cu into the Pt catalyst (0.8Cu-0.1Pt/MMT) enhanced its electronic environment, resulting in a higher isomerization yield of 29.6% and selectivity of 77.5% at the same temperature. Additionally, the Cu-Pt/MMT catalyst demonstrated robust long-term stability, maintaining an isomer yield of approximately 28.1% and selectivity of 75.3% after 50h of continuous operation at 350°C. This study highlights the improved performance of the Cu-Pt/MMT catalyst and offers valuable insights for optimizing bimetallic catalysts in hydrocarbon isomerization applications.

Graphical abstract



Introduction

As environmental regulations become stricter to minimize the impact of gasoline on the environment, the need to reduce aromatics and olefins in fuels has become increasingly critical. While these compounds enhance fuel properties, they pose environmental and health risks [1], [2], [3]. Reducing aromatics can decrease the octane number of gasoline, which is essential to maintain efficient engine performance [4]. To counteract this challenge, researchers are exploring alternative strategies to compensate for the octane loss associated with reduced aromatic content.

One promising solution is the isomerization process, which enhances gasoline quality by converting straight-run naphtha fractions- primarily composed of linear aliphatic hydrocarbons- into branched isomers that significantly boost the octane rating of fuel [5], [6]. Fuels with higher octane resist knocking, enabling smoother, and more efficient engine performance. By producing high-octane gasoline without the need for environmentally harmful additives, isomerization helps refineries fulfill environmental standards and enhancing fuel quality, effectively compensating for reduced aromatic content [7], [8].

Isomerization uses bifunctional catalysts featuring both metal and acidic sites [8], [9], [10]. Metals like platinum, nickel, or palladium, convert alkanes into form alkenes via dehydrogenation, while the acidic sites promote the protonation and rearrangement of these alkenes into branched isomers [9], [10], [11], [12]. These acid sites are typically provided by solid acids, such as amorphous silica-alumina [13], metal oxides [14], silicon aluminum molecular sieves [15], and silicoaluminophosphate (SAPO) molecular sieves [16]. Montmorillonite (MMT), a high surface area acidic clay, also serves as a robust support, facilitating metal dispersion, and provides necessary acidic sites for isomerization.

Platinum (Pt) is widely used in hydroisomerization catalysts due to its excellent dehydrogenation capabilities [3], [17], which efficiently convert linear alkanes, such as n-heptane, into more reactive intermediates that can be rearranged into higher-octane branched isomers. However, using Pt as a monometallic catalyst tend to promote cracking [18], reducing the yield and selectivity of the desired isomers. Recent studies suggest that introducing a second metal, such as copper (Cu), can improve their catalytic performance by modifying the electronic environment around Pt. This modification enhances Pt dispersion on the support, reduces the size of Pt ensembles, and lowers the rate of undesirable side reactions, such as cracking. Bimetallic Pt-Cu catalysts demonstrate improved stability, selectivity for isomerization, and reduced coking tendencies, due to the synergistic interaction between Pt and Cu, making them highly effective for n-heptane hydro-isomerization.

In a study by Sayed et al. [19], Pt nanoparticles with loadings of 0.1 wt%, 0.3 wt%, and 0.6 wt% were synthesized on montmorillonite (MMT) and tested for n-heptane isomerization. At 350 °C, 1 bar atmospheric pressure, LHSV of $1\,h^{-1}$, and a H_2/n-heptane ratio of 50 ml/ml, the 0.1 wt% Pt/MMT catalyst exhibited the highest isomerization activity. Higher Pt loadings of 0.3 and 0.6 wt% decreased isomerization performance and increased cracking. Building on these findings, this study explores the effects of incorporating different Cu loadings into the 0.1 wt Pt/MMT catalyst. By analyzing the impact of Cu on catalytic performance and selectivity, this research aims to optimize bimetallic catalysts for n-heptane hydro-isomerization, focusing on balancing catalyst activity, selectivity, and stability.

Section snippets

Materials

Cu $(NO_3)_2 \cdot 3H_2O$, formaldehyde, tetrahydrofuran, and K10-Montmorillonite (MMT; Si/Al=40), purchased from Sigma-Aldrich, K10-Montmorillonite was used as a support for platinum and copper nanoparticles. Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), ethanol (99.8%), and n-heptane (used as the model hydrocarbon feed) were also obtained from Sigma-Aldrich. …

Preparation of Cu-Pt/MMT catalyst

The Cu-Pt/MMT catalysts with varying Cu loadings were synthesized following the same procedure used for preparing the monometallic Pt catalyst [23]. …

X-ray diffraction (XRD)

The XRD patterns of MMT and all prepared samples are presented in Fig. 1. The diffraction patterns display distinct peaks at 2θ values of 8.87°, 17.8°, 19.9°, 20.82°, 26.6°, 35.03°, 45.53°, and 62.31°, which are characteristic of MMT. These peaks correspond to the (110), (020), (004), (130), (200), (330), and (060) diffraction planes (JCPDS card no. 03-0015), indicative of the layered structure typical of MMT. Notably, the XRD analysis reveals that the peaks of MMT remain sharply defined, and …

Conclusion

The study highlights the crucial role of copper in enhancing the catalytic performance and selectivity of Cu-Pt/MMT catalysts for the isomerization of n-heptane. Comprehensive characterization techniques, such as XRD, BET analysis, HR-TEM, TPR, and

FT-IR, provided detailed insights into the structural and electronic properties of the catalysts. Amongst the tested formulations, the 0.1% Pt-0.8% Cu/MMT emerged as the most effective, exhibiting superior catalytic activity and selectivity at …

CRediT authorship contribution statement

M.A. Sayed: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Muhammad A. Abo El-Khair:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **A.A. Ragab:** Visualization, Validation, Software, Resources, Methodology. **Ahmed O. Abo El Naga:** …

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. …

Dr/Asmaa Said Morshedy Mohammed is an Assistant Professor of Applied Physical Chemistry at the Egyptian Petroleum Research Institute (EPRI). She is the head of one Refinery department labs. She holds a PhD in Applied Physical Chemistry from Ain Shams University (2016) and a Master's in Organic Chemistry from Minufiya University (2008). Her research focuses on Photocatalysis, Environmental chemistry, and Sustainable materials. Dr. Asmaa has published extensively on Diesel fuel desulfurization, …

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Dr/Asmaa Said Morshedy Mohammed is an Assistant Professor of Applied Physical Chemistry at the Egyptian Petroleum Research Institute (EPRI). She is the head of one Refinery department labs. She holds a PhD in Applied Physical Chemistry from Ain Shams University (2016) and a Master's in Organic Chemistry from Minufiya University (2008). Her research focuses on Photocatalysis, Environmental chemistry, and Sustainable materials. Dr. Asmaa has published extensively on Diesel fuel desulfurization, Hydrogen production and storage, and Water purification. She has received prestigious awards, including the Prof. Osama Elkholy Prize in Environmental Studies (2020) from Academy of Scientific Research and Technology (ASRT), and is a member of the Royal Society of Chemistry. Renowned for her contributions to science, she continues to advance sustainable solutions in Energy and the Environment.

[1] These authors are equally contributed.

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