



7th International Conference on Energy and Environment Research, ICEER 2020, 14–18
September, ISEP, Porto, Portugal

Effect of acidic MCM-41 mesoporous silica functionalized with sulfonic acid groups catalyst in conversion of methanol to dimethyl ether

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Received 22 October 2020; accepted 22 October 2020

Abstract

The global issue of contamination and power reserves has given dimethyl ether (DME) considerable attention. It is an encouraging and clean green material for the future resulting from its clean combustion properties. In this paper, a novel MCM-41-propyl-SO₃H catalyst was successfully prepared with tethering of the active sulfonic acid groups onto the support via covalent bonds. This material was investigated as catalyst for DME synthesis via methanol dehydration in a fixed bed flow reactor at different experimental settings. TGA, NH₃-TPD, SEM, XRD and BET techniques were utilized to characterize the synthesized material. MCM-41 sulfonated catalyst showed great thermal stability, high surface area and significant acid loading. The catalytic tests also demonstrated that the maximum methanol conversion was observed at 350 °C and catalyst contact time of 8 s. In addition, the catalyst showed a total selectivity to DME; light hydrocarbons and higher oxygenated compounds were not formed at temperatures above 300° C.

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Keywords: Dimethyl ether; MCM-41; Methanol dehydration; Power-to-X; Sulfonic acid catalyst

1. Introduction

Power-to-X (PtX) technologies have generated great interest, since renewable resource is currently being converted to chemical products and fuels which can be stocked and transferred lot further quickly [1]. The PtX technology consists of two principal phases: the development of H₂ through water electrolysis using renewable resource and CO₂ hydrogenation to chemicals and fuels. Then, dimethyl ether (DME) synthesis is a very interesting strategy since it can be utilized as a heating and transport fuel and as an intermediate in olefin, petrol and aromatic production [2]. One-step DME process from syngas or methanol dehydration can be used to obtain DME. The direct

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<https://doi.org/10.1016/j.egy.2020.10.042>

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synthesis uses a dual function catalyst in a one stage for the formation and dehydration of methanol; particularly, methanol dehydration is essential to control the thermodynamic restriction of alcohol synthesis. Dimethyl ether is currently produced at industrial scale from methanol using dehydration catalysts such as γ - Al_2O_3 as a result of its great surface area, excellent thermal stability, high mechanical resistance and catalytic activity for DME formation because of its surface acidity; unfortunately it rapidly deactivates with water [3].

H-ZSM-5 is a very interesting alternative but the formation of hydrocarbon byproducts during the methanol dehydration reaction, leads to a decrease of the activity [4]. Materials grafted with sulfonic groups were described for methanol to DME process as catalysts with high catalytic performance, selectivity and stability [5]. In particular, the catalytic performances of sulfonated MCM-41 catalyst were close to those of γ - Al_2O_3 , commercial reference for this reaction. The goal of the present investigation is to develop a synthesis for high surface area MCM-41 with sulfonic acid groups catalyst with high activity toward DME production. The catalytic features of MCM-41-propyl- SO_3H were analyzed under various experimental settings. The catalyst's structure is also investigated using thermogravimetry (TGA), NH_3 -TPD (temperature programmed desorption) of ammonia, and N_2 adsorption–desorption isotherm techniques. The catalyst activity is associated with its surface characteristics and acid properties. The dehydration process is performed in a continuous fixed bed flow reactor. The optimum operating condition for DME synthesis is determined.

2. Material and methods

2.1. Catalyst preparation

Sulfonic acid-incorporated-MCM-41 mesoporous catalyst was prepared as reported by Piscopo et al. [6], utilizing the silane bis (3-triethoxysilylpropyl)-tetrasulfide (TESPT), which contains polysulfide linkages. In Fig. 1 there is the scheme of the catalyst preparation [7].

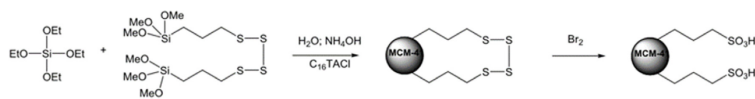


Fig. 1. Incorporation of $-\text{SO}_3\text{H}$ into MCM-41 mesoporous material using TESPT.

2.2. Characterization techniques

The procedures for thermogravimetry, scanning electron microscopy and Brunauer–Emmett–Teller techniques were reported elsewhere [8]. For the investigation of catalyst's acidic properties, we utilized the temperature programmed desorption of ammonia (NH_3 -TPD) technique. A ThermoScientific TPD/R/O 1100 analyzer equipped with a thermal conductivities detector (TCD) was used for this analysis. The material was deposited in a quartz tube for nitrogen treatment. Then, it was warmed at $100\text{ }^\circ\text{C}$ under a NH_3 flow (30 ml/min, 2% in helium) for 1 h and lastly it was cooled to room temperature and then purged with helium. During the analysis the catalyst was warmed from room temperature to $700\text{ }^\circ\text{C}$ (heating rate $5\text{ }^\circ\text{C}/\text{min}$) under a 30 ml/min helium flow, the desorbed NH_3 is detected by means of the TCD detector.

2.3. Catalytic performance evaluation

A schematic representation of the experimental setup is reported in the following Fig. 2 [5].

Experimental results are presented in terms of methanol conversion (X_{MeOH}) and selectivity (S_{DME}), defined as it follows:

$$X_{\text{MeOH}} = \text{mol}_{\text{MeOH converted}} / \text{mol}_{\text{MeOH initial}} \quad (1)$$

$$S_{\text{DME}} = 2 * \text{mol}_{\text{DME}} / \text{mol}_{\text{MeOH converted}} \quad (2)$$

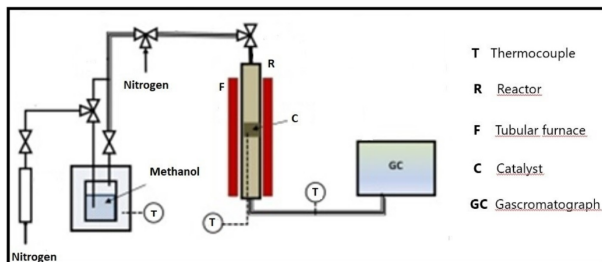


Fig. 2. A simplified flow diagram of the experimental unit for catalytic production of DME from methanol.

3. Results and discussion

3.1. Catalyst characterization

The SEM picture (Fig. 3) demonstrates a chemically porous morphology of the prepared catalyst. The micrograph shows that the functionalized powder MCM-41 has a uniform size and has a low agglomeration tendency.

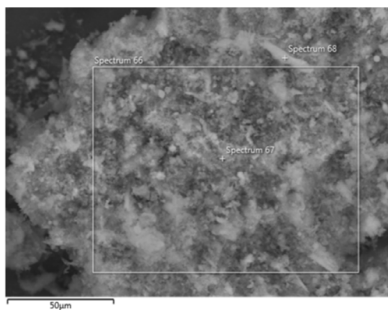


Fig. 3. The SEM image of MCM-41-propyl-SO₃H catalyst.

In the methanol dehydration to DME reaction, catalyst's acidity which makes a significant contribution in material durability, DME productivity and production costs. Temperature programmed desorption NH₃-TPD measurement was utilized to quantify the acid loading of organic functional groups incorporated in the catalyst, using ammonia as an adsorbate and the data are exhibited in Fig. 4.

The synthesized sulfonic material displayed two desorption peaks at 120 and 190 °C, indicating the presence of relatively weak acid sites on MCM-41-propyl-SO₃H. The acid loading of the studied catalyst was 8.36 µmol/g.

The TGA profile in Fig. 5 shows the first peak lower than 100 °C due the desorption of water followed by an intense broad peak between 400-600 °C corresponding to the degradation of sulfonic acid groups. The weight loss in the temperature range 200-350 °C could be due to the release of remaining surfactant molecules, unoxidized thiol groups and ethoxy groups adsorbed on the solid surface during the surfactant extraction process [9]. However, these processes are unlikely to occur at the temperature used for our catalytic process.

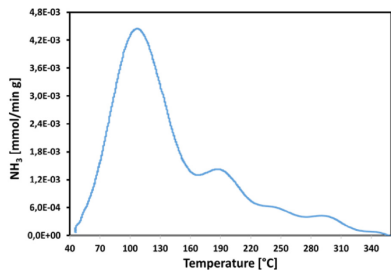


Fig. 4. NH₃-TPD profile of MCM-41-propyl-SO₃H catalyst.

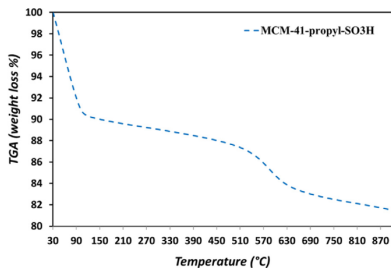


Fig. 5. TGA profile of MCM-41-propyl-SO₃H catalyst.

Small angle X-ray diffractogram of the propyl-SO₃H-functionalized mesoporous material is exhibited in Fig. 6. In particular, the solid-acid MCM-41-propyl-SO₃H showed the characteristic peak which coincides to the 100 preferred orientation.

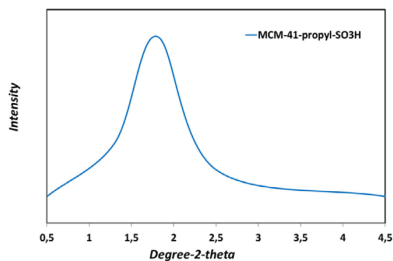


Fig. 6. XRD pattern of MCM-41-propyl-SO₃H catalyst.

The textural properties, including surface area, total pore volume, and average pore diameter of the sulfonated MCM-41 catalyst, are calculated on the basis of nitrogen adsorption and are indicated in Table 1. The sample was

Table 1. BET surface area, average pore radius, and pore volume of the catalyst.

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
MCM-41-propyl-SO ₃ H	970	0.68	2.1

found to have a BET surface area of 970 m²/g with a pore diameter of 2.1 nm very similar to that calculated from XRD analysis, 2.3 nm.

3.2. Catalytic activity

Temperature is a critical parameter, which makes a significant contribution in catalytic reactions. With the objective to evaluate the trend of variation of methanol conversion over operating temperature, a series of experiments were performed under a temperature range of 200 to 360 °C. Fig. 7a and b reported the effects of the reaction temperature on the conversion of methanol over this catalyst. The maximum methanol conversion and DME selectivity were reached by a temperature of 350 °C. The selectivity to DME at temperatures beyond 350 °C was decreased as a consequence of the development of higher hydrocarbons within the series of DME dehydration reaction, as well as hydrocarbon formation.

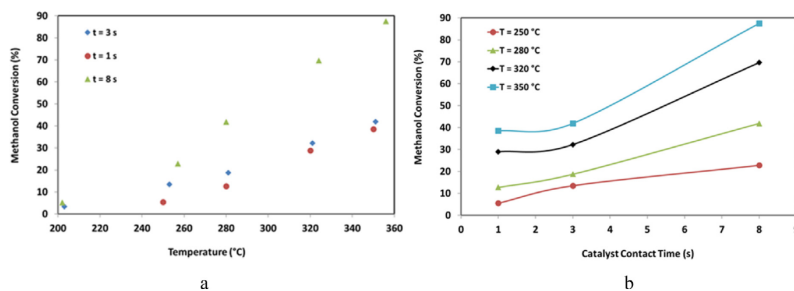


Fig. 7. (a) Variation of methanol conversion vs. temperature at different residence times; (b) Effect of catalyst contact time on methanol dehydration at different temperatures.

The influence of residence time within a range of 1–8 s was also investigated in Fig. 7a and b because it is one of the main governing factors that affect methanol dehydration to DME. At high value of residence contact catalyst the methanol conversion was high. Based on the results, decreasing residence time had a negative effect on conversion and an optimum conversion was obtained at high contact time, which is not practical or economical for the industrial interest. Hence, in order to access optimum commercial space velocity range, a trend of variation of conversion with residence time was studied at operating temperature range.

Experimental results show that maximum performance can be reached (conversion greater than 85%) under catalyst contact time of more than 8 s at temperatures of 350 °C.

The catalyst's DME selectivity with time on stream was reported in Fig. 8. It has been noticed that the selectivity of DME decreased very slowly with an increase of time on stream. After the reaction completed, the coke deposition on the MCM-41-propyl-SO₃H material was analyzed by TGA and the small quantity of carbon was 5.8%.

4. Conclusion

This study focused on influences of reaction temperatures and catalyst contact times on the methanol conversion and DME selectivity of MCM-41-propyl-SO₃H catalyst. The novel material was prepared by a new synthetic

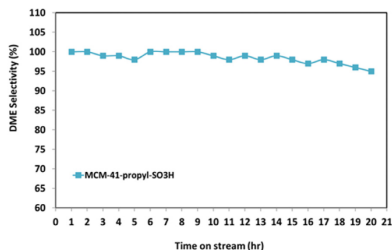


Fig. 8. DME selectivity of MCM-41-propyl-SO₃H catalyst as a function of time on stream at T = 350°, P = 1 bar, and t = 8 s.

strategy and it showed high performances in the synthesis of DME via methanol dehydration. The introduction of –SO₃H groups in the solid significantly enhanced the total acidity by increasing the concentration of weak acidity and consequently modifying the material behavior in the methanol to DME transformation. This material possesses particles of 2.1 nm in size with a surface area 970 m²/g and total pore volume of 0.68 ml/g. The methanol conversion was subject to the reaction temperature and residence times. Particularly, the MCM-41 sulfonated showed remarkable performances with a methanol conversion as high as 88% at 350 °C (100 vol.% MeOH; 41 mg of sample; t = 8 s) and a total selectivity to DME.

CRediT authorship contribution statement

Rosanna Viscardi: Investigation, Formal analysis, Validation, Writing - original draft, Writing - review & editing. **Vincenzo Barbarossa:** Investigation, Formal analysis, Validation. **Raimondo Maggi:** Data curation, Investigation, Writing. **Francesco Pancrazzi:** Resources, Validation.

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.

Acknowledgments

The authors wish to thank Raffaele Pirone and Fabio Deorsola of Politecnico of Torino for their support to NH₃-temperature programmed desorption analysis.

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