

# Selective synthesis of 2,6-triad dimethylnaphthalene isomers by disproportionation of 2-methylnaphthalene over mesoporous MCM-41

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## Abstract

2,6-Dimethylnaphthalene (2,6-DMN) is one of the crucial intermediates for the synthesis of polybutylenenaphthalate and polyethylene naphthalate (PEN). The complex synthesis procedure and the high cost of 2,6-DMN production significantly reduce the commercialisation of PEN even though PEN demonstrates superior properties compared with polyethylene terephthalate. 2,6-DMN can be produced by methylation of 2-methylnaphthalene (2-MN) and/or naphthalene, disproportionation of 2-MN, and/or isomerisation of dimethylnaphthalenes (DMNs). In this study, synthesis of 2,6-triad DMN isomers consisting of 2,6-DMN, 1,6-DMN, and 1,5-DMN have been investigated with the disproportionation of 2-MN over unmodified and Zr-modified mesoporous MCM-41 zeolite catalysts. In contrast to other DMN isomers, both 1,5-DMN and 1,6-DMN can be effectively isomerised to be profitable 2,6-DMN. The disproportionation of 2-MN experiments were carried out in a catalytic fixed-bed reactor in the presence of 1 g of catalyst at a temperature range of 350–500 °C and weight hourly space velocity between 1 to 3  $h^{-1}$ . The results demonstrated that mesoporous MCM-41 zeolite catalyst has a selective pore shape for 2,6-triad DMN isomers, which may allow a decrease in the production cost of 2,6-DMN. Additionally, 2,6-DMN was successfully synthesised by the disproportionation of 2-MN over MCM-41 zeolite catalyst. Furthermore, both the conversion of 2-MN and the selectivity of 2,6-DMN were considerably enhanced by the Zr impregnation on MCM-41.

Keywords 2-Methylnaphthalene  $\cdot$  2,6-Dimethylnaphthalene  $\cdot$  Disproportionation  $\cdot$  MCM-41  $\cdot$  PEN

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## Introduction

Polyethylene naphthalate (PEN) is a thermoplastic polyester which demonstrates superior properties such as thermal and mechanical stability, oligomer extraction, gas barrier, heat resistance, tensile strength, and stability against UV light compared with polyethylene terephthalate (PET) [1-6]. These properties clearly reveal that PEN is expected as an alternative material for innovative applications [1, 3, 5] such as high-performance containers for carbonated beverages, advanced photosystems, films, textile and industrial fibres, storage of water and other liquids, etc. [3-5, 7]. It also has a wide application possibility for the modern electronic devices in view of its thermal and mechanical stability. The PEN synthesis process involves three main parts; (1) the oxidation of 2,6-dialkylnaphthalenes (2,6-DKN) to synthase dicarboxylic acid (2,6-NDA), (2) the esterification of 2,6-NDA to produce dimethyl 2,6-naphthalene dicarboxylate (2,6-NDC), and (3) copolymerization of 2,6-NDC with ethylene glycol to PEN [3, 8]. 2,6-Dimethylnaphthalene (2,6-DMN) is preferred over dialkyl naphthalene thanks to the fact that no carbon atoms are lost in the oxidation step [8]. However, the complex synthesis procedure and the high cost of 2,6-DMN production significantly reduce the industrial applications of PEN [1, 3, 4, 7-9]. To produce 2,6-DMN, a few synthesis pathways have been investigated, such as disproportionation of methylnaphthalenes [4, 10], methylation of naphthalenes [6, 11-19], and isomerisation of dimethylnaphthalenes (DMNs) [7, 20].

In the methylation of 2-methylnaphthalene (2-MN), a higher ratio of 2,6-DMNto-2,7-DMN and higher selectivity of β,β-DMN were observed over Fe- and Znmodified ZSM-5 silicates while ZSM-5 demonstrated higher MN conversion and less deactivation than metal silicates [6]. However, both lifetime and catalytic activity of ZSM-5 zeolite catalyst were enhanced by NaOH treatment [16]. Furthermore, a higher ratio of 2,6-DMN-to-2,7-DMN and selectivity and yield of 2,6-DMN were observed over ZSM-5 modified by Pt and Zr [16, 19]. Although 2-MN is one of the widely used starting materials in methylation reaction, naphthalene is also another alternative starting material for the production of 2,6-DMN [5, 14, 21]. The methylation of naphthalene was investigated over Al, Ga, and Al/Ga impregnated ZSM-12 by Wu et al. [21]. According to their results, the highest naphthalene conversion was obtained over ZSM-12 modified by Al-Ga, whereas the highest ratio of 2,6-DMN-to-2,7-DMN was observed over Ga-modified ZSM-12. Song et al. [14] also revealed that Fe-impregnated ZSM-5 demonstrated higher naphthalene conversion and better catalytic activity as to compare with Tiand Co-modified ZSM-5. In the isomerisation of DMNs, Motoyuki et al. [7] state that an effective synthesis process of 2,6-DMN is possible by utilising a nonvaluable feed stream that mainly includes naphthalene and DMN isomers in which 2,6-DMN can be effectively enriched with isomerisation reaction over MCM-22 zeolite catalyst [7].

As for the disproportionation of 2-MN, Güleç et al. [4] revealed that Zr modification efficiently enhanced the disproportionation activity of ZSM-5. Moreover, it was found by Matsuda et al. [22] that while ZSM-5 was

stable against deactivation for the disproportionation of 2-MN, the catalyst was deactivated in the isomerisation of MNs and disproportionation of 1-MN. However, although HZSM-5 was defined as one of the most selective catalysts for the synthesis of 2,6-DMN and 2,7-DMN, these two isomers were easily isomerised to other DMN isomers [23]. On the other hand, isomerisation of 2,6-DMN and 2,7-DMN was suppressed by removal of external acid sites by dealumination using  $(NH_4)SiF_6$  with the disproportionation activity being unchanged [23]. However, catalysts, such as H-ZSM-5, H-ZSM-11, H-ZSM-48, and H-mordenite, having medium pores, demonstrated lower disproportionation activity compare with H-Y and H-beta zeolite catalysts [23]. Niftaliyeva and Karaduman [10] also investigated the disproportionation of 2-MN over mesoporous Y zeolite catalyst. Although mesoporous MCM-41 aluminosilicate zeolite catalyst has never been tested in the disproportionation of 2-MN reaction, it is a promising catalyst in the disproportionation reactions. The particular selectivity of MCM-41 was attributed by Morin et al. to its regular non-interconnected long channels where the xylene molecules undergo, before desorption, successive reactions of disproportionation and transalkylation [24].

Although disproportionation of 2-MN is an alternative pathway for the synthesis of DMN isomers, especially 2,6-triad DMN isomers, there is a relatively small number of studies which have been concerned with the shape-selective conversion of 2-MN to 2,6-triad DMN isomers. Investigations into different zeolite catalysts with different pore shapes are therefore of utmost importance to find a selective catalyst for the disproportionation of 2-MN. In previous studies, neither MCM-41 nor Zr-impregnated MCM-41 zeolite catalysts have been used for the disproportionation of 2-MN which is the novelty of the present work. In this study, the disproportionation of 2-MN was carried out over Zr-modified MCM-41 (Zr/MCM-41) and un-modified MCM-41 zeolite catalysts. The conversion of 2-MN, the ratio of 2,6-DMN-to-2,7-DMN, and the selectivity of 2,6-DMN were investigated to demonstrate the disproportionation activity of non-modified MCM-41zeolite catalysts.

# Materials and method

## Preparation of Zr/MCM-41 zeolite catalyst

MCM-41 zeolite catalysts, supplied from Zeolyst (surface area of 900 m<sup>2</sup>/g), were modified with about 10 wt% of Zr using ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Acros Organics, purity of 99.5%) by the wet impregnation method. Before the impregnation, the powder MCM-41 zeolite catalysts were firstly pelletized using the following process; 15 g of MCM-41 zeolite catalyst was mechanically mixed with 3 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder with a mass ratio of 5:1. The mixture was then mixed with deionized water before it was extruded to cylindrical pellets. The cylindrical pellets were then dried at room temperature for 24 h and then at 120 °C for 4 h in an oven. To investigate the baseline experiments of MCM-41, the pelletized MCM-41 zeolites were calcined at 550 °C for 6 h. The impregnation method of Zr, which has also been presented in a previous study [5], was used as follows: approximately 9 g of the pelletized MCM-41 zeolite catalyst was placed in a beaker and then an aqueous solution of 2.53 g of  $ZrO(NO_3)_2 \cdot 2H_2O$  was added onto the MCM-41 catalysts. The impregnation was carried out at 25 °C for 20 h. The samples were then dried at 110 °C for 4 h before the calcination at 550 °C for 6 h. The zeolite catalyst having a cylindrical shape (2-mm diameter, 10-mm length) was, finally, designated as Zr/MCM-41. The activity of the MCM-41 zeolite catalyst would, therefore, be expected to be enhanced by the impregnation of Zr as active sites of the catalyst.

## Characterisation of Zr/MCM-41 zeolite catalyst

To characterise Zr-impregnated MCM-41 and un-modified MCM-41 zeolite catalysts, the textural properties of zeolite catalysts were derived from nitrogen sorption measurements at liquid nitrogen temperature, -196 °C (77 K), using a Quantachrome NOVA 2200 N<sub>2</sub> sorption instrument. The specific surface area and the pore volume of the zeolite catalysts were calculated according to Brunauer-Emmett-Teller (BET) [25, 26] and Barrett-Joyner-Halenda (BJH) [25] methods, respectively. The wide-angle X-ray diffraction (XRD) analysis of the prepared catalysts was investigated using an Inel Equinox 1000 instrument with Cu-Ka radiation at 40 kV and 100 mA. The patterns were recorded under the  $2\theta$  range of  $5^{\circ}$ - $60^{\circ}$  with a step size of 0.02 Å. The energy-dispersive X-ray (EDX) and scanning electron microscopy (SEM) were performed using a ZEISS EVO 40 microscope operated at 20 kV. Additionally, the amount of Zr impregnated in the pore surfaces of MCM-41 zeolite catalyst was measured using a Spectra XLAB-2000 PED X-ray fluorescence (XRF) spectrometer. Furthermore, the infrared analyses of Zr/MCM-41 and un-modified MCM-41 were investigated using a spectrometer (Mattson 1000). The MCM-41 and Zr/MCM-41 zeolite pellets were prepared by pressing the sample powders at 10 kPa, and each pellet was then scanned 30 times per analysis at a  $16 \text{-cm}^{-1}$  resolution within the 400–4000-cm<sup>-1</sup> infrared region. The nature of acid sites of the prepared catalysts was characterised by the same FTIR spectroscopy (Py-IR). In the Py-IR experiments, pyridine was used as a probe molecule and it was dosed onto the samples till saturation and kept in a desiccator for 24 h.

## **Disproportionation of 2-MN**

The disproportionation tests of 2-MN were investigated in a fixed-bed experimental set-up which consisted of a high-pressure liquid pump, a flow meter controlling the carrier gas flow rate, a specially designed steel fixed-bed flow reactor with a 30-cm length and inner diameter of 1 cm, surrounded by a tubular furnace with a PID temperature controller, a condenser (working at -5 °C), and a phase separator. A schematic diagram of the experimental set-up was supplied in the previous publications [5, 10]. A mixture of 2-MN and benzene having a mole ratio of 1:1 was prepared as the disproportionation feed stream. Approximately 2 ml (nearly 1 g) of zeolite catalyst (MCM-41 or Zr/MCM-41) was located in the centre of the fixed-bed reactor, and the catalysts were then activated at 500 °C for 30 min with a nitrogen flow rate of 5 ml/min. The disproportionation feed was then injected into the fixed-

bed reactor by the liquid pump just after the catalyst activation. The disproportionation of 2-MN was carried out at different temperatures of 350–500 °C and various weight hourly space velocities (WHSVs) of  $1-3 \text{ h}^{-1}$ . The reaction products were then condensed and collected in glass vials. The disproportionation feed stream and liquid products were analysed using a gas chromatograph (GC; Thermo Finnigan DSQ250) with a Zebra brand mass spectroscopy (60 m long, 0.25-mm internal diameter, 0.25 µm film thickness, from – 60 to 370 °C). DMN isomers in the product stream were easily separated using a temperature programme; from 95 °C to 125 °C with a heating rate of 1 °C/min, then from 125 to 200 °C with a heating rate of 5 °C/min, and then finally from 200 to 230 °C with a heating rate of 20 °C/min. The conversion of 2-MN [4, 5, 13], the ratio of 2,6-DMN-to-2,7-DMN, and the selectivity of 2,6-DMN [4] were calculated using the following equations;

Conversion of 2-MN = 
$$\frac{W_{2-MN,0} - W_{2-MN,t}}{W_{2-MN,0}} * 100$$
 (1)

$$S_{2,6-\text{DMN}} = \frac{W_{2,6-\text{DMN}}}{W_{\text{DMNs}}} * 100$$
(2)

$$R_{2,6-/2,7-\text{DMN}} = \frac{W_{2,6-\text{DMN}}}{W_{2,7-\text{DMN}}}$$
(3)

where  $W_{2-MN,0}$ , and  $W_{2-MN,t}$  are the weight of 2-MN in the feed and product mixtures, respectively.  $S_{2,6-DMN}$  shows the selectivity of 2,6-DMN.  $W_{2,6-DMN}$ ,  $W_{2,7-DMN}$ , and  $W_{DMNs}$  represent the weight percentage of 2,6-DMN, 2,7-DMN, and total DMN isomers, respectively.

## **Results and discussion**

#### Proposed reaction mechanism

It is known that the zeolite catalysts are widely used for methylation [9, 11, 15, 27], isomerisation [1–3, 7, 28], and disproportionation [4, 10] processes. Because of the pore shape of zeolite catalysts and the structure of the model feed, both isomerisation and disproportionation reactions could be observed in this study as demonstrated in Fig. 1. The isomerisation reaction may occur among MN isomers and DMN isomers. DMN isomers may be produced by either disproportionation of 2-MN or 1-MN which is produced by isomerisation of 2-MN as seen in Fig. 1. The experimental results supported the proposed disproportionation reaction from 2-MN or 1-MN to DMNs (more information is presented in the "Disproportionation of 2-methylnaphthalene" section).





Fig. 1 Possible disproportionation and isomerisation reaction pathways of 2-MN

#### Characterisation of prepared catalysts

#### N<sub>2</sub> adsorption-desorption isotherms and XRD analysis

Nitrogen sorption isotherms of MCM-41 and Zr/MCM-41 zeolite catalysts are presented in Fig. 2. The isotherms consist of three well-distinguished regions; (1) adsorption of monolayer-multilayer, (2) capillary condensation, and (3) multilayer adsorption on the outer particle surfaces [29]. According to IUPAC classification, the isotherms may be defined as "type IV", typical isotherm of mesoporous materials, as porous materials having a diameter of 20–500 Å are classified as mesoporous [30]. Additionally, the isotherms contain a hysteresis loop at high  $P/P_0$  values (higher than 0.4) which is typical for mesoporous materials [31]. The BET surface area, BJH pore volume, and pore diameter of MCM-41 were found as



833 m<sup>2</sup>/g, 0.8833 cm<sup>3</sup>/g, and 33.96 Å, respectively. For Zr/MCM-41, the BET surface area and BJH pore volume, however, decreased to 759.80 m<sup>2</sup>/g and 0.7822 cm<sup>3</sup>/g, respectively, whereas the BJH pore diameter was insignificantly affected (33.89 Å). The decrease on the surface area and pore volume may be attributed to the blocking of some pores by Zr impregnation into the catalyst pores.

Figure 3 illustrates the wide-angle XRD patterns of the catalysts; MCM-41 and Zr/MCM-41. The wide-angle XRD patterns of both MCM-41 and Zr/MCM-41 are quite similar with the wide-angle XRD patterns of MCM-41 zeolite catalysts presented in the literature [29, 32, 33]. There is no clear diffraction peak corresponding to the Zr compound in Fig. 3b which may be explained by high dispersion of Zr compounds in the catalyst [29]. The hump at 27.13° may be attributed to the amorphous nature of MCM-41 zeolite catalyst.

#### SEM, EDX mapping, and XRF analysis

SEM images of the zeolite catalysts are presented in Fig. 4. The SEM images reveal no morphological decomposition on the MCM-41 zeolite with the modification of Zr. Additionally, the MCM-41 zeolite surface looks much smoother after Zr modification compared with unmodified MCM-41.

EDX mappings of Zr/MCM-41 and MCM-41 zeolite catalysts are presented in Fig. 5. Figure 5b proves the successful impregnation of Zr on the MCM-41 zeolite surface. Additionally, the dispersion of Zr metal on the surface seems quite homogenous. Both SEM and EDX mapping results demonstrate that there was no agglomeration on the zeolite surface after Zr impregnation. The amount of impregnated Zr was measured by XRF analysis before and after disproportionation of 2-MN. According to the XRF analysis, fresh Zr/MCM-41 zeolite catalyst consisted of approximately 9.0 wt% of Zr, 40 wt% of Si, and 1.5 wt% of Al. However, the XRF analysis of used Zr/MCM-41 demonstrated a slightly lower Zr





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Fig. 4 SEM images of a MCM-41 and b Zr/MCM-41 zeolite catalysts before testing on the disproportionation reaction of 2-MN



Fig. 5 EDX mapping of a MCM-41 and b Zr/MCM-41 zeolite catalysts before testing on the disproportionation reaction of 2-MN

content of 8.7 wt%. Although the chemical composition of MCM-41 consists of Si and O, the other metal, Al, comes from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used in the pelletizing process.

### FTIR analysis

Figure 6 shows that the FTIR spectrums contain a group of absorption bands where the peak at around  $805 \text{ cm}^{-1}$  indicates the symmetric stretching modes of Si–O–Si

Fig. 6 FTIR spectrum of the MCM-41, Zr/MCM-41, and used MCM-41



groups [29, 33]. Additionally, the shoulder band at 968  $\text{cm}^{-1}$  may be attributed to stretching vibration of either Si-O-Si or M-O-Si [29]. The other band around 1090 cm<sup>-1</sup> indicates the internal asymmetric stretching of the Si-O-Si bond [29, 33, 34] and the shoulder on the right side of the peak may be attributed to the external asymmetric stretching of Si-O-Si [29]. The other wide band at about  $3100-3700 \text{ cm}^{-1}$  may be linked with H-bonded hydroxyl groups at  $3530 \text{ cm}^{-1}$ [35-38]. As neither the bridging hydroxyl groups, SiOHAl, which are usually characterised by a sharp band at 3550-3650 cm<sup>-1</sup> [39], nor isolated SiOH groups characterised by a band at 3745  $\text{cm}^{-1}$  [39] were observed. These peaks are the same for both MCM-41 and Zr/MCM-41 zeolite catalyst. Additionally, the structure of used MCM-41 zeolite catalyst remains the same after the disproportionation reaction, as demonstrated in Fig. 6 where the external and internal symmetric stretching modes of Si-O-Si groups still remain. The Py-IR results of MCM-41 and Zr/MCM-41, which has not been presented in this paper, demonstrate that Zr impregnation has clearly decreased the absorbance values for Lewis (about  $1450 \text{ cm}^{-1}$ ), Lewis + Brönsted (about  $1495 \text{ cm}^{-1}$ ), and Brönsted (about  $1550 \text{ cm}^{-1}$ ) acidities. Similarly, Jin et al. [13] have mentioned that the total acidic amount and proportion of strong acid sites decrease with increase in the ratio of Zrto-Al.

## **Disproportionation of 2-MN**

## Catalytic activity of Zr/MCM-41

The activity of MCM-41-type zeolite catalysts is identified by the conversion of 2-MN, the selectivity of 2,6-DMN, and the ratio of 2,6-DMN-to-2,7-DMN with using Eqs. 1–3. Figure 7 shows that an increase in temperature leads to an increase in the conversion, although it decreases with an increase in the WHSV. When the MCM-41 was used in the disproportionation of 2-MN, the conversion values were found lower than 4 wt% as shown in Fig. 7a. However, the conversion was clearly enhanced by the modification of Zr. For instance, the conversion of 2-MN clearly



Fig. 7 Conversion of 2-MN at different WHSVs and temperatures for a MCM-41 and b Zr/MCM-41

increased to about 20 wt% at 400 °C and nearly 30 wt% at 500 °C for WHSV1, as observed in Fig. 7b, when Zr/MCM-41 was used as a catalyst. A similar increase was also observed for WHSV2 and WHSV3 in Fig. 7. It is known that the reaction rate constant (k) depends on the temperature because of the exponential term of the Arrhenius equation  $(k = k_0 * \exp(-E_A/RT))$ . According to the equation, the increase in the temperature can increase the value of the exponential term that may result in an increase in the reaction rate. Additionally, the activity increase may be attributed to the reaction mechanism of disproportionation on the catalyst surface. The acid sites may be attached to the weak C-C bound on the 2-MN molecules adsorbed on the active site of the catalyst and result in a bond cleavage. As it is known that the weakest C-C bond on the 2-MN is the methyl bond which is connected to the 2nd carbon of the naphthalene molecule. Thus, the conversion of 2-MN may be enhanced thanks to the transfer of methyl group to another 2-MN molecule. Furthermore, the increase in the conversion may also be attributed to both the weakening of Lewis and Brönsted acidities and the constriction of the pore dimension of MCM-41 after Zr modification. These findings correlate with those of Jin et al. [13], where the improvement in the catalytic performance on methylation reaction of 2-MN was also mainly attributed to both the weakening of acid strength and the expansion of pore dimension that occurred after Zr impregnation into ZSM-5. Additionally, Morin et al. [24] suggested that the particular selectivity of MCM-41 samples was most likely due to the presence of regular non-interconnected long channels, where the molecules undergo successive reactions of disproportionation and transalkylation before desorption.

The selectivity of 2,6-DMN demonstrated an increasing trend with an increase in temperature, but a decreasing trend with an increase in WHSV for MCM-41 and Zr/MCM-41 zeolite catalysts, as seen in Fig. 8. For instance, the selectivity of 2,6-DMN increased from about 7–18 wt% with temperature increasing from 350 to 450 °C for WHSV1 for MCM-41. A similar increase was observed for both WHSV2 and WHSV3, as seen in Fig. 8a. However, the selectivity of 2,6-DMN decreased from about 7 wt% to approximately 1 wt% with WHSV increasing from 1 to 3 h<sup>-1</sup> at 350 °C. Additionally, a similar decrease in the selectivity was clearly observed at 400 and 450 °C. These decreases may be attributed to the decreasing



Fig. 8 The selectivity of 2,6-DMN at different WHSVs and temperatures for a MCM-41 and b Zr/MCM-41

residence time in the catalyst bed with increasing WHSV. The decrease in the interaction between catalyst and reactant may also decrease the selectivity of 2,6-DMN. As for Zr/MCM-41, the selectivity of 2,6-DMN was found to be higher than that for MCM-41. It is clear that Zr modification enhanced both the conversion of 2-MN shown in Fig. 7b, and the selectivity of 2,6-DMN illustrated in Fig. 8b. The selectivity of 2,6-DMN for Zr/MCM-41 was found mostly higher than 20 wt% at 400, 450, and 500 °C for WHSV1, WHSV2, and WHSV3. On the contrary of MCM-41 and Zr/MCM-41 can almost keep the selectivity of 2,6-DMN values at the same level regardless of different temperatures and WHSV used in these experiments.

Figure 9 shows the ratio of 2,6-DMN-to-2,7-DMN for MCM-41 and Zr/MCM-41 at different temperatures and WHSVs. The ratio of 2,6-DMN-to-2,7-DMN is generally greater than 1.5 for MCM-41 and Zr/MCM-41 zeolite catalysts. The higher ratio of 2,6-DMN-to-2,7-DMN can enable an easy subsequent separation because an eutectic mixture would be formed at a ratio of 0.7 [8]. Similarly, the



Fig. 9 The ratio of 2,6-DMN-to-2,7-DMN at different WHSVs and temperatures for a MCM-41 and b Zr/MCM-41

ratio of 2,6-DMN-to-2,7-DMN was found to be higher than 1.0 in the disproportionation reaction over Zr-modified ZSM-5 zeolite catalyst in our previous study [4]. However, the great increase in the ratio by about 2.5–3.0 of 2,6-DMN-to-2,7-DMN after Zr impregnation on ZSM-5 was investigated on methylation of 2-MN by Jin et al. [13]. The ratio of 2,6-DMN-to-2,7-DMN is among 1.4–2.4 for MCM-41 and 1.3–1.6 for Zr/MCM-41 as shown in Fig. 9.

## Dimethylnaphthalene distribution

The weight % distributions of DMN isomers in the products stream is another crucial issue in this study for the synthesis of 2,6-DMN. 2,6-DMN has nine other DMN isomers that can be produced as by-products in the disproportionation reaction of 2-MN, as demonstrated in Fig. 1. These DMN isomers can be divided into three main triads: (1) 2,6-triad; 1,5-DMN, 1,6-DMN, and 2,6-DMN, (2) 2,3triad; 1,4-DMN, 1,3-DMN, and 2,3-DMN, and (3) 2,7-triad; 1,8-DMN, 1,7-DMN, and 2,7-DMN [1]. Among these three triads, the 2,6-triad has the utmost importance as both 1,5-DMN and 1,6-DMN can be effectively isomerised to be profitable 2,6-DMN [1, 2]. 1,6-DMN can be supplied by a single methyl shift of 1,5-DMN and then 2,6-DMN can be produced by one more methyl shift of 1,6-DMN [1, 3]. The DMN distributions are presented in Table 1 for WHSV1 space velocity in which the highest conversion of 2-MN and selectivity of 2,6-DMN were achieved. The 2,6-DMN and other DMN isomers such as 2,7-DMN, 1,3-DMN, 1,4-DMN, 1,7-DMN, 1,5-DMN, 1,6-DMN, 1,2-DMN, 2,3-DMN, and 1,8-DMN were synthesised with disproportionation of 2-MN over MCM-41 and Zr/MCM-41. It is clear that Zr modification enhanced the selectivity of 2,6-DMN at low temperature (400 °C). Additionally, the disproportionation of 2-MN over the Zr/MCM-41 catalyst mainly leads to 2,6-DMN, 2,7-DMN, 1,5-DMN, and 1,6-DMN in very high proportions compared with the thermodynamically attainable level. A similar contribution was

Catalyst type Temperature (°C)	MCM41			ZrMCM41			Thermodynamic
	350	400	450	400	450	500	equilibrium [23]
Composition of DMNs (wt%	%)						
2,6-DMN	6.8	12.4	18.3	19.3	19.8	23.1	9.0
2,7-DMN	3.6	8.2	12.7	13.5	15.8	16.5	9.0
1,3-, 1,4- and 1,7-DMN	5.9	12.7	19.1	20.7	13.6	10.2	45.6
1,5- and 1,6-DMN	74.8	56.2	40.9	29.2	31.9	35.2	27.3
1,2-DMN	1.9	3.4	5.6	7.2	9.8	9.3	5.7
2,3-DMN	1.5	2.3	3.4	6.4	8.1	5.4	2.9
1,8-DMN	5.5	4.5	0	0.5	0.9	0.1	-
Unknown	-	0.3	-	2.2	-	-	-
Sum	100	99.7	100	97.8	100	100	99.5

 Table 1
 DMN isomer distributions over MCM-41 and Zr/MCM-41 at different temperatures for WHSV1

also investigated with disproportionation of 2-MN over H-ZSM-11 and H-Mor by Kikuchi et al. [23]. The disproportionation of 2-MN demonstrates that MCM-41 zeolite catalyst has a selective pore shape for 2,6-triad isomers; 1,5-DMN, 1,6-DMN, and 2,6-DMN. These three isomers have the highest percentage among the other DMN isomers for both MCM-41 and Zr/MCM-41 zeolite catalysts.

# Conclusions

The selective synthesis of 2,6-triad DMN isomers has been investigated with the disproportionation of 2-MN over both MCM-41 and Zr-modified MCM-41 zeolite catalysts. This is the first study in which the MCM-41 zeolite catalyst has been investigated in the disproportionation of 2-MN reaction to synthesize 2,6-triad DMN isomers. The conversion of 2-MN is considerably enhanced by the Zr modification on MCM-41 zeolite catalyst, and reaches a peak level of 30 wt% at 500 °C and WHSV1. In addition to the improvement in the conversion, the selectivity of 2,6-DMN is also increased substantially by the Zr modification. It was increased to nearly 20-25 wt% after Zr modification at 400, 450, and 500 °C. Furthermore, the ratio of 2,6-DMN-to-2,7-DMN is about 1.5 for both MCM-41 and Zr/MCM-41 zeolite catalysts. Additionally, in terms of the synthesis of 2,6-tirad isomers, MCM-41 zeolite catalyst shows a selective pore shape for 2,6-triad isomers; 1,5-DMN, 1,6-DMN, and 2,6-DMN, which can allow for a decrease in the production costs of 2,6-DMN. Thanks to its selective pore shape for 2,6-triad isomers, the other transition metals can also be impregnated onto MCM-41 zeolite catalyst and investigated in the disproportionation reaction as a future study. Furthermore, a cheap naphthalene source, such as coal tar naphthalene oil fractions, which is a sub-product of the iron-steel industry, could be used as a raw material which could also reduce the production cost of 2,6-DMN.

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