

The use of Uio-66 Metal-Organic Frameworks as a high-performance catalyst for the isomerization process of endo- to exo-dicyclopentadiene in a solvent-free condition

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Research Article

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Abstract

Exo-tetrahydrodicyclopentadiene (tricyclo[5.2.1.0^{2,6}]decane) or JP-10 is a synthetic jet fuel, which can be used as a high-density fuel in the air-breathing missile engines and supersonic combustion ramjets. It can be produced from the fully saturated version of *exo*-dicyclopentadiene (*exo*-DCPD). This work introduces a new green method for isomerization of *endo*-dicyclopentadiene (*endo*-DCPD) to *exo*- form in the presence of Metal-Organic Frameworks (MOFs). The synthesized UiO-66 and UiO-66-vac as two suitable MOF catalysts are used for the isomerization process in a solvent-free condition. The design of the experiment is used to optimize reaction conditions including time, temperature and catalyst loading. High yield and excellent conversion of *endo*- to *exo*-DCPD are obtained by reacting with UiO-66-vac at lower levels of time and temperature. Solvent-free, environmentally friendly, simple reaction process, reusable catalyst, and availability of materials are advantages of this process.

1. Introduction

Meta-Organic Frameworks (MOFs) are a category of porous materials containing inorganic nodes (metal cations or clusters of metal cations) and organic linkers [30]. Since MOFs are crystalline materials containing a vast area of effective properties, they can be introduced as heterogeneous catalysts in contrast to the other porous materials. They have some advantages such as tunable pores, high surface area, high porosity, good stability in different conditions, ease to functionalize, and flexible structure [8]. Due to these properties, MOFs have had wide applications in recent years, e.g. isomerization [9], drug delivery [24], hydrogenation/isomerization [25], condensation reactions [7], benzylation [19], and alkylation [22].

Cyclic hydrocarbons can provide a much larger heat of combustion than similar non-cyclic compounds because they contain strain energy [12]. Moreover, synthetic jet fuels with bridged cyclic and multicyclic hydrocarbon structures can provide high strain energy, which are attractive candidates as jet fuels or liquid fuels in liquid bipropellants [18]. It is essential to use synthetic jet fuels with low values of melting point [15] and enthalpy of fusion [14] to prevent their freezing in cool weather. JP-10, a pure component: *exo*-tetrahydrodicyclopentadiene (tricyclo[5.2.1.0^{2,6}]decane), is a synthetic jet fuel, which was developed to use as a super fuel in the air-breathing missile engines and supersonic combustion ramjets [20]. It is a high volumetric density fuel with many unique properties such as low and appropriate freezing point, thermal stability, and specific impulse [13]. Dicyclopentadiene (DCPD) and tetrahydrodicyclopentadiene (THDCP) are important initial reactants for producing JP-10 that have two *endo*- and *exo*- stereoisomers [26]. *Exo*- and *endo*-THDCP have the same chemical and physical properties but the freezing point *endo*-THDCPD (80°C) is more than its *exo*-isomer (-79°C). Thus, *endo*-THDCPD is not suitable to use as a liquid fuel. Since DCPD exists naturally in the form of *endo*- isomer, its isomerization to *exo*- form as well as optimizing reaction conditions and improving efficiency are essential and valuable [26].

Bratlett and Goldstein [3] have introduced a two-step method in which iodo-dihydro-*endo*-DCPD was obtained by increasing HI to DCPD then isomerization is done to *exo*-form in the presence of alcoholic

potassium hydroxide and eliminates HI. Bakke and Lundquist [2] presented the isomerization of *endo*-DCPD in the gas phase. They used Pt-containing silica-alumina as a suitable catalyst but their method did not show a good yield. Zhang and coworkers [29] have investigated *endo*- to *exo*-isomerization of DCPD using thermal treatment at optimum conditions for temperature (180 °C) and pressure (4 MPa). In another report, they performed the alteration of *endo*-DCPD to *exo*-form using Al-grafted MCM-41 [31]. They found that the porous structure and high dosage of catalysts give better results at relatively low reaction temperatures with the addition of inert solvent. Commercial zeolites can be used as a catalyst for isomerization *endo*-DCPD in the liquid phase. Han et al. [10] found that acidic zeolites (H β) usefully promote the isomerization reaction with good activity. Kim and coworkers [17] indicated that MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) can be used as catalysts for the isomerization of *endo*- to *exo*-DCPD. Since the nature of the active metal center is effective in the conversion and selectivity of the reaction, the MIL-100 (Fe) showed the highest catalytic activity.

It is important to improve the performance and strategies for isomerization of *endo*- to *exo*-DCPD. The use of solvents has some problems for environmental and human health. Moreover, the processes containing solvents are complicated for industrial usage because isomerization requires high pressure, high temperature, and long reaction time. The use of zeolites has some shortcomings such as easy deactivation, coke formation, and obstruction of micropores, which can decrease the yield [16]. The changes such as solvent-free reactions and mild conditions may be attractive for chemical industries. Thus, MOFs containing a well-ordered structure and a high surface area (till 5000 m²/g) are appropriate for isomerization reaction because they can provide a suitable pore size with a high surface area to solve the problem.

Zirconium (Zr) has three times more abundant in the earth's crust than copper and zinc [27]. UiO-66 and UiO-66-vac (Zr-cluster-based MOFs) have excellent thermal and chemical stability and acidity properties. Both catalysts are composed of Zr as a node and terephthalic acid as a linker that can be utilized as MOFs for isomerization. UiO-66-vac has missing linkers that result in vacancy sites, which are useful for catalytic activity [5]. The existence of strong bonding between Zr (IV) and carboxylate is an effective factor for the stability of UiO-66-vac. The high oxidation number of the Zr (IV) in comparison with MOFs based on a lower oxidation number is a key property, which provides high charge density and polarity [28].

To obtain a high yield and improve the selectivity of *exo*-DCPD, it is essential to select the optimal reaction conditions such as catalyst, temperature, and time. The design of experiments (DOE) is very efficient because it can adjust several factors and interactions that lead to process optimization [1]. The purpose of this work is to introduce UiO-66(Zr) and UiO-66(Zr) vac as favorable new heterogeneous catalysts for isomerization of *endo*- to *exo*-DCPD without using solvents. The optimized reaction conditions are specified to maximize conversion of *endo*- to *exo*-DCPD using a central composite design. Furthermore, catalysts regeneration is also studied.

2. Experimental

2.1. Materials

ZrCl₄, terephthalic acid (BDC, 98%), dimethylformamide (DMF, 99%), hydrogen chloride (37%), dichloromethane (99%), isopropanol (99%), *endo*-DCPD (93%), *exo*-DCPD (96%) were bought from Merck Co. and Sigma-Aldrich. All materials were used without further purification.

The solvothermal method was used to prepare UiO-66 (Zr) and UiO-66-vac [5].

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns were recorded with AW-XDM300 X-ray Diffractometer at a step size of 0.05° with a Cu K α radiation ($\lambda = 1.5406\text{\AA}$). Brunauer–Emmett–Teller (BET) surface area was analyzed by N₂ sorption/desorption using at 77 K with a Belsorp mini instrument and degassing at 200°C under vacuum. The Fourier transform infrared (FT-IR) spectra were recorded on an Infracum-08 spectrophotometer in the range of 400–4000 cm⁻¹. Gas chromatography-mass spectrometry (GC-MS) was analyzed using Agilent 6890 by 30 m length packed HP5((5%-phenyl)-methylpolysiloxane) column and mass selective detector.

2.3. Catalytic experiments and analysis

The catalytic isomerization was performed based on the primary results of DOE. In an autoclave, 4 mL of *endo*-DCPD was added to the proper amount of catalysts without stirring and solvent. The reactions proceeded at a specified temperature and time. The autoclave was cooled slowly after completing the reaction. The catalysts were easily separated from the solution with filtration by increasing dichloromethane. Gas chromatography (GC) was used to analyze the conversion of *endo*- to *exo*-DCPD. GC analysis was done using Agilent 68 gas Chromatograph by 30 m packed HP5 ((5%-phenyl)-methylpolysiloxane) column and flame-ionization detector (FID). The yield was computed based on the standard addition method.

2.4. DOE

One-factor-at-a-time (OFAT) was used to investigate the effect of different factors on a result wherein only one of the factors is altered at a time and others are kept fixed. The influences of the interactions between the variables cannot be considered here. It was tried to determine the optimized conditions for the catalytic isomerization of *endo*- to *exo*-DCPD with catalysts UiO-66 and UiO-66-vac using DOE (Design Expert 10 software) and quadratic model.

2.5. Design of process

The central composite design (CCD) with three independent variables was chosen to evaluate the activity of the UiO-66 catalyst. Reaction time (hour), reaction temperature (°C), and weight percentage catalyst (Wt% catalyst) were selected as process variables. Influential variables and their variation levels have been selected according to the values used in other references and some preliminary experiments [6]. The

measured response is the yield of the *exo*-DCPD, which was obtained from the isomerization reaction. The models were computed by multiple linear regression (MLR) and analysis of variance (ANOVA).

3. Results And Discussion

3.1. Specification of catalysts

XRD, FTIR spectroscopy, and N₂ sorption isotherm were used to identify UiO-66 and UiO-66-vac catalysts. Figure S1 shows the XRD results for UiO-66 and UiO-66-vac where the synthesized MOFs are highly crystalline. They exhibited mainly three broad 2θ peaks at around 7, 9, and 26°. No additional peaks were observed and their pattern is according to XRD results in the literature [11]. For FTIR spectrums of UiO-66 (Zr) and UiO-66-vac (Figure S2), carboxylate asymmetric and symmetric stretch in BDC appears as strong bands at 1589 and 1396 cm⁻¹, the weak band at 1504 and 1658 cm⁻¹ shows a double bond in the benzene ring. The Zr-O band is observed at wavenumber 744 cm⁻¹ [5]. UiO-66-vac presents a wider pore volume and higher specific surface area than UiO-66. The surface area of the synthesized UiO-66 (Zr) and UiO-66-vac are 553 and 982 m²/g respectively. The pore volumes for UiO-66 and UiO-66-vac are 0.213 and 0.322 cm³/g⁻¹, respectively. The BET and Barrett-Joyner-Halenda (BJH) data show that both catalysts are mesoporous. N₂ adsorption-desorption isotherm of both catalysts is shown in Figure S3.

3.2. Isomerization catalysis and statistical analysis

The DOE based on the effective factors and CCD method for *endo*-DCPD to *exo*-DCPD conversion using UiO-66 and UiO-66-vac are shown in Table 1. Based on the results of the estimated yields, UiO-66-vac is more efficient as compared to UiO-66. The higher yield of *exo*-DCPD was obtained when UiO-66-vac was used as a catalyst. Isomerization of DCPD is an important step in JP-10 synthesis, which is related to time, temperature and catalyst. The software analyzes the data and provides several key plots.

The results of one-factor plots show that time is the most effective factor with a negative effect. A long reaction time leads to undesired side reactions such as oligomerization of *exo*-DCPD. Some products have more opportunities to combine and form different (cyclic) compounds [17]. Mild changes in yield occur as the temperature or the weight percent of the catalyst increases. The effects of temperature and weight percent catalyst are negative and positive, respectively. Thermal oligomerization of raw material molecules at higher temperatures reduces the isomerization efficiency [17]. Since similar behavior was observed for both UiO-66-vac and UiO-66, Figure S4 shows the effects of temperature, time, and Wt% catalyst only for UiO-66-vac.

Figure 1 shows contour diagrams for better investigation of the effects of the parameters of temperature, time, and Wt% catalyst (UiO-66-vac) on each other and the yield, which show simultaneous changes in the parameters. One variable in each of the contour diagrams is taken constantly. The study of the effect of reaction time in the presence of catalyst UiO-66-vac shows that the highest yields are achieved in the time range of 3.4 to 4.5 hours (Figures 1a and c). Increasing the amount of loaded catalyst can increase

the total number of active sites of the catalyst, which provides better access for *endo*-DCPD to improve higher yield (Figure 1a). For lower temperatures, higher percentages of *exo*-DCPD product are obtained in the presence of the UiO-66-vac catalyst, which shows the optimal amount of catalyst (Figure 1b). In general, middle and lower levels of temperature and reaction time, respectively, along with a higher percentage of catalysts have the greatest impact on the isomerization of *endo*-DCPD to *exo*-DCPD. Figure S5 shows contour plots for UiO-66 catalyst in which the effect of the mentioned parameters on isomerization is similar to UiO-66-vac.

Table S1 gives the results from ANOVA, which validates the model and the selected factors. These parameters show the conversion of *endo*-DCPD to *exo*-form significantly. The significance of factors is shown by p-value because factors with a p-value less than 0.05 are significant [23]. The assessment of the p-value and lack-of-fit test for the yield indicates the validity of the model in this study. All main factors in this model are significant, and the lack of fit is not significant. As shown in Table 2, values of coefficient of determination (R^2) demonstrate a good correlation between experimental and predicted values.

3-3 Reactivity of UiO-66 and UiO-66-vac catalyst in the isomerization of *endo*-DCPD

As mentioned earlier, UiO-66-vac is more efficient in the isomerization of *endo*-DCPD as compared to UiO-66. Both catalysts can perform the isomerization at mild reaction conditions without solvent. They have higher efficiency in comparison to commercial catalysts such as zeolites [10] or other MOFs [17]. As seen in Table 1, the best yield for *exo*-DCPD is obtained from run 7 under the conditions of temperature 116 °C, time 3.4 h, and weight percent catalyst 8.4. Due to the presence of the missing BDC²⁻ linkers in UiO-66-vac, the surface area of this catalyst is greater than UiO-66 which this agent can be effective in the isomerization process. Charge balance in this catalyst is provided by hydroxide anions that are bonded to μ_3 -OH groups in the parent UiO-66 and at the missing linkers. Zr atoms are ended to water molecules that are likely to develop the number of Brønsted acid sites in the UiO-66-vac [4, 21]. The significant activity of UiO-66-vac in isomerization *endo*-DCPD has arisen from the mentioned agents.

The effects of three factors on *endo*-DCPD conversion and *exo*-DCPD selectivity in the presence of UiO-66-vac are shown in Figure 2. An excellent conversion is observed for most reactions and the highest percentage of selectivity is shown for run 16, which is equal to 72. Thus, selectivity decreases with increasing temperature and time, which may be due to the in-situ consumption of *exo*-DCPD and its decomposition to CPD and thermal oligomerization of *endo*-DCPD [17].

Table 3 compares the results of previous works with this study for the kind and activity of catalysts on isomerization of *endo*-DCPD. It confirms a high percentage conversion of *endo*-DCPD to *exo*-DCPD in this study by the significant activity of UiO-66 and UiO-66-vac. Thus, both catalysts show excellent activity toward zeolites as well as MOFs with Fe and Cr metal.

The results of GC-MS show that in addition to *exo*-DCPD the mixture may contain small amounts of tricyclopentadiene, 1,3a,3b,4,6a,6bHexahydrocyclopenta[3,4]cyclobuta[1,2] cyclopentene and

pentacyclo[5.3.0.02,5.03,9.04,8]decane as well as other cyclic and linear compounds like 9-methylidenetricyclo[4.2.1.12,5]decane and tetraisobutylene. Recycling the catalyst is favorable from the viewpoint of environmental and economic. Thus, the used catalysts are washed with carbon tetrachloride to eliminate the products from the catalyst surface. Fortunately, there is no loss of the yield with the reused catalyst after three times.

4. Conclusions

A green process was introduced in this work for single-step isomerization of *endo*- to *exo*-DCPD in the presence of UiO-66 and UiO-66-vac (Zr) with high yield in mild reaction conditions. The catalysts are synthesized easily and reusable for this reaction. The DOE with three factors including temperature, time, and %Wt catalyst is effectively used to optimize conditions. Temperature and time at lower levels as well as catalyst dosage at higher levels have better performance on reaction yield. The surface area and acidity properties of the UiO-66 catalysts are also important to further factors to obtain a higher yield. Since UiO-66-vac has more surface area, it is more active in the isomerization of *endo*-DCPD to *exo*-DCPD. Since the new method has some advantages such as solvent-free, eco-friendly, easy reaction procedure, and availability of materials, it is superior to previous works.

Declarations

Supplementary Information

Characterization of catalysts, X-ray diffraction spectra, N₂ isotherms, Fourier-transform infrared spectra, ANOVA results, effects of main factors, and Contours plots for UiO-66 are given as supplementary data.

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Statements & Declarations

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Competing Interests The authors declare no competing interests.

Author Contributions All authors (Narjes Khaton Maghsoodi and Mohammad Hossein Keshavarz) made substantial contribution.

Data Availability Data can be obtained from the corresponding authors through email.

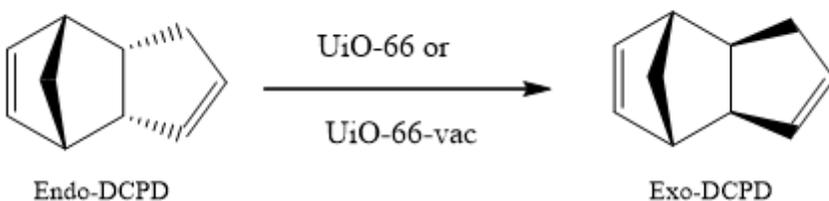
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Tables

Table 1. Factors and levels of CCD and yields for the conversion of *endo*- to *exo*-DCPD in the presence of UiO-66 and UiO-66-vac as catalysts



Run	Variables and levels			Yield%	
	Temp(°C)	Time (h.)	Wt% ¹ Cat	UiO-66	UiO-66-vac
1	116	3.4	3.6	11	35
2	140	5.5	6	15	47
3	116	7.5	3.6	10	30
4	140	9	6	9	27
5	164	3.4	8.4	14	42
6	164	7.5	3.6	13	39
7	116	3.4	8.4	19	51
8	164	7.5	8.4	9	25
9	164	3.4	3.6	14	42
10	116	7.5	8.4	13	37
11	180	5.5	6	12	36
12	140	5.5	6	15	46
13	140	5.5	10	14	40
14	140	5.5	6	16	47
15	140	5.5	2	12	34
16	100	5.5	6	14	43
17	140	5.5	6	15	47
18	140	2	6	15	45
19	140	5.5	6	16	46
20	140	5.5	6	15	45

¹Weight percentage

The best conditions: temperature 116 °C, time 3.4 h ND catalyst 8.4 Wt%

Table 2. Statistical parameters to prove the adequacy of the model

Catalyst	R-Squared	Adj ^a R-Squared	Pred ^b R-Squared
UiO-66	0.980	0.961	0.914
UiO-66-vac	0.983	0.967	0.884

^a Adjusted

^b Predicted

Table 3. Comparison of catalyst activity our study and previous studies

Entry	Catalyst	%Conversion	%Selectivity	Ref.
1	No catalyst	5	-	This work
2	H β ^a	21	38	[31]
3	Al-MCM-41 ^a	33	58	[31]
4	MIL-100(Fe) ^b	17.3	48.6	[17]
5	MIL-100(Cr) ^b	7.3	41.2	[17]
6	MIL-101(Fe) ^b	4.3	40.5	[17]
7	MIL-101(Cr) ^b	4.2	40.7	[17]
8	UiO-66 ^c	58	32	This work
9	UiO-66-vac ^c	93	55	This work

^a Reaction conditions: catalyst= 5 wt%, temperature= 150 °C and reaction time = 3 h

^b Reaction conditions: 5 g *endo*-DCPD, catalyst = 5 wt.%, temperature = 140 °C and reaction time = 3 h.

^c Reaction conditions: catalyst= 8.4 wt%, temperature= 116 °C and reaction time = 3.4 h.

Figures

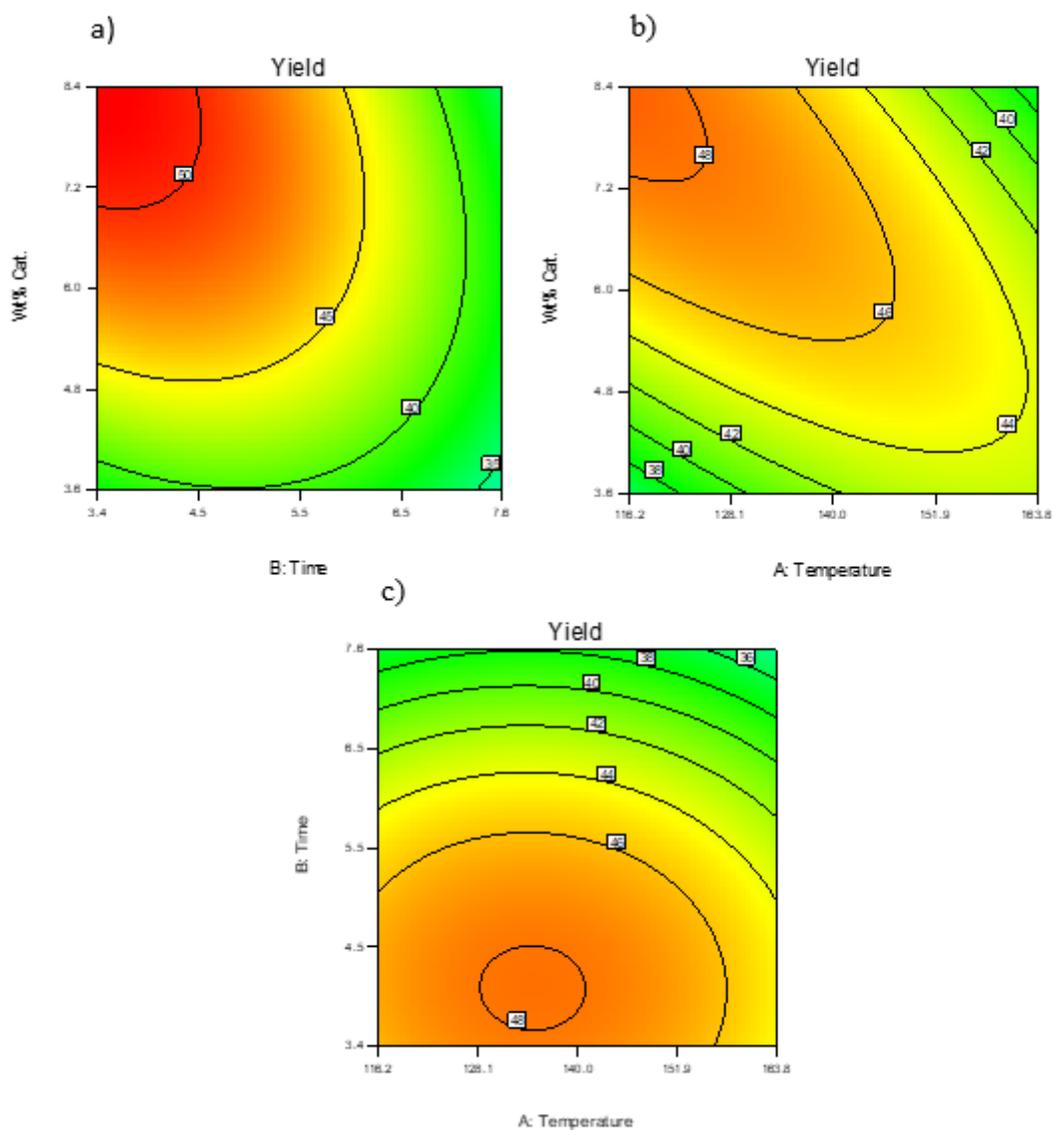


Figure 1

Contours plots for main factors interactions on the the yield of isomerization *endo*-DCPD in the presence of UiO-66-vac: a) Time-%Wt cat., b) Temperature-%Wt cat., and c) Temperature-Time

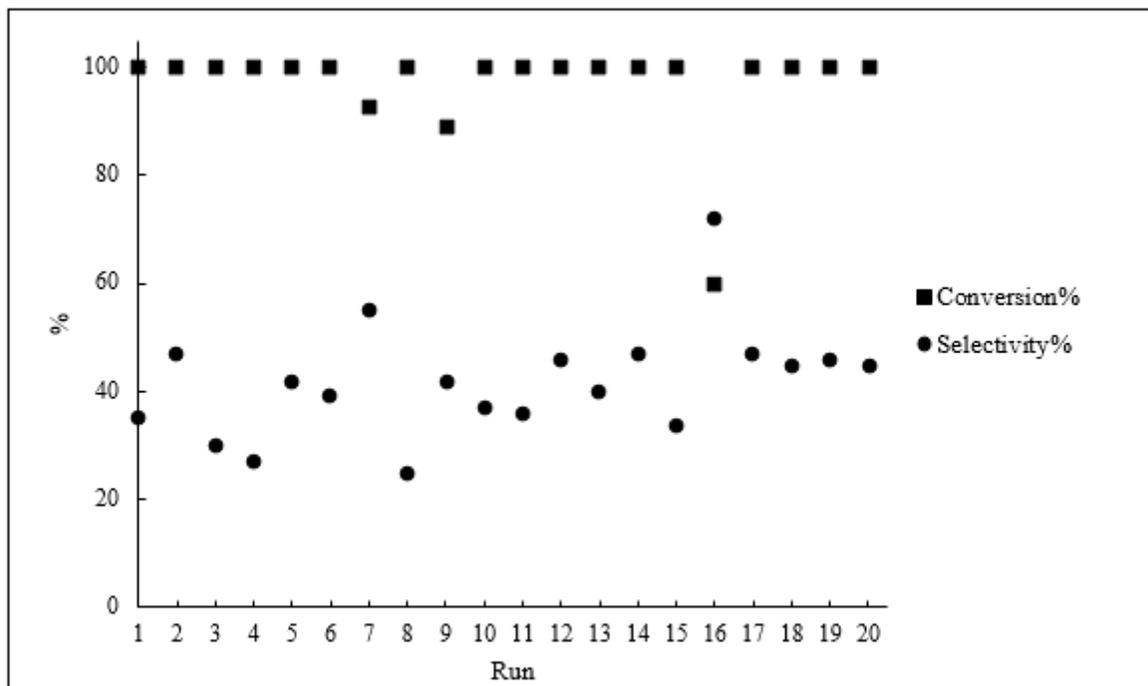


Figure 2

Effect of three factors on the *endo*-DCPD conversion and *exo*-DCPD selectivity in the presence of UiO-66-vac. (Run numbers in table 1 versus conversion & selectivity percentage)

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