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Using Catalysts with ZSM-48 Zeolite support and MOF-5 Organic-metallic Framework in the Oxidative Dehydrogenation Process of Propane to Produce Propylene

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Abstract

In this research, catalysts with zeolite bases ZSM-48 and organic-metallic framework MOF-5 were used as catalytic bases in the process of oxidative dehydrogenation of propane to produce propylene. The experimental design of the central composition method was used to investigate the effect of different parameters in the oxidative dehydrogenation process of propane. For this purpose, loading of chromium in the range of 2-6% by weight, ratio of propane to carbon dioxid in the range of 1:1-3:1 and temperature in the range of 500 to 700 degrees Celsius, and loading ratio of chromium to vanadium in the range of 2:1 to 5 1: was used as the input variables of the central composition method. After conducting the reactor test and analyzing the results, the design of the experiment was done by Design expert software. Also, with the increase in temperature, the percentage of propane conversion and the percentage of efficiency increase and the percentage of selectivity of propylene decreases. Although with increasing chromium loading percentage, propane conversion percentage and oxidative dehydrogenation efficiency percentage first increase and then decrease and selectivity percentage decreases. By reducing the propane-to-oxygen ratio with the Cr-V@MOF-5 organometallic framework catalyst, the percentage of propane conversion and the percentage of efficiency decrease and the percentage of selectivity increases. The optimal conditions obtained for the performance of the organometallic framework catalyst, the amount of chromium loading in the catalyst construction, the reaction temperature, the ratio of propane to CO_2, and the loading ratio of chromium to vanadium were determined as 4%, 500 degrees Celsius, 1:1, 3.5:1, respectively. Under these conditions, the area under the propylene peak is estimated to be 93.3%. So that in optimal conditions Cr-V@ZSM-48, the amount of chromium loading in the catalyst construction, the reaction temperature, the propane to CO_2 ratio, and the chromium to vanadium loading ratio were determined as 4%, 600°C, 3:1, and 3.5:1, respectively, and under these conditions, the area under propylene was obtained91. 1% is achievable.

Keywords: Catalyst Selectivity, Zeolite ZSM-48, MOF-5, Propane Oxidative Dehydrogenation Process, Experimental Design.

1- Introduction

The increasing growth of global demand for propylene requires extensive research to find alternative sources. The process of oxidative dehydrogenation of propane is a reliable method to produce propylene, which does not have any of the disadvantages of recent propylene production processes. However, controlling the selectivity is the only major challenge facing the industrialization of this process, as propane and propylene can be converted to carbon oxides and other products [1].

Orlick and his colleagues in (2023), conducted studies on the oxidative conversion of propane to propylene. They stated that in today's world, propylene is one of the most important petrochemical materials. Propylene, as an important and vital substance, is produced by various methods, the most important of which is the oxidative dehydrogenation of propane, which is exothermic [10]. In the pioneering research, this method was used to produce propylene and CO_2 was used as an oxidant. The obtained results were studied using XRD, Raman, TEM, SEM, BET analysis. At the beginning of the work, BEA zeolite base was synthesized by inoculation method, and after synthesis, zinc metal modifier was loaded on the catalyst as an improved. In the conducted studies, the great value of CO_2 as an oxidant is that it prevents oxidation of the final product [11-13]. In the analyzes performed by Raman and XRD tests, the prepared nano catalyst shows the presence of anatase phase. SEM and TEM tests also confirmed the structure of the base nano catalyst and the absence of impurities in it. The zinc improver was loaded with 1% by weight of zinc oxide on the zeolite nanotube base by inoculation method. The selectivity of the obtained propylene was equal to 86-94% at the temperature of 293 K and the production efficiency of propylene was 30-33%. This improvement and high efficiency can be due to the higher specific surface area and better distribution of zinc on the zeolite-based sample [14].

Wang et al. (2023) studied the CrOx-Fe-CeO_2 catalyst for the oxidative hydrogenation of propane. They used CO_2 oxidizer and iron and cesium modifiers on the catalyst base [15]. Catalysts for dehydrogenation processes are usually based on modified chromium [16]. Since chromium-containing catalysts are environmentally problematic, the tendency to use other improving metals has increased. Iron and cesium modifiers were used in this study [17-19]. In order to increase the selectivity and stability of these catalysts, inactive metals are often added as promoters, but the addition of inactive metals reduces the activity of chromium metal. Studies have shown that at low temperatures, the selectivity of propane to propylene conversion is higher, and at high temperatures, the selectivity is lower [20-22].

Chromium-containing catalysts are one of the most widely used bases for the dehydrogenation process, and the reason for this is the extraordinary ability it has for the high degree of distribution of other metal modifiers, which is necessary to achieve high activity in the dehydrogenation process [23-25]. But because the acid sites on the primary base cause side reactions and coke formation, it is necessary to add iron and cesium metals in order to poison the acid sites to reduce the isomerization reaction without affecting the dehydrogenation capacity of the catalytic system [25-27].

In (2022), Ilya and his colleagues prepared studies on zinc-nickel bimetallic catalyst based on zeolite ZSM-5 by combined sol-gel method and wet inoculation and investigated its performance in the oxidative dehydrogenation reaction of propane [28, 29]. The characteristics of the catalysts were determined by XRD, BET, FT-IR and SEM tests. They carried out oxidative dehydrogenation reactions of propane in a fixed bed reactor and all the samples made were examined in the temperature range of 350-550 degrees Celsius with a temperature step of 50 degrees Celsius [30-32]. The highest activity and surface area were also obtained in the case where these two bases were

prepared with a weight ratio of 1:1. By increasing the loading of vanadium from 5wt% to 10wt%, the activity increased, but the selectivity first increased up to 7.5wt% and then decreased slightly. For all manufactured catalysts, with increasing temperature, propane conversion and propylene yield increased, but propylene selectivity decreased [30-32].

Mubaraka and his colleagues (2022) used vanadium based on nanostructured ZrO_2 for the oxidative dehydrogenation of propane to propylene. They used an organic fabrication method to obtain a well-distributed structure of V_2O_5 on TiO_2. In the samples prepared by the organic method, lower oxidation numbers of vanadium were observed, while the absence of such a state in the sample prepared by the wet loading method was suggested as another reason for the low activity [33].

In this study, our Target is catalysts with zeolite bases ZSM-48 and organic-metallic framework MOF-5 were used as catalytic bases in the process of oxidative dehydrogenation of propane to produce propylene. The experimental design of the central composition method was used to investigate the effect of different parameters in the oxidative dehydrogenation process of propane.

2- **Consumable raw materials and method**

Synthesis method: In the synthesis method of Cr-V@MOF5 catalyst, a combination of several previous studies was used, and it can be said that the presented synthesis method is not repetitive.

In this research, deionized distilled water and aluminum sulfate octadehydrate ($AL_2(SO_4)3.18H_20$) with 99% purity and 99% ethanol from Merck, Germany was used for the synthesis of the catalyst. From sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) 90% from Sigma Aldrich Company, hexamethylene diamine ($H_2N(CH_2)6NH_2$ 99%, colloidal silica (SiO_2) 40%, NH_4NO_3 (99% from Sigma Aldrich Company, chrome Chloride hexahydrate ($CrCl_3.6H_2O$) 96% was obtained from PubChem Co. and ammonium metavanadate (NH_4VO_3) 98% was obtained from Prolab Co. H2BDC (benzene-1,4-dicarboxylate) 99% and zinc nitrate Zn $(NO_3)2.6\ H_2O$ 99% and vanadyl sulfate ($VOSO_4$) were purchased from Merck. Hydrazine 45% was purchased from Prolab Chemical Company. Also, propane gas with 97% purity from Maron Petrochemical and dry air with grade 5 and 99.99% purity gas Oxygen and carbon dioxide with a purity of 99.99% were prepared for use in the oxidative dehydrogenation system Figure 1 & 2).

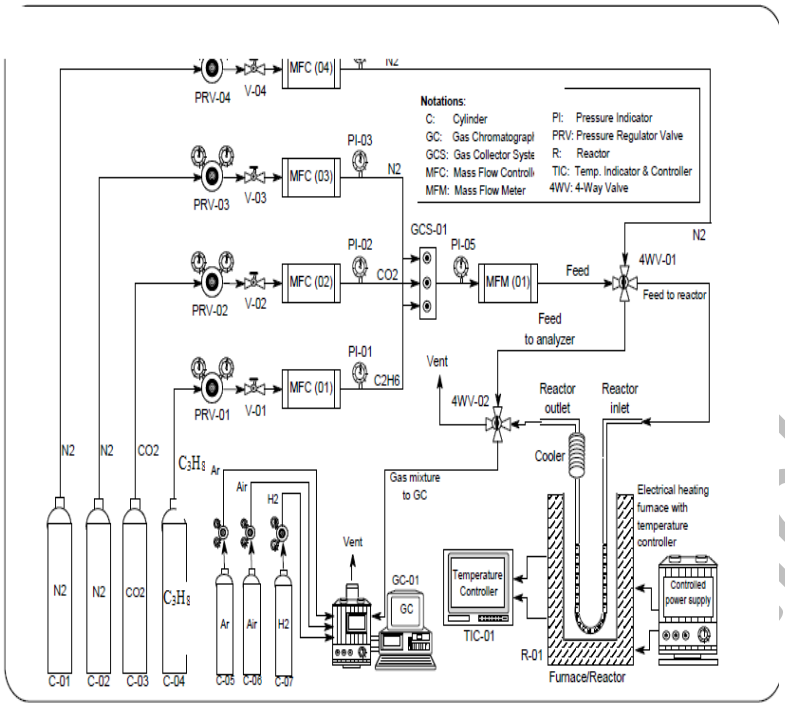


Figure (1). The laboratory system for evaluating the performance of chromium vanadium catalysts with zeolite base ZSM-48 and MOF-5 in the process of oxidative hydrogenation of propane and its conversion to propylene.

Figure (2). Propane oxidative dehydrogenation laboratory system

To check the activity and selectivity of catalysts in oxidative dehydrogenation of propane, 0.1 g of catalyst was used in each experiment. In order to have a better temperature distribution, the samples were mixed with 0.1 g of silicon carbide. After being placed in the reactor, the catalyst was heated to a temperature of 300°C and then cooled to a temperature of 200°C under an air flow with a flow rate of 20sccm and a heating rate of 100 C/min. Then, a mixture of air and propane with a flow intensity of 100sccm entered the reactor in such a way that the molar ratio of propane to oxygen is equal to the required value.

According to the output results from the GC device, the conversion percentage and selectivity calculations have been done as follows. The percentage of conversion is equal to the fraction of propylene output from the reactor (the level below the GC output peak diagram) to propane input to the reactor (the level below the GC peak of propane before the reaction) is defined and calculated. The selectivity is defined and calculated as the fraction of propylene output from the reactor to the sum of the reaction output products (sum of the levels under the peak diagram of all the reaction products). MOF-5 The process efficiency is equal to the product of the conversion percentage by the selectivity. The main ones seen by the detectors were propane, propylene, carbon oxides. To ensure the correctness of the reactor results, all the outlet flow analyzes were performed after 20 minutes of feed

passing through the catalytic bed with 2 repetitions. The range of experiments and different levels of variables were designed as 29 experiments.

1- Model Results

After analyzing the variance table and finding significant and effective variables on propylene yield, a polynomial model with statistical value is obtained for each answer. The graph of the experimental values of propylene production against the predicted results are shown in figures (3A) respectively. These graphs show that the laboratory values are almost on the Y=X line. Therefore, the presented models have been able to predict the laboratory results well.

In the following, the effect of chromium loading parameters, temperature, ratio of propane to carbon dioxide and ratio of chromium to vanadium dosage in catalyst synthesis on the rate of conversion of propane to propylene will be investigated.

2-1- Effect of operational parameters

In this section, the mutual influence of all parameters on the percentage of propane conversion is analyzed.

2-1-1- Temperature effect

In figure (3 A & B), the trend of temperature increase changes on the conversion rate, selectivity and conversion efficiency of propane to propylene can be seen. As we know, temperature is a very important variable to increase products. As can be seen in the figure below, at a temperature of 500 degrees Celsius, the selectivity of propylene is increasing, and with the increase in temperature, the efficiency of propylene production has decreased.

But at 600°C, the maximum selectivity occurs, and then with the increase in temperature, the selectivity has decreased. Since fracture reactions are generally endothermic reactions and increasing temperature always increases the speed of reactions and conversion rate. An increase in temperature always increases the number of olefins such as propylene. But it should be considered that this increase in temperature can be accompanied by an increase in coke production, which will decrease the unit's operation time. By increasing the temperature from 500 to 600 degrees Celsius, the amount of feed conversion increases and more propylene is produced. If at higher temperatures, it leads to the formation of coke and blockage of the catalyst, and the efficiency of propylene production tends from a maximum point to a minimum [34-36].

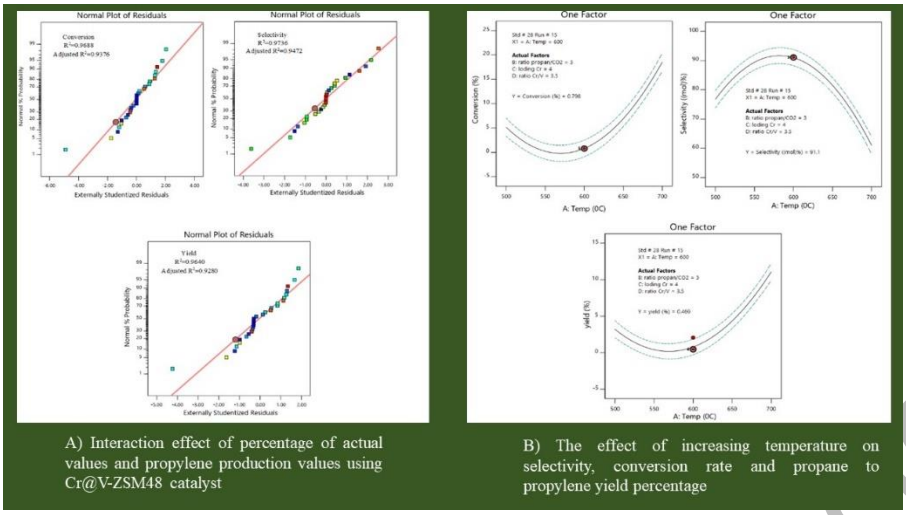


Figure (3). A) Interaction effect of percentage of actual values and propylene production values using Cr@V-ZSM48 catalyst & B) The effect of increasing temperature on selectivity, conversion rate and propane to propylene yield percentage

2-1-2- The effect of propane to carbon dioxide ratio

Oxidative dehydrogenation is an exothermic reaction and does not have the limitations of previous processes for propylene production. The presence of oxygenated compounds such as carbon dioxide in the reaction limits the formation of coke and allows more catalyst to be used. The existence of a stable product of water also removes the thermodynamic limitation. Of course, the presence of many side reactions causes carbon oxides to be produced and the selectivity of producing the desired product (propylene) is not very high. Using CO_2 as an oxidizer easily increases the conversion power up to 10%. Therefore, because of the positive things mentioned about the use of CO_2 as an oxidant, it has gained more power.

As can be seen in the figure, when the ratio of propane to carbon dioxide is 3:1, the highest selectivity has occurred in the conversion of propane to propylene. On the other hand, by reducing the ratio of propane to carbon dioxide due to the presence of more oxygen to oxidize propane and propylene, the selectivity of propylene decreases because propane compounds are more involved in the oxidation reaction with carbon dioxide and play a lesser role in dehydrogenation. and cause a decrease in the selectivity of propane and its conversion to propylene. By increasing the amount of propane more than the 3:1 ratio, the volume of propane entering the pilot increases and the amount of oxidant is greatly reduced. Due to the imbalance in the propane feed and the amount of CO_2 oxidant, it will reduce the selectivity in the production of propylene from propane (Figure 4A).

Propane dehydrogenation in the presence of carbon dioxide is a stable and valuable approach and an attractive catalytic pathway for the production of propylene with less environmental impact than the conventional oxidative dehydrogenation pathway with oxygen. Carbon dioxide as an oxidant has special features such as not oxidizing final products, using CO_2 in the atmosphere to reduce the harmful effects of this pollutant in the atmosphere, the possibility of using it in the presence of more available catalysts, slow and efficient decomposition, etc. This has caused this oxidant to predict C-H bonds in new researches to attract several times the value [37-39].

As can be seen in the figure above, with the increase of propane from 1 to 3, the amount of propylene production has increased. With the increase in the ratio of propane to carbon dioxide, due to the presence of less oxygen for the oxidation of propane and also the production of propylene, it decreases the conversion percentage and

decreases the selectivity. As the ratio of propane to oxygen increases, the percentage of conversion and selectivity decreases due to the presence of less oxidizer to oxidize propane and propylene.

2-1-3- Effect of chromium loading rate in catalyst synthesis

The presence of chromium particles with oxidation states and high re general ability as well as the presence of weak to moderate acid sites are key factors in achieving better efficiency of these catalysts. On the other hand, it has been stated that the proper distribution of chromium particles can somehow indicate the presence of reductive oxidation particles with high re general ability. Based on this, it can be said that the base strongly affects the catalytic efficiency because it affects not only the distribution and structure of the active phase, but also the nature of the active centers, reactivity, acidity, accessibility, etc. As can be seen in the figure, the selectivity of propane to propylene conversion increases with the increase of chromium loading from 2% by weight to 4% by weight. It has been found that by adding cream promoters to the catalyst base (Figure 4B)., the surface area of the catalyst will increase and as a result, the selectivity will increase [40-42].

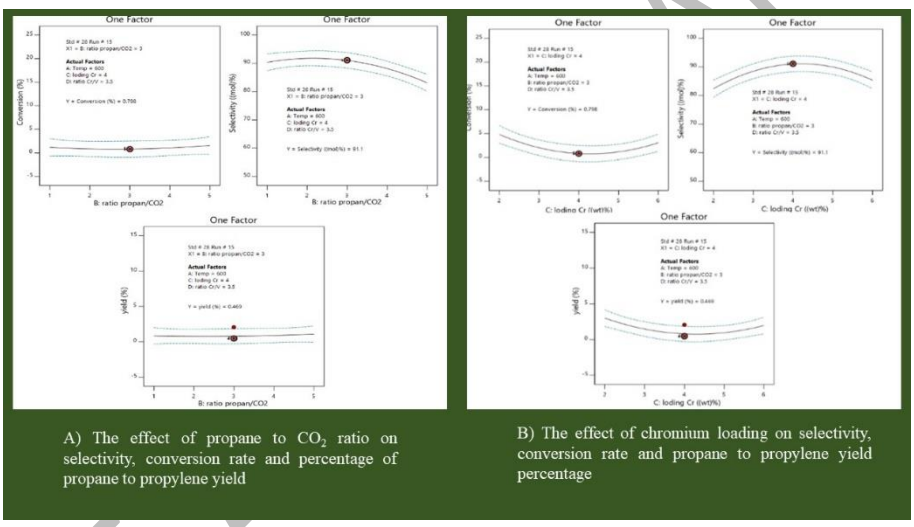


Figure (4). A) The effect of propane to CO_2 ratio on selectivity, conversion rate, percentage of propane to propylene yield & B) The effect of chromium loading on selectivity, conversion rate and propane to propylene yield percentage

2-1-4- The effect of loading ratio of chromium to vanadium in catalyst synthesis

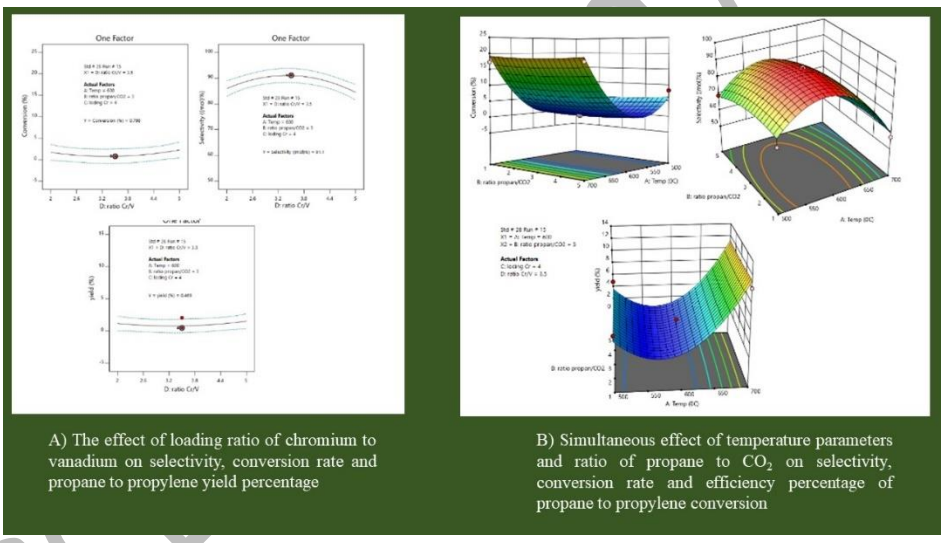
In the current research, two types of promoters (enhancers) have been used on the catalyst base to increase the improvement of the catalyst performance. The loading ratio of chromium to vanadium was higher in the synthesized catalysts. When the loading rate of chromium to vanadium is 3:1, the selectivity is increasing, but with the increase in the loading ratio of chromium to vanadium, clumping and accumulation has occurred in the catalyst structure, it decreases because in the consumed amounts Chromium with a higher dose in the structure of the catalyst, agglomeration has occurred in the structure of the catalyst, and the active sites of the catalyst are blocked due to agglomeration, as a result, the area of the active surface of the catalyst is reduced and the percentage of the produced product is reduced [43-45] (Figure 5A).

2-2- Investigating the simultaneous effect of effective parameters in the oxidative dehydrogenation of propane

The effect of variable AB (A temperature and B ratio of propane to CO_2)

The graphs below show the simultaneous effect of temperature parameters and propane to CO_2 ratio. According to the diagram, increasing the temperature from 500 to 600 degrees Celsius has increased the selectivity, and at higher temperatures, the selectivity decreases due to the formation of coke and the blockage of the catalyst pores and the reduction of the surface area. As mentioned in the previous section, when the ratio of propane to carbon dioxide is 3:1, the most selective conversion of propane to propylene has occurred.

On the other hand, by reducing the ratio of propane to carbon dioxide due to the presence of more oxygen to oxidize propane and propylene, the selectivity of propylene decreases because propane compounds are more involved in the oxidation reaction with carbon dioxide and play a lesser role in dehydrogenation and cause a decrease in the selectivity of propane and its conversion to propylene. Therefore, according to the graph below, it can be stated that with the increase in temperature from 500 to 600 °C and the decrease in propane ratio from 5:1 to 3:1, the selectivity has increased, and also at temperatures lower than 600 °C, there is no interaction between parameters of temperature and the ratio of carbon dioxide to propane, but the interaction increases with increasing temperature (Figure 5B).



A) The effect of loading ratio of chromium to vanadium on selectivity, conversion rate and propane to propylene yield percentage

B) Simultaneous effect of temperature parameters and ratio of propane to CO_2 on selectivity, conversion rate and efficiency percentage of propane to propylene conversion

Figure (5). A) The effect of loading ratio of chromium to vanadium on selectivity, conversion rate and propane to propylene yield percentage & B) Simultaneous effect of temperature parameters and ratio of propane to CO_2 on selectivity, conversion rate and efficiency percentage of propane to propylene conversion

2-3- The effect of AC variable (A temperature and C chromium loading rate in catalyst synthesis)

In the figure (6A), the mutual influence of parameters of chromium loading percentage and temperature simultaneously on the percentage of propane conversion is investigated. It can be said that by increasing the loading percentage of chromium from 2 to 4 and decreasing the ratio of propane to carbon dioxide from 5:1 to 3:1, the percentage of propane conversion increases and also by increasing the loading percentage of chromium, the active surface of the catalyst increases and as a result selectivity increases. But with the increase of temperature more than 600 degrees Celsius and the formation of more coke, the surface-active sites decrease and the selectivity decreases (Figure 6A).

2-4- The effect of variable AD (A is temperature and D is loading rate of chromium compared to vanadium in catalyst synthesis)

Due to the increase in loading of the modifier ratio of chromium to vanadium on the base surface of the catalyst, the selectivity rate increases with a ratio of 3.5 because the specific surface area of the catalyst increases, but with an increase in the ratio of chromium to vanadium more than the ratio of 3.5, the empty spaces and porous cavities of the catalyst are smaller and is limited and as a result leads to a decrease in selectivity. As the reaction temperature decreases from 600°C to 500°C and the loading percentage of chromium is higher, the percentage of selectivity decreases. The highest selectivity was possible at a temperature of 600 degrees Celsius and a ratio of chromium to vanadium of 3.5:1 (Figure 6B).

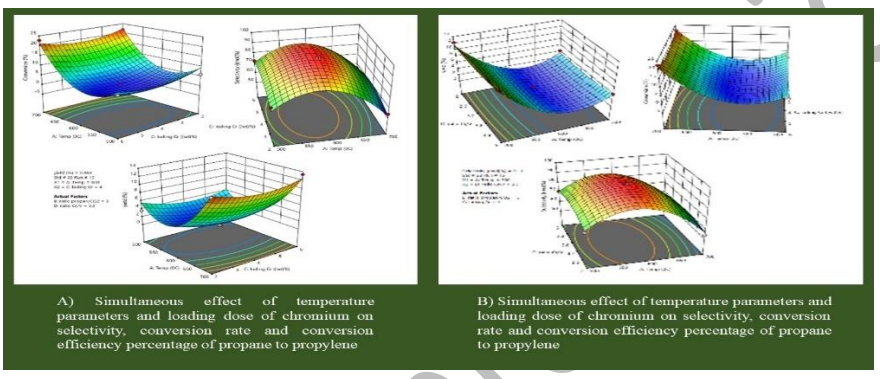


Figure (6). A) Simultaneous effect of temperature parameters and loading dose of chromium on selectivity, conversion rate and conversion efficiency percentage of propane to propylene & B) Simultaneous effect of temperature parameters and loading dose of chromium on selectivity, conversion rate and conversion efficiency percentage of propane to propylene

2-5- Experimental design for the oxidative dehydrogenation of propane to propylene with an organic-metallic framework catalyst

In the continuation of the current research, to investigate the behavior of the ODHP process by the Cr-V@MOF-5 organometallic framework catalyst in the laboratory unit, experiments have been designed based on the box Behnken design method. Using preliminary experiments and based on the study of past researches, four factors of reaction temperature inside the reactor, loading amount of Cr metal, ratio of propane to CO_2 and ratio of Cr to V composition in the synthesis of Cr@V-MOF-5 catalyst as the most important operating variables in this process and conversion percentage, selectivity percentage are considered as responses. The design of the experiment was done by design expert (11) software. The range of experiments and different levels of variables were designed as 29 experiments. To evaluate the appropriateness of the model, the design of the experiment and the value of the regression coefficient (R^2) were presented in table (1), respectively. In table (1) the way of conducting experiments was done randomly and based on statistical principles. R^2 and R^2Adjusted coefficients were used to determine the quality of the presented model. In the second part of the research, the aim of the experiment design is to find a combination of variable levels that can produce the maximum amount of propylene from propane by using oxidative dehydrogenation with Cr-V@MOF-5 catalyst.

Table (1). Model evaluation and variance coefficient

Std. Dev.	1.89	R^2	0.9239
Mean	46.35	Adjusted R^2	0.8477
C.V. %	4.08	Predicted R^2	0.5645
		Adeq Precision	13.1283

2-6- Analysis of variance and checking the appropriateness of the model using Cr-V@MOF-5 catalyst

The results of variance analysis for conversion percentage, propylene selectivity and efficiency are given in tables (2), (3) and (4) respectively. F-test and p-test methods were used to analyze the results of variance analysis and check the importance of independent variables on propylene yield.

Table (2). Results of analysis of variance based on the response of conversion percentage

Source	Sum of Squares	df	Mean Square	F-value	P-value	Column1
Model	606.88	14	43.35	12.13	< 0.0001	significant
A-Temp	433.12	1	433.12	121.25	< 0.0001	
B-ratio propan/CO_2	64.37	1	64.37	18.02	0.0008	
C-loding Cr	5.73	1	5.73	1.6	0.2261	
D-ratio Cr/V	6.07	1	6.07	1.7	0.2134	
AB	6.04	1	6.04	1.69	0.2143	
AC	0.04	1	0.04	0.0112	0.9172	
AD	0.0702	1	0.0702	0.0197	0.8905	
BC	0.0016	1	0.0016	0.0004	0.9834	
BD	0.1354	1	0.1354	0.0379	0.8484	
CD	12.57	1	12.57	3.52	0.0817	
A^2	55.43	1	55.43	15.52	0.0015	
B^2	4.7	1	4.7	1.32	0.2704	
C^2	4.6	1	4.6	1.29	0.2756	
D^2	3.06	1	3.06	0.8552	0.3707	
Residual	50.01	14	3.57			
Lack of Fit	49.53	10	4.95	41.21	0.0014	significant
Pure Error	0.4808	4	0.1202			
Cor Total	656.89	28				

It can be concluded from the model that the greatest effect in increasing the conversion percentage is related to the increase in temperature.

$$\text{Conversion}=+47.28+6.01*A+2.32*B+0.6908*C-0.7113*D-1.23*AB-0.1000*AC+0.1325*AD+0.0200*BC+0.1840*BD+1.77*CD-2.92*A^2-0.8516*B^2+0.8420*C^2+0.6863*D^2$$

2-7- Evaluation of the predicted statistical model of propylene selectivity percentage response

In the table (3), various statistical data (sum of squared errors, degree of freedom, mean square, F. Value and P. Value) calculated by the software are reported. The value of F and P was 120.49 and <0.0001, respectively, and it shows that the model is statistically significant and can be used to predict the desired goals.

Table (3). Results of analysis of variance based on selectivity response

Source	Sum of Squares	df	Mean Square	F-value	P-value	Column1
Model	712.67	14	50.9	120.49	< 0.0001	significant
A-Temp	612.08	1	612.08	121.25	< 0.0001	
B-ratio propan/CO_2	48.07	1	48.07	18.02	< 0.0001	
C-loding Cr	0.3675	1	0.3675	1.6	0.3668	
D-ratio Cr/V	0.056	1	0.056	1.7	0.7212	
AB	5.31	1	5.31	1.69	0.0032	
AC	0.0306	1	0.0306	0.0112	0.7917	
AD	0.0784	1	0.0784	0.0197	0.6732	
BC	0.198	1	0.198	0.0004	0.5048	
BD	1.3	1	1.3	0.0379	0.1013	
CD	1.37	1	1.37	3.52	0.0934	
A^2	27.45	1	27.45	15.52	< 0.0001	
B^2	0.0051	1	0.0051	1.32	0.9142	
C^2	3.28	1	3.28	1.29	0.0146	
D^2	4.95	1	4.95	0.8552	0.0041	
Residual	5.91	14	0.4225			
Lack of Fit	5.91	10	0.5914	41.21	< 0.0001	significant
Pure Error	0.0011	4	0.0003			
Cor Total	718.58	28				

Table (4). Evaluation of the model and coefficient of variance for the selectivity of propylene

Std. Dev.	0.65	R^2	0.9918
Mean	79.96	Adjusted R^2	0.9835
C.V. %	0.8129	Predicted R^2	0.9526
		Adeq Precision	39.2632

Selectivity=+79.77-7.14*A-2.00*B-0.1750*C+0.0683*D+1.15*AB+0.0875*AC-0.1400*AD-0.2225*BC+0.5700*BD+0.5850*CD+2.06*A^2-0.0280*B^2-0.7109*C^2-0.8734*D^2

2-8- Evaluation of the predicted statistical model of the propylene yield response

In the table (5), various statistical data (sum of squared errors, degree of freedom, mean square, F. Value and P. Value) calculated by the software are reported. The value of F and P was 10.17 and <0.00029, respectively, and it shows that the model is statistically significant and can be used to predict the desired goals.

Table (5). Results of analysis of variance based on the response of propylene yield

Source	Sum of Squares	df	Mean Square	F-value	P-value
Model	149.5	14	10.68	10.17	< 0.0001
A-Temp	1.05	1	1.05	0.9981	0.3347
B-ratio propan/CO_2	9.5	1	9.5	9.05	0.0094
C-loding Cr	10.38	1	10.38	9.88	0.0072
D-ratio Cr/V	0.3913	1	0.3913	0.3728	0.5513
AB	1.46	1	1.46	1.39	0.2586
AC	10.52	1	10.52	10.02	0.0069
AD	0.431	1	0.431	0.4105	0.532
BC	0.354	1	0.354	0.3372	0.5707
BD	0.1156	1	0.1156	0.1101	0.7449
CD	0.7396	1	0.7396	0.7045	0.4154
A^2	111.35	1	111.35	106.07	< 0.0001
B^2	3.47	1	3.47	3.31	0.0905
C^2	0.0954	1	0.0954	0.0908	0.7675
D^2	4.91	1	4.91	4.68	0.0483
Residual	14.7	14	1.05		
Lack of Fit	14	10	1.4	8.08	< 0.0029
Pure Error	0.6933	4	0.1733		
Cor Total	164.19	28			

Table (6). Evaluation of model and coefficient of variance for propylene efficiency

Std. Dev.	1.02	R^2	0.9105
Mean	34.01	Adjusted R^2	0.821
C.V. %	3.01	Predicted R^2	0.5021
		Adeq Precision	10.5597

Yeild=+36.44-0.2955*A-0.8898*B-0.9298*C-0.1806*D-0.6032*AB-1.6*AC-0.3283*AD-0.2975*BC-0.1700*BD-0.4300*CD-4.14*A^2-0.7314*B^2-0.1213*C^2-0.8701*D^2

2-9- Examining the predicted model with laboratory results in the oxidative hydrogenation of propane

After analyzing the variance table and finding significant and effective variables on propylene yield, a polynomial model with statistical value is obtained for each answer. The graph of the experimental values of propylene production against the predicted results are shown in figures (7A) respectively. These graphs show that the laboratory values are almost on the Y=X line. Therefore, the presented models have been able to predict the laboratory results well 9Figure 7 A).

2-10- The effect of operating parameters

In this section, the mutual influence of all parameters on the percentage of propane conversion is analyzed (Figure 7 a)

.

2-10-1- Temperature effect

Figure (7B) shows the trend of temperature increase on the conversion rate, selectivity and conversion efficiency of propane to propylene. As we know, temperature is a very important variable to increase products. As can be seen in the figure below, at a temperature of 500 degrees Celsius, the selectivity of propylene is increasing, and with the increase in temperature, the efficiency of propylene production has decreased. It should be considered that this increase in temperature can be accompanied by an increase in coke production, which will decrease the operation time of the unit. By increasing the temperature from 500 to 600 degrees Celsius, the feed conversion rate increases and more propylene is produced. If at higher temperatures, it leads to the formation of coke and blockage of the catalyst, and the efficiency of propylene production tends from a maximum point to a minimum [44].

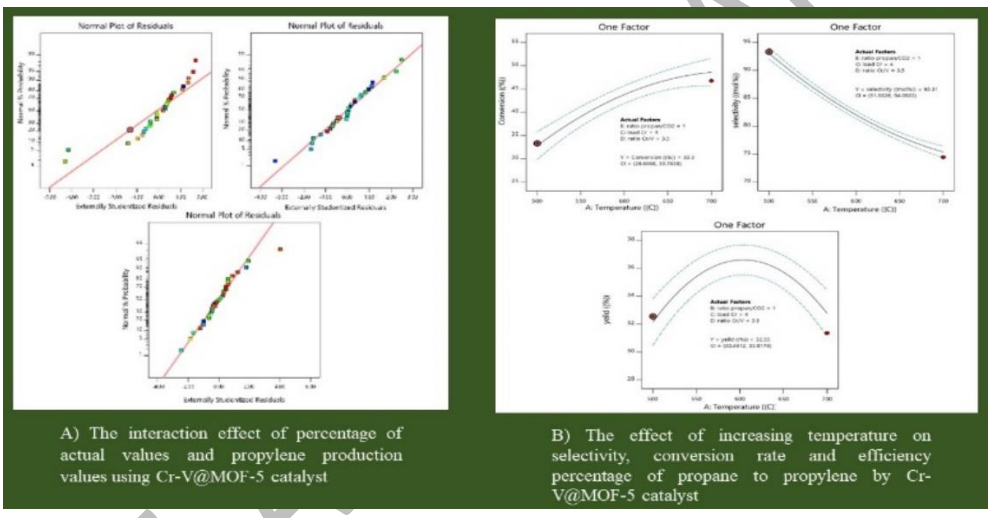


Figure (7). A) The interaction effect of percentage of actual values and propylene production values using Cr-V@MOF-5 catalyst & B) The effect of increasing temperature on selectivity, conversion rate and efficiency percentage of propane to propylene by Cr-V@MOF-5 catalyst

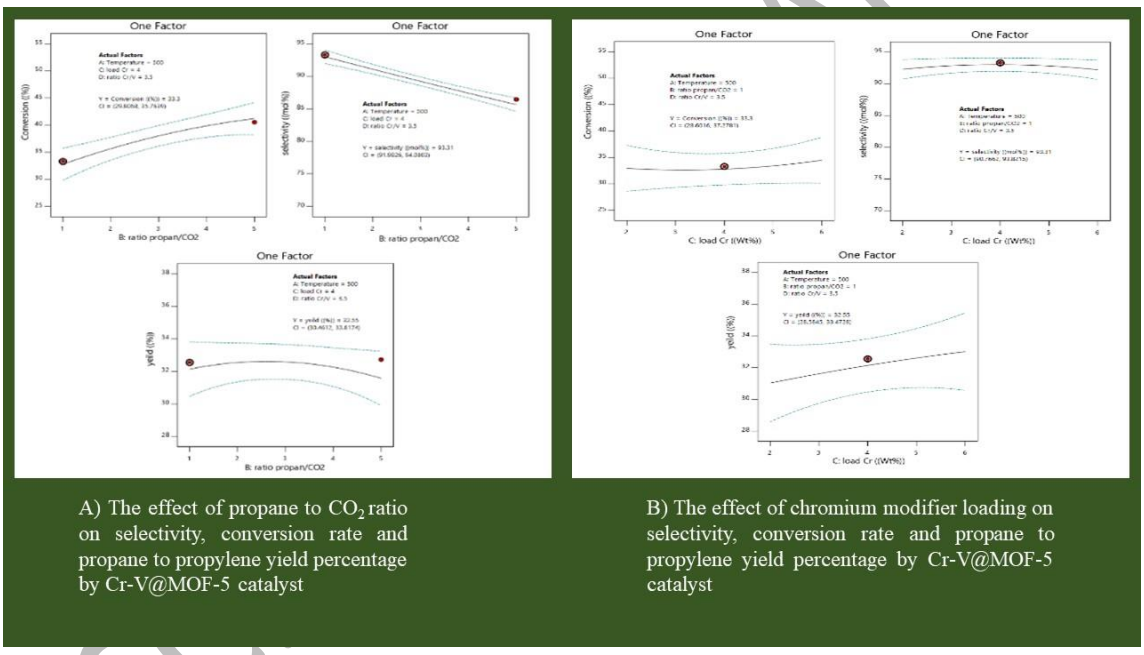
2-11- Effect of ratio of propane to carbon dioxide

The presence of oxygenated compounds such as carbon dioxide in the reaction limits the formation of coke and allows more catalyst to be used. Of course, the presence of many side reactions causes carbon oxides to be produced and the selectivity of producing the desired product (propylene) is not very high. Using CO_2 as an oxidizer easily increases the conversion power up to 10%. Therefore, because of the positive things mentioned about the use of CO_2 as an oxidant, it has gained more power [45]. As can be seen in the figure, when the ratio of propane to carbon dioxide is 1:1, the highest selectivity in converting propane to propylene has occurred. On the other hand, with an increase in the ratio of propane to carbon dioxide, due to the presence of more oxygen to carry out propane oxidation, the selectivity of propylene decreases because propane compounds are more involved in the oxidation reaction with carbon dioxide and play a lesser role in dehydrogenation, causing a decrease selectivity of propane and its conversion to propylene. By increasing the amount of propane more than the 3:1 ratio, the

volume of propane entering the pilot increases and the amount of oxidant is greatly reduced. Due to the imbalance in the propane feed and the amount of CO_2 oxidant, the selectivity in the production of propylene from propane will decrease (Figure 8A). [46-48]

2-12- The effect of chromium loading in the synthesis of Cr-V@MOF-5 catalyst

Considering the mechanism of the process and the strong role of the base on the catalytic performance, it can be said that one of the ways to obtain chromium oxide catalysts with better activity and efficiency in this process is to obtain a high distribution of chromium oxide nanoparticles through a base with acidic properties. The game and structure is suitable. As can be seen in the figure (8B), by increasing the amount of chromium loading from 2% to 4% by weight, the selectivity of propane to propylene conversion has increased, because by adding cream promoters to the catalyst base, the surface area of the catalyst has increased, and as a result, the selectivity will increase. By increasing the loading of chromium more than 4% by weight, it was found that the surface area is decreasing and it causes the accumulation of chromium in the overall structure of the catalyst and the blocking of the inter-pore space and reduces the selectivity performance in propane to propylene conversion [49-51].



A) The effect of propane to CO_2 ratio on selectivity, conversion rate and propane to propylene yield percentage by Cr-V@MOF-5 catalyst

B) The effect of chromium modifier loading on selectivity, conversion rate and propane to propylene yield percentage by Cr-V@MOF-5 catalyst

Figure (8). A) The effect of propane to CO_2 ratio on selectivity, conversion rate and propane to propylene yield percentage by Cr-V@MOF-5 catalyst & B) The effect of chromium modifier loading on selectivity, conversion rate and propane to propylene yield percentage by Cr-V@MOF-5 catalyst

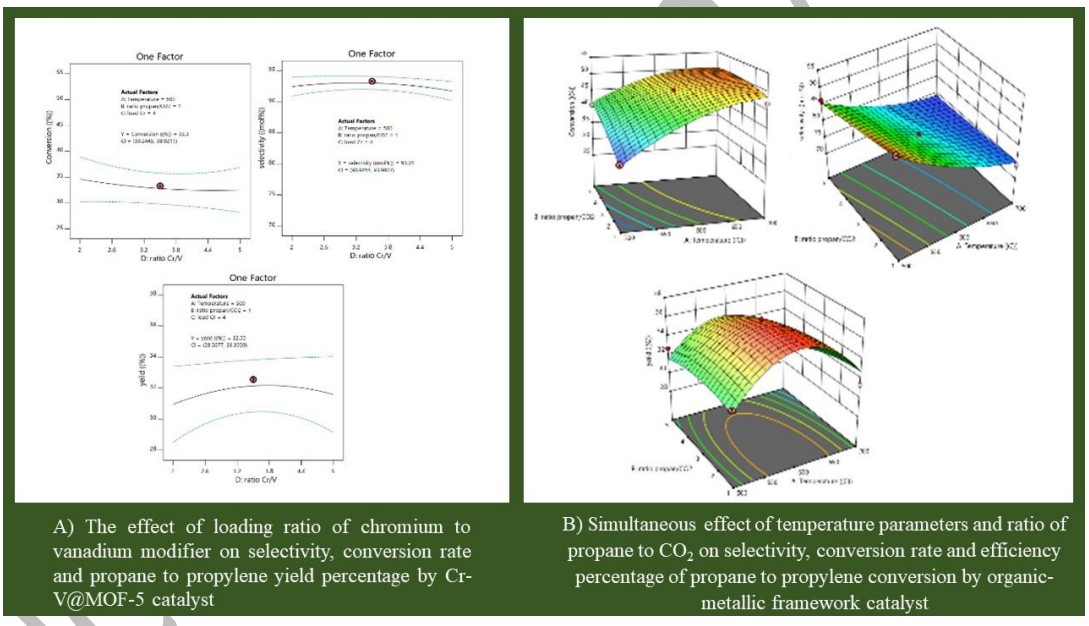
2-13- The effect of loading ratio of chromium to vanadium in catalyst synthesis

As can be seen in figure (9A), the loading ratio of chromium to vanadium was higher in the synthesized catalysts. When the loading ratio of chromium to vanadium is 3.5:1, the selectivity is increasing, but with the increase of the loading ratio of chromium to vanadium, clumping and accumulation has occurred in the catalyst structure and the selectivity decreases. This is because in the consumption amounts of chromium with a higher dose, clumping has occurred in the catalyst structure and the active sites of the catalyst are blocked due to clumping [52-54].

2-14- Investigating the simultaneous effect of effective parameters in the oxidative dehydrogenation of propane with organic-metallic framework catalyst

The effect of variable AB (A temperature and B ratio of propane to CO_2)

The graphs below show the simultaneous effect of temperature parameters and propane to CO_2 ratio. According to the diagram, increasing the temperature from 500 to 600 degrees Celsius has increased the selectivity, and at higher temperatures, the selectivity decreases due to the formation of coke and the blockage of the catalyst pores and the reduction of the surface area. According to the graphs below (Figure 16), when the ratio of propane to carbon dioxide is 1:1, the most selectivity has occurred in the conversion of propane to propylene. On the other hand, increasing the ratio of propane to carbon dioxide due to the presence of less oxygen to oxidize propane and propylene reduces the selectivity of propylene because propane compounds are involved in the dehydrogenation reaction on the one hand. On the other hand, lack of oxidizer causes more coke formation and hinders the progress of propane to propylene conversion [48]. Therefore, according to the graph below, it can be stated that with increasing temperature from 500 to 600°C and decreasing the ratio of propane from 5:1 to 1:1, the selectivity has increased, and also at temperatures lower than 600 °C, there is no interaction between parameters of temperature and ratio of carbon dioxide to propane, but the interaction increases with increasing temperature (Figure 9B).



A) The effect of loading ratio of chromium to vanadium modifier on selectivity, conversion rate and propane to propylene yield percentage by Cr-V@MOF-5 catalyst

B) Simultaneous effect of temperature parameters and ratio of propane to CO_2 on selectivity, conversion rate and efficiency percentage of propane to propylene conversion by organic-metallic framework catalyst

Figure (9). A) The effect of loading ratio of chromium to vanadium modifier on selectivity, conversion rate and propane to propylene yield percentage by Cr-V@MOF-5 catalyst & B) Simultaneous effect of temperature parameters and ratio of propane to CO_2 on selectivity, conversion rate and efficiency percentage of propane to propylene conversion by organic-metallic framework catalyst

2-15- The effect of AC variable (A temperature and C chromium loading rate in catalyst synthesis)

In the figure below (Figure 10A), the mutual influence of parameters of chromium loading percentage and temperature simultaneously on the percentage of propane conversion is investigated. It can be said that by increasing the loading percentage of chromium from 2 to 4 and decreasing the ratio of propane to carbon dioxide from 5:1 to 1:1, the percentage of propane conversion increases, and also by increasing the loading percentage of chromium, the surface area of the catalyst and the active surface of the catalyst increase found and the ratio

increases as a result of the selectivity. But with the increase of temperature more than 600 degrees Celsius, the formation of coke increases and it will cause the reduction of active catalytic levels.

2-16- The effect of variable AD (A temperature and D loading rate of chromium compared to vanadium in catalyst synthesis)

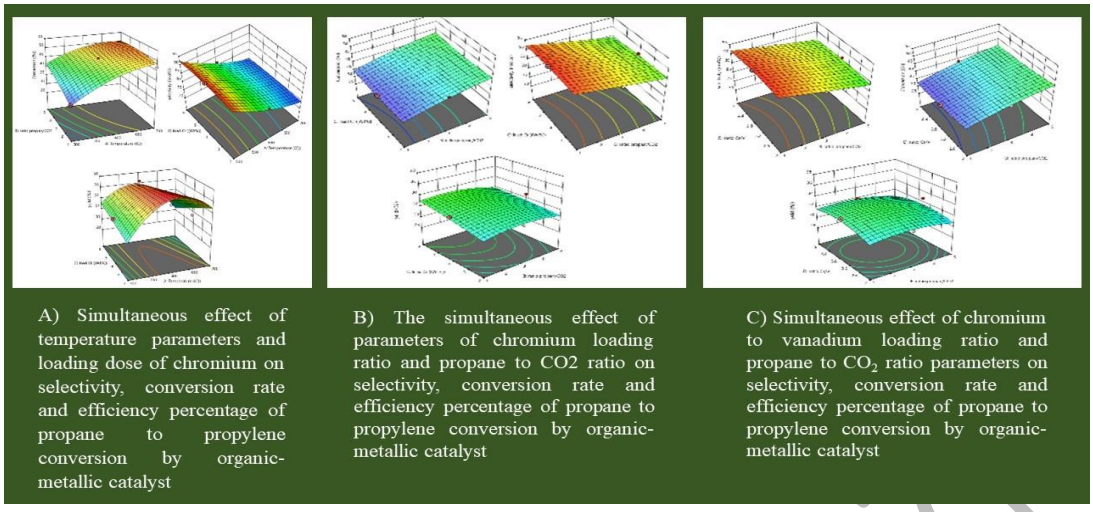
Due to the increase in the load of the modifier ratio of chromium to vanadium on the base surface of the catalyst and the formation of a solid and even crystalline structural framework, the selectivity increases with a ratio of 3.5 because the specific surface area of the catalyst increases, but with an increase in the ratio of chromium to vanadium, more than the ratio 3.5. The empty spaces and porous cavities of the catalyst are smaller and limited, thus leading to a decrease in selectivity. As the reaction temperature decreases from 600 °C to 500 °C and the loading percentage of chromium is higher, the percentage of selectivity decreases. The highest selectivity was possible at a temperature of 600 degrees Celsius and a ratio of chromium to vanadium of 3.5:1.

2-17- The effect of BC variable (B ratio of propane to carbon dioxide and C loading amount of chromium in catalyst synthesis)

The figure (10 B) shows the effect of the simultaneous parameters of the ratio of propane to CO_2 and the amount of chromium loading. According to the figure, it can be concluded that the greatest simultaneous effect of these two parameters has occurred in selectivity and the least effect can be seen in efficiency and conversion percentage. The best ratio for the propane/CO_2 parameter is 1:1 and the best chromium loading is 4% by weight.

2-18- The effect of BD variable (B is the ratio of propane to carbon dioxide and D is the loading ratio of chromium to vanadium in the synthesis of organic-metallic framework catalyst)

The figure (10 C) shows the effect of the simultaneous parameters of the ratio of propane to CO_2 and the ratio of chromium to vanadium loading. According to the figure, it can be concluded that the greatest simultaneous effect of these two parameters has occurred in selectivity and the least effect can be seen in efficiency and conversion percentage. The best ratio for propane/CO_2 parameter is 1:1 ratio and the best loading rate of chromium compared to vanadium is at the point of 3.5% by weight.



A) Simultaneous effect of temperature parameters and loading dose of chromium on selectivity, conversion rate and efficiency percentage of propane to propylene conversion by organic-metallic catalyst

B) The simultaneous effect of parameters of chromium loading ratio and propane to CO2 ratio on selectivity, conversion rate and efficiency percentage of propane to propylene conversion by organic-metallic catalyst

C) Simultaneous effect of chromium to vanadium loading ratio and propane to CO_2 ratio parameters on selectivity, conversion rate and efficiency percentage of propane to propylene conversion by organic-metallic catalyst

Figure (10). Simultaneous effect of some parameters

According to the design, in the next chapter, the optimal reaction conditions and the effect of operational parameters will be concluded.

3- Discussion

The physical properties of the synthesized catalysts play a very effective role in the oxidative dehydrogenation reactions of propane and its conversion to propylene. In these reactions, the method of loading the modifiers and the structural resistance of the catalyst determine the amount of the final propylene product. Reducing the resistance of the catalyst, increasing or decreasing the disproportionate diameter of the catalyst pores can be effective during the lifetime of the catalyst. Therefore, in this chapter, it was tried to briefly examine the physical properties of catalysts and then discuss the final results and draw conclusions.

3-1- Identification tests

The synthesized catalysts were investigated and identified by mechanical analysis methods in terms of their structure.

3-2- Optimization of reaction conditions: Catalysts were synthesized with different weight percentages. Then they were placed in the operating conditions obtained in the experimental design. The summary of the obtained results is according to the table (7).

Table (7). Optimization test resulting from experiment design with synthesized catalysts with different percentages

Catalyst	Temp(^{0}C)	ratio propane/CO_2	Cr	ratio Cr/V	Selectivity(mol)%
Cr-V/ZSM-48(2%)	600	3	4	3.5	88.71
Cr-V/ZSM-48(4%)	600	3	4	3.5	91.1
Cr-V/ZSM-48(6%)	600	3	4	3.5	88.89
Cr-V/ZSM-48(8%)	600	3	4	3.5	88.64
Catalyst	**Temp(^{0}C)**	**ratio propane/CO_2**	**Cr**	**ratio Cr/V**	**Selectivity(mol)%**
Cr-V/MOF-5(2%)	500	1	4	3.5	90.18
Cr-V/MOF-5(4%)	500	1	4	3.5	93.31
Cr-V/MOF-5(6%)	500	1	4	3.5	91.25
Cr-V/MOF-5(8%)	500	1	4	3.5	89.78

Evaluation of the ability of catalysts: Cr-V@ZSM-48 and Cr-V@MOF-5 catalysts were investigated for reusability and to evaluate the catalytic power after several times of reproducibility. Catalysts were used 5 times in other experiments with the same optimal conditions after performing the test under optimal conditions in the reactor. After 5 periods of use and analysis, the products obtained from the reaction were analyzed by a chromatographic device and it was found that the catalytic activity was preserved and no significant decrease in their activity was observed.

3-3- Examining the analysis results of the test design tests with the chromatography device

In order to analyze the product sample and identify the peaks, first the raw materials of the reaction were injected separately into the chromatography machine to determine the time of each peak. The peak of propane sample was observed at 6.77 and some ethylene at 3.2. The peak of the final product of propylene also appeared in the area of 11.105. Then the products obtained from the operating conditions that were carried out according to the experimental design were injected into the chromatography machine. The figure below briefly shows the result of the analysis with the chromatography device.

3-4- XRD analysis of catalysts based on ZSM-48

According to the shape of the black spectrum related to ZSM-48 precursor, it shows that the dominant crystalline phase is anatase. According to the blue and red spectra, there are distinct peaks that appear at precise angles. The peaks at angles of 8.9, 9.5, 15.3, 24.8, 30.1, 45.2=2θ indicate the extreme crystallinity of these catalysts. By increasing the loading of chromium and vanadium on the surface of the catalyst base, this substance tends to be placed on the base in a crystalline form, which is consistent with other research results (Figure 11 & 12).

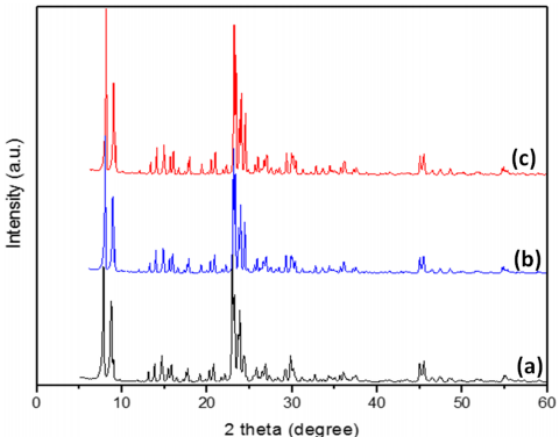
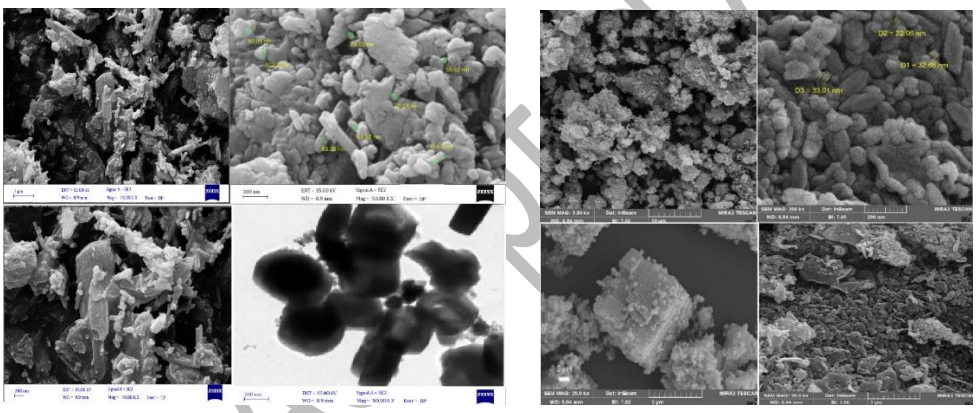


Figure 11: XRD sample ZSM-48 black, XRD sample Cr@ZSM-48 blue, XRD sample Cr-V@ZSM-48 red

3-5- SEM analysis

By using the scanning electron microscope image, it is possible to identify the morphology, the distribution of the accumulation, the shape and the average size of the particles.



A B

Figure 12. A) SEM image of Cr-V@ZSM-48 composition and B) SEM image of Cr-V@MOF-5 composition

4- Conclusion

The results showed and obtained from comparing the performance evaluation of catalysts based on organic-metallic framework and zeolite, based on the conversion rate of propane feed along with the obtained selectivity and also the efficiency of propylene production at different temperatures. The general trend of the results shows that the selectivity decreases with increasing temperature. Considering the structural instability of the catalyst at temperatures higher than 600 degrees Celsius and the intensification of side reactions at high temperatures, it is a natural thing.

As the results illustrate:

- Due to the closeness of propane conversion rate and propylene selectivity, it is possible to realize the high selectivity of the prepared samples even at a temperature of 500 degrees Celsius, which is different from the performance of these two catalysts due to the desirable acidic properties. With a brief look at the results, it can be seen that at all temperatures, the Cr-V@MOF5 catalyst has a

remarkable advantage in terms of performance compared to other catalysts. NH_3-TPD analysis indicates the presence of strong acid sites using MOF-5 base.

- According to the statistical analysis performed with design expert software for the production of propylene with Cr-V@MOF_5 catalyst, the optimal conditions are in accordance with the effective parameters such as the amount of chromium loading in the catalyst, the reaction temperature, the ratio of propane to CO_2, and the ratio of loading of chromium to vanadium, respectively. The ratio was determined to be 4%, 400 degrees Celsius, 1:1, 3.5:1. Under these conditions, the amount of propylene obtained is estimated at 95.3%.
- According to the results of analysis of variance obtained from the software, it was found that the temperature parameter has the greatest impact compared to other parameters such as the amount of chromium loading and the ratio of propane to CO_2. Also, the coefficient of variance (R^2) obtained by the software is 0.9936, which indicates the high accuracy of the proposed model. In optimal conditions, Cr-V@ZSM-48 catalyst performance was investigated and the results showed that the amount of chromium loading in the catalyst, the reaction temperature, the ratio of propane to CO_2, and the loading ratio of chromium to vanadium are respectively equal to 4%, 500 degrees Celsius, 3: 1, 3.5:1 was determined and under these conditions the amount of propylene obtained is 91.1%.
- After obtaining the optimal conditions for the conversion of propane to propylene, the stability of the produced catalysts with the passage of time and reproducibility were investigated and their conversion percentage under these conditions was found to be 32.3%.
- According to the evaluations and the results obtained in this study, it was shown that the main reason for the presence of catalytic properties in nanomaterials is their high surface-to-volume ratio, and other factors such as the shape and substrate used are very effective. The network structure of these nano cavity catalysts is three-dimensional, which consists of tetrahedra containing trivalent or tetravalent metal ions.
- As a result of electric charge balance in the structure of these catalysts, Bronsted acid sites are created in the vicinity of oxygen atoms. Appropriate acid strength and small pore size are the most important features of these catalysts, which increases the catalytic activity and selectivity to light olefins. The main problem of these catalysts in industrial processes is their short life due to the formation of coke. Larger olefins and branched isomers are formed inside the empty spaces of the catalyst and irreversibly adsorbed on the acid sites, as a result, the concentration of the acid sites of the catalyst decreases.
- The use of different metals, including transition metals, as improvers by creating new acid sites, corrects the acidity of the catalyst and increases the lifespan of these catalysts. Based on the results of XRD analysis, unit cell parameters have increased with the increase in the weight percentage of chromium and vanadium metal, which indicates the change of the crystal structure and the improvement of the catalytic properties. Also, according to FTIR and NH3-TPD analyses, the number of acidic sites, especially strong acidic sites, has decreased. The results of SEM analysis in the synthesis of catalysts with different ratios of chromium to vanadium have shown that the size of the catalyst particles has decreased with the increase in the amount of chromium. Based on the results obtained from the reactor tests, with the distribution of chromium and vanadium metals in the

structure of the catalysts, a significant increase in the selectivity of the propylene ratio has been observed.

- In the Cr-V@MOF5 catalyst, due to the shrinking of the pores to the nano level (the factor of improving the selectivity compared to zeolites), the increase of the external surface (the factor of increasing the number of acidic active points and increasing the activity) and the reduction of the residence time of the molecules ultimately lead to a decrease in production coke in the channels and increased the selectivity. Improving the performance of catalysts using organic-metallic framework nanoparticles promises that if these nano catalysts can be prepared on an industrial scale, we can witness a huge transformation in industries, especially the oil and petrochemical industries.

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