

Evaluation of catalytic activity of chromium oxide by activated carbon obtained from olive trash

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Abstract

This study was to investigate and compare the catalytic activity of supported and unsupported chromium oxide on chemically activated carbon due to the properties of this oxide and its economic importance as a distinct and widespread catalyst. Chemically activated carbon was used as a support prepared from the remnants of pressing olive fruits, due to the availability of this substance in abundance in olive presses. To study the catalytic activity of the prepared samples, the dissociation reaction of hydrogen peroxide was chosen as a model reaction for a catalytic process to clarify the relationship between the volume of oxygen rising against time on supported and unsupported chromium oxide catalysts. The support and also on the unsupport of pure activated carbon (AC) for comparison at a constant temperature of 25°C, as well as the effect of the mass of the catalyst (10Cr / AC) on the rate of decomposition of hydrogen peroxide, and the effect of the reaction temperature on the rate of decomposition of hydrogen peroxide catalyst to calculate the activation energies of the reaction using the Arrhenius equation In order to determine the thermodynamic function that explains the dissociation reaction. When comparing the obtained results, it was found that the values of the hydrogen peroxide dissociation reaction rate constant are consistent with the values of the activation entropy more than the values of the activation energies.

Keywords: Catalyst, Chromium Oxide, Activated Carbon, Hydrogen Peroxide, Entropy.

المخلص:

اختيرت هذه الدراسة لتقييم النشاط التحفيزي لأكسيد الكروم المدعم والغير المدعم على الكربون المنشط كيميائياً نظراً لخواص هذا الأكسيد وأهميته الاقتصادية كعامل محفز متميز واسع الانتشار. واستخدم الكربون المنشط كيميائياً كدعامة تم تحضيره من مخلفات عصر ثمار الزيتون لتوفر هذه المادة بكثرة في معاصر الزيتون، ولدراسة النشاط الحفزي للعينات المُحضرة تم اختيار تفاعل التفكك لأكسيد الهيدروجين كتفاعل نموذج لعملية حفزية لتوضيح العلاقة بين حجم الأكسجين المتساعد مقابل الزمن على حفازات أكسيد الكروم المدعم والغير المدعم وأيضا على الدعامة للكربون المنشط (AC) النقية للمقارنة عند درجة حرارة ثابتة 25°C ، وكذلك تأثير كتلة العامل الحفاز (10Cr/AC) على معدل تفكك فوق أكسيد الهيدروجين، وتأثير درجة حرارة التفاعل على معدل التفكك لأكسيد الهيدروجين المحفز لحساب طاقات التنشيط للتفاعل باستخدام معادلة ارهينوس بهدف تحديد الدالة الديناميكية الحرارية المفسرة لتفاعل التفكك. عند مقارنة النتائج المتحصل عليها وجد أن قيم ثابت معدل تفاعل تفكك فوق أكسيد الهيدروجين تتفق مع قيم انتروبيا التنشيط أكثر من قيم طاقات التنشيط، يبين لنا هذا أن (ΔS) تلعب دور رئيسي لتحديد رتبة النشاط التحفيزي لمثل هذه النوعية من الحفازات.

1. Introduction

The term catalyst refers to certain materials that rely on changing the rate and direction of or initiating a specific reaction, and it was used to explain a group of experimental observations on some chemical transformations that he attributed to a catalytic force, referring to the decomposition of bodies by this force [1]. A catalyst is defined as any substance that changes the rate of a chemical reaction without changing its quantity or chemical properties, with the exception that its physical properties may change, and that physical changes may differ from one reaction to the next [2]. and that this change is only in the crystal structure without changing the chemical composition. Catalysts work to change the speed of many reactions, either positively or negatively, and the positive catalyst works to increase the speed of the reaction, whereas the negative

catalyst works to slow down the speed of the chemical reaction, and the negative catalyst may break down the original catalyst and prevent it from performing its function as it changes the status of reaction mechanics [3,4].

There are some types of catalysts that induce some reactions that would not occur naturally in the absence of them, and there are some reactions to which no type of catalyst is added, where the reaction speed changes as a result of one of the materials resulting from the reaction, which is considered a catalyst, and the reaction speed changes with the concentration of this resulting substance. This sort of catalysis is known as autocatalysis or autocatalysis, and it results from an increase in the speed of a chemical reaction caused by one of the products of the reaction [5,6].

In this study, the catalytic activity of supported and unsupported chromium oxide on chemically activated carbon was investigated and compared due to the properties of this oxide and its economic and technological importance as a distinct and widespread catalyst and its various and multiple industrial applications.

2.Preparation of supported and unsupported chromium oxide catalysts

Each of the following steps has been taken:

- A sample of chemically activated carbon was prepared using zinc chloride from the remnants of pressing olives, due to the abundance of this raw material in olive presses.
- Preparation of supported and unsupported chromium oxide catalysts from a sample of chromium nitrate, because this salt gives chromium oxide (Cr_2O_3) by burning.
- Preparation of an unsupported chromium oxide catalyst with a concentration of 10% by weight chromium on activated carbon. The prepared sample was treated thermally to compare the catalytic activity of the two samples of the supported and unsupported oxide. This sample was called (10Cr/AC).
- Choosing the appropriate weight of the catalyst, the effect of the reaction temperature on the decomposition rate of hydrogen peroxide was studied, the activation energies for the reaction were calculated using the Arrhenius equation, then a calculation of the thermodynamic functions of the decomposition reaction was performed in order to

determine the thermodynamic function that explains the catalytic activity.

3. Result and discussion

3.1. The relationship between the volume of oxygen rising (V_t) cm^3 and the time (t) per minute

To clarify this relationship, a separate experiment was carried out for each of the chromium oxide sample (Cr_2O_3) supported and unsupported (10Cr/AC) as well as on the pure support for comparison, at a reaction temperature of 30C, The obtained results are shown in the following tables:

Table 1: Unsupported chromium oxide (Cr_2O_3) sample at reaction temperature 25°C - weight used 51mg

time (min)	V_t (cm^3)
1.19	3.0
2.95	4.0
4.07	5.0
7.37	6.0
10.05	7.0
13.65	8.0
17.27	9.0
21.27	10.0
24.59	11.0
29.33	12.0

Table 2: Supported chromium oxide sample (10Cr/AC) at reaction temperature 25°C- weight used 51mg

time (min)	V_t (cm^3)
0.65	4.0
1.38	8.0
1.57	9.0
1.91	11.0
2.91	17.0
3.07	18.0
3.98	24.0
4.43	27.0
5.16	33.0
5.71	37.0
6.01	39.0
6.23	41.0

6.98	47.0
7.38	50.0

Table 3: Pure Activated Carbon Sample AC at Reaction Temperature 25°C - Weight Used 51mg

time (min)	Vt (cm ³)
3.07	2.0
12.87	4.0
14.90	4.5
17.84	5.0
22.13	5.5
27.64	6.0

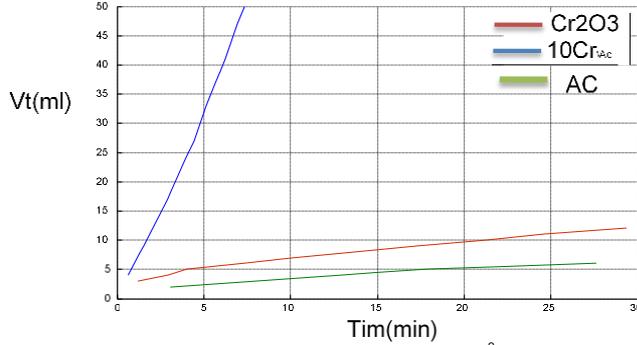


Figure 1: The volume of oxygen released at 25°C and the weight used is 51mg

it is noted that the relationships represented are all linear relationships in the studied time range, it is clear that the effect of Chromium oxide catalyst supported on activated carbon on the catalytic decomposition of hydrogen peroxide has a positive effect.

Table 4: The values of hydrogen peroxide dissociation rate constant for unsupported chromium oxide (Cr₂O₃) and supported (10Cr/AC) and pure support AC

K x 10 ²	Sample
4.67	Cr ₂ O ₃
192.23	10Cr / AC
2.99	AC

3.2. Studying the effect of 10Cr/AC catalyst mass on the decomposition rate of hydrogen peroxide

The effect of the weight of the catalyst on the disintegration rate constant H_2O_2 was chosen in order to investigate the effect of this factor on the disintegration rate as well as the appropriate conditions for conducting this reaction in order to select the catalytic activity of the samples. In the catalyst mass in the range (10–102mg), the results obtained are shown in the following tables:

Table 5: Supported chromium oxide sample (10Cr/AC) at reaction temperature 25°C - weight used 10mg

time (min)	Vt (cm ³)
3.85	3.0
5.85	4.0
7.90	5.0
10.11	6.0
12.16	7.0
15.95	9.0
18.05	10.0
19.92	11.0
22.42	12.0
24.33	13.0
28.60	15.0

Table 6: Supported chromium oxide sample (10Cr/AC) at reaction temperature 25°C - used weight 32mg

time (min)	Vt (cm ³)
0.97	2.5
2.16	4.5
2.44	5.0
3.03	6.0
3.65	7.0
4.18	8.0
4.76	9.0
5.33	10.0
5.81	11.0
6.33	12.0

Table 7: Supported chromium oxide sample (10Cr/AC) at reaction temperature 25°C - weight used 71mg

time (min)	Vt (cm ³)
0.61	4.0
0.80	5.0
1.16	7.0
1.56	9.0
1.96	11.0
2.35	13.0
2.71	15.0
3.10	17.0
3.45	19.0
3.78	21.0

Table 8: Supported chromium oxide sample (10Cr/AC) at reaction temperature 25°C - weight used 102mg

time (min)	Vt (cm ³)
0.42	4.0
0.68	6.0
0.97	8.0
1.23	10.0
1.52	12.0
1.78	14.0
2.03	16.0
2.28	18.0
2.53	20.0
2.72	22.0
2.97	24.0

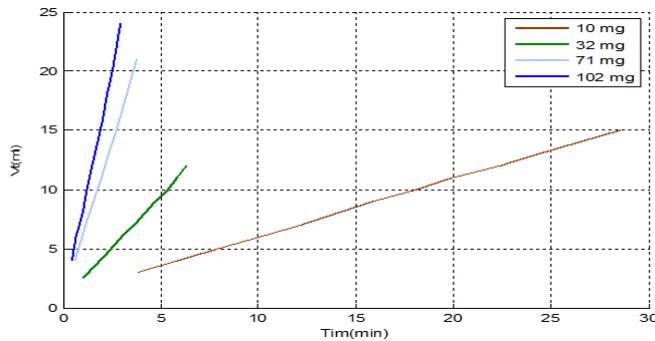


Figure 2: The volume of oxygen released for the supported chromium oxide sample (10Cr/AC) at a constant temperature

Table 9: Relationship between disintegration reaction rate (k) and catalyst weight (10Cr/AC)

$K \times 10^3 \text{ (sec}^{-1}\text{)}$	weight mg
8.15	10
29.63	32
88.05	71
133.33	102

Through the experimental results obtained, as well as after calculating the reaction rate constant corresponding to the different weights of the catalyst used, it is clear that the dissociation rate constant is directly proportional to the mass of the catalyst.

3.3. Effect of reaction temperature on the rate constant of hydrogen peroxide dissociation catalyzed by unsupported chromium oxide sample (Cr_2O_3).

To investigate the influence of reaction temperature on the dissociation rate constant of H_2O_2 equal weights of 20mg of chromium oxide (Cr_2O_3) at a concentration of 30% were taken. When the reaction rate constants were obtained in the thermal range of 25 - 45 degrees Celsius:

Table 10: Unsupported chromium oxide (Cr_2O_3) sample at reaction temperature 25°C - weight used 20mg

time (min)	$V_t \text{ (cm}^3\text{)}$
8.80	4.0
13.63	5.0
17.75	5.5
21.63	6.0
25.38	6.5
29.92	7.0
34.01	7.5

Table 11: Unsupported chromium oxide (Cr_2O_3) sample at reaction temperature 30°C - weight used 20mg

time (min)	$V_t \text{ (cm}^3\text{)}$
1.16	4.0
2.75	4.5
4.25	5.0
6.30	5.5
8.51	6.0
11.28	6.5

13.03	7.0
15.78	7.5
18.98	8.0
22.05	8.5

Table 12: Unsupported chromium oxide (Cr_2O_3) sample at reaction temperature 35°C - weight used 20mg

time (min)	Vt (cm^3)
1.96	4.0
4.13	5.0
5.63	5.5
7.76	6.0
10.43	6.5
11.71	7.0
14.85	7.5
17.98	8.0
20.21	8.5
22.71	9.0
24.05	9.5

Table 13: Unsupported chromium oxide (Cr_2O_3) sample at reaction temperature 40°C - weight used 20mg

time (min)	Vt (cm^3)
5.06	8
6.41	9
7.76	10
9.21	11
10.93	12
12.53	13
14.06	14
15.91	15
17.61	16
19.31	17
21.06	18
22.95	19

Table 14: Unsupported chromium oxide (Cr_2O_3) sample at reaction temperature 45°C - weight used 20mg

time (min)	Vt (cm^3)
3.83	6
4.98	7

5.98	8
7.28	9
8.88	10
10.13	11
11.86	12
13.20	13

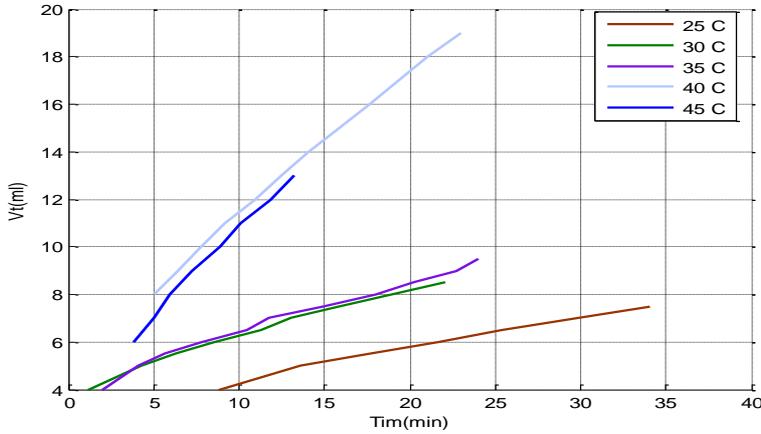


Figure 3: The volume of oxygen released for the unsupported chromium oxide (Cr_2O_3) sample

Table 15: Relationship between $\ln k$ and reciprocal of absolute temperature ($1/T$) for unsupported chromium oxide (Cr_2O_3) catalyst

T (°C)	T (K)	$\frac{1}{T} \times 10^5$	K	Lnk
26	299	334.45	0.1000	-2.3026
30	303	330.03	0.1515	-1.8872
33	306	326.80	0.1667	-1.7916
40	313	319.48	0.3846	-0.9556
45	318	314.47	0.5556	-0.5877

We note that the rate constant (k) increases with the increase in the reaction temperature according to the Arrhenius equation. The activation energy of the hydrogen peroxide catalyzed dissociation reaction was calculated using the Arrhenius equation, and the thermodynamic functions of the reaction (ΔS , ΔH , ΔG) were calculated by the Ehring's Equation. Table 17 illustrates this:

Table 16: Thermodynamic functions for the catalytic decomposition of hydrogen peroxide on unsupported chromium oxide (Cr₂O₃) catalyst

Ea (Kj . mol ⁻¹)	75.512
ΔG (Kj . mol ⁻¹).30C	78.933
ΔH (Kj . mol ⁻¹).30C	72.995
ΔS (j .K ⁻¹ . mol ⁻¹).30C	-19.60

3.4. The effect of reaction temperature on the rate constant of hydrogen peroxide dissociation catalyzed by a chromium oxide sample supported on activated carbon (10Cr/AC)

To investigate the influence of reaction temperature on the dissociation rate constant of H₂O₂, equal weights (20mg) of a sample (10Cr/AC) and 5ml of 30% H₂O₂ were used. Temperatures (45, 35, 30, 25) °C were used in the experiments.

Table 17: Supported chromium oxide sample (10Cr /AC) at reaction temperature 25°C - weight used 20mg

time (min)	Vt (cm ³)
1.55	5
2.37	6
3.85	8
4.53	9
5.28	10
6.70	12
9.51	16
12.21	20
13.63	22
16.55	26

Table 18: Supported chromium oxide sample (10Cr/AC) at reaction temperature 30°C - weight used 20mg

time (min)	Vt (cm ³)
1.28	6
2.33	8
3.34	10
4.28	12
5.16	14
6.08	16
7.05	18

7.90	20
8.76	22
9.73	24
10.63	26

Table 19: Supported Chromium Oxide Sample (10Cr/AC) at Reaction Temperature 35°C - Weight Used 20mg

time (min)	Vt (cm ³)
0.30	3
1.65	8
2.33	10
2.97	12
3.55	14
4.13	16
4.76	18
5.27	20
5.86	22
6.44	24
6.92	26
7.45	28
8.02	30
8.60	32

Table 20: Supported chromium oxide sample (10Cr/AC) at reaction temperature 45°C - weight used 20mg

time (min)	Vt (cm ³)
0.56	3
0.96	6
1.33	9
1.66	10
1.98	12
2.30	15
2.60	16
2.91	18
3.23	20
3.53	22
3.83	24
4.18	26

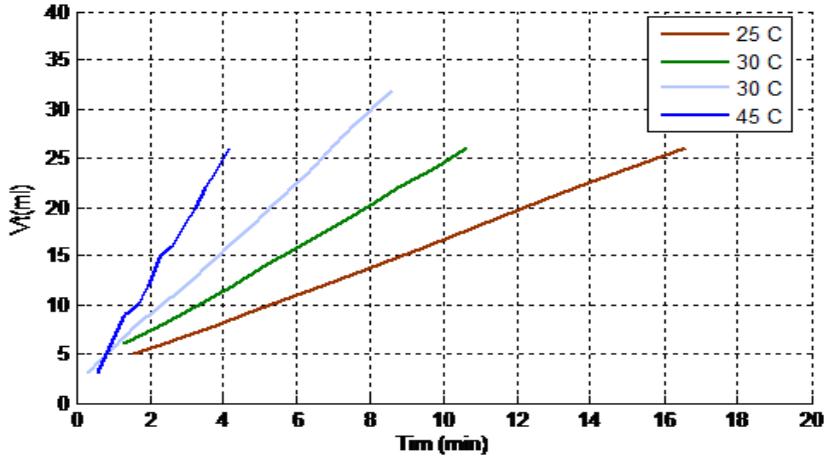


Figure 4: The volume of oxygen released for the supported chromium oxide sample (10Cr/AC) at constant volume

The collected data showed that the reaction rate constants were between 25 and 45 degrees Celsius. According to the Arrhenius equation, the rate constant (k) increases as the reaction temperature rises. Using the Arrhenius equation, the activation energy for the catalytic dissociation process of hydrogen peroxide was computed. Ering's equation was also used to compute the thermodynamic functions of the reaction (ΔS , ΔH , and ΔG). The following tables illustrate this:

Table 21: Relationship between LNK vs. Reciprocal Absolute Temperature (1/T) for Supported Chromium Oxide (10Cr /AC) Catalyst

T (C)	T(k)	$\frac{1}{T} \times 10^5$	K (sec ⁻¹)	Lnk
26	299	334.45	0.9195	-0.0839
30	303	330.03	1.4167	0.3483
35	308	324.68	2.2857	0.8267
42	315	317.46	4.3590	1.4722

Table 22: Thermodynamic functions for the catalytic decomposition of hydrogen peroxide on a catalyst (10Cr/AC)

Ea (Kj . mol ⁻¹)	76.675
ΔG (Kj . mol ⁻¹).30C	73.320

ΔH (Kj . mol ⁻¹).30C	74.158
ΔS (j . k ⁻¹ . mol ⁻¹).30C	2.77

The reaction study for the catalytic decomposition of supported and unsupported chromium superoxide Cr₂O₃ on activated carbon (10Cr/AC) shows that the activity towards the dissociation reaction is superior in the case of the supported catalyst compared to the unsupported catalyst, and the distinct catalytic activity of the supported chromium oxide is revealed by the values of the dissociation reaction's rate constant. This result is predicted when compared to unsupported chromium oxide synthesized under the same conditions since the pure Cr₂O₃ oxide sample comprises the majority of the chromium element with a triple valence Cr⁺³ While the chromium oxide is supported on activated carbon, the chromium element on carbon undergoes a partial reduction from the triple valence Cr⁺³ to par zero Cr. Thus, oxidation-reduction centers of the type Cr⁰ - Cr⁺³ are formed, on which the catalytic cracking of the hydrogen oxide difference occurs, and the proof of the arrangement of the catalytic activity of the samples in this study is to exploit a kinetic function that does not depend on the surface area of the samples, as the internal space (gaps) does not participate in the dissolution of hydrogen peroxide in aqueous media. The activation energy or change in the activation entropy of the dissociation reaction, which depends on the type of catalyst and its electronic composition more than the morphology of the surface, is the optimal test for such a function, as the activation energy represents the true self-catalytic activity. The activity of the samples can be compared based on which catalysts are most effective. H₂O₂ dissociation has the lowest activation energy.

The activation energies of unsupported chromium oxide catalyst Cr₂O₃ [75.5 kj. mol⁻¹] and fortified (10Cr/AC) [76.7 kj. mol⁻¹] obtained by plotting the results lnk vs. (1/T) according to the Arrhenius equation show non-essential differences despite the large differences in catalytic activity, and the slight differences in the activation energy can be explained on the basis of diffusion effects and The reaction is occurring near the catalyst's surface. As a result

of the solid dispersing in the liquid, a thin coating of liquid with a thickness of about 10m adheres to the solid's surface. In order for the reaction to continue, the diffusion control will govern the overall reaction kinetics of heterogeneous hydrogen peroxide dissociation. As a result, the observed rate law is the diffusion law for hydrogen peroxide under the experimental conditions used, and as the catalyst mass increases, there are more granules around which diffusion layers can form, which explains the dependence of the dissociation reaction rate constant on the catalyst mass and that the diffusion kinetics is unaffected by the catalyst composition. The results show the importance of using the Arrhenius equation to estimate the change in the activation entropy of the catalytic dissociation, and that the values of the activation entropy depend more on the composition of the catalyst and can be attributed to the entropy of adsorption of the reactants on the surface of the catalyst. The obtained results show that the entropy values differ and are positive ($2.77 \text{ Jol.k}^{-1}.\text{mol}^{-1}$) for a supported chromium oxide catalyst and negative ($-19.60 \text{ Jol.k}^{-1}.\text{mol}^{-1}$) for an unsupported chromium oxide catalyst. Because the supported and reaction rate values are compatible with the related activation entropy values, it performs the primary role in determining the rank.

4. Conclusions

We demonstrated that, when interpreting the relationship between the volume of oxygen rising against time on catalysts for unsupported and supported chromium oxide, as well as on pure activated carbon (AC) support, it was found that the catalytic activity increased $10\text{Cr}/\text{AC} > \text{Cr}_2\text{O}_3 > \text{AC}$. And according to that:

- The rate of catalytic dissociation is directly proportional to the mass of the catalyst.
- The supported chromium oxide samples have distinct catalytic activity compared to the unsupported sample, which shows the effect of chromium oxide support on the activated carbon in increasing its catalytic activity.

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