A kinetic study of acetone acidic oxidation with KMnO₄ in the absence and presence of CuO/γ-Al₂O₃ as a heterogeneous nano-catalyst

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Acetone oxidation; Reaction kinetics; Heterogeneous nano-catalyst; CuO; γ-Al₂O₃; Reaction rate law.

Abstract. A kinetic study of acetone acidic oxidation with aqueous KMnO₄ in the absence and presence of CuO nanocatalysts was carried out. The rate laws and activation energies were evaluated in case of reaction with no catalyst and with 0, 2.5, 5, and 10 wt.% of CuO on γ-Al₂O₃. Catalysts were prepared by the impregnation method and characterized by ICP-OES, XRD, BET, and TEM. Products were analyzed by UV-VIS and examinations were performed by changing concentrations of a reactant and keeping the rest constant to determine the order of the reaction for the targeted one. Results showed that, in the absence and presence of nano-catalysts, the order of the reaction for all KMnO₄, (CH₃)₂CO, and H₂SO₄ was one. The rate constants for the reaction in the absence of catalyst and in the presence of 0, 2.5, 5 and 10 wt% CuO were 0.0022, 0.0023, 0.0025, 0.0026, and 0.0029 L².mole⁻².min⁻¹; in addition, the activation energies for them were 56.767, 56.807, 53.978, 50.075, and 46.774 kJ.mol⁻¹, respectively. Moreover, there was no relationship between the product concentrations and the rate of reaction. Therefore, the results showed that CuO on γ-Al₂O₃ had a significant effect on the reaction kinetics and can be a reliable heterogeneous catalyst for it.

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1. Introduction

Acetone is a very useful material in many chemical and non-chemical industries. It is used as solvent and reagent for many reactions such as synthesis of methyl-methacrylate and bisphenol-A, which are both intensive products. It also has medical, cosmetic, and domestic uses. However, the presence of acetone as a toxic, colorless, volatile and flammable liquid in the aqueous and gaseous wastes of these industries causes environmental problems [1–3]. It has been demonstrated that acetone inhalation can negatively affect the central nervous system of humans, and also its anticonvulsant effect has been proven for the model animal [4].

Recently, environmental problems have become the reason for researchers to pay closer attention to acetone oxidation in gaseous and aqueous media and to the optimization of this process. In the gaseous medium, the process has proceeded in the presence of different catalysts such as platinum, palladium, cobalt, copper, nickel, and manganese [5–9]. Many chemical industrial reactions are run in the presence of solid catalysts. To increase the exposed surface area, the catalyst is commonly distributed on the surface of a porous support (or carrier). Common supports include silica gel (SiO₂), alumina (Al₂O₃),
carbon (in the form of charcoal), and diatomaceous earth. The support may be inert or may contribute to catalytic activity [10-12]. In a liquid medium, the oxidation of organic compounds in the presence of potassium permanganate has been widely investigated. Aqueous acetone oxidation has also been performed in the presence of KMnO₄ in different conditions.

Metallc copper and its different oxidation states have been used as catalysts for the oxidation of organic compounds. They are highly effective in carbon monoxide oxidation in different conditions [13,14]. The performance of CuO/Cu₂O nanoparticles as the electro-catalyst of formaldehyde oxidation in the liquid phase has been studied. Results have introduced these nanoparticles as promising catalysts for formaldehyde oxidation [15]. The oxidation of hydrogen peroxide has been carried out on the CuO/zeolite nano-catalyst. The effect of CuO loading on the performance of the nano-catalyst has been investigated. Results showed more oxidation levels up to 100% for higher loadings of CuO on zeolite [16]. The copper (II) oxide was used for acetone gas sensing based on acetone oxidation reaction at the operation temperatures of 200–300°C. Results showed that, in such a condition, CuO exhibited a good tendency for acetone oxidation in the presence of NH₃ and methanol gases [17]. The CuO nanoparticles supported on γ-Al₂O₃, pillared clay, and TiO₂ were used as catalysts for phenols oxidation in aqueous phases. The largest amount of produced CO₂ and the lowest amount of Cu leaching were in the presence of CuO/γ-Al₂O₃ nano-catalyst. It was also the most economically favorable catalyst [18].

In this research, a kinetics study of the acidic oxidation of acetone is carried out in the absence and presence of CuO nanoparticles supported on γ-Al₂O₃. The CuO amount varies by 0 (only γ-Al₂O₃), 2.5, 5, and 10% weights of the catalyst, and the kinetic parameters of the reaction are evaluated in their presence. The reaction rate laws are assumed as Rate = k[A]ⁿ, and the data related to reactant concentrations versus time extracted and [A]⁻¹, [A]¹⁻, and ln[A] versus time are plotted so as to find a linear relationship. Afterward, the relationship between the rate constants and temperature is investigated through Arrhenius equation to find activation energies of the reactions.

2. Experimental

2.1. Materials

Sulfuric acid 98%, acetone, and potassium permanganate as reagents were purchased from Merck. Cu(NO₃)₂·3H₂O was purchased from Sigma-Aldrich and used as a CuO precursor. Condea Vista Catalox γ-alumina with 212.4 m²·g⁻¹ specific surface area and sodium oxide (Na₂O) < 0.05 (ppm). Silica (SiO₂) < 0.9 (ppm). Sulfate (SO₄) < 1.5 (ppm) impurities was provided and treated. Deionized water was used as the water content of the reaction medium.

2.2. Methods

2.2.1. Catalyst preparation

Catalysts were prepared via the impregnation method. Firstly, gamma alumina was treated in a laboratory furnace at 400°C to burn and remove possible organic impurities. Suitable solutions of Cu(NO₃)₂·3H₂O were prepared in deionized water. For the preparation of CuO/γ-Al₂O₃ with 2.5, 5, and 10% weights of CuO, the prepared solutions were added to γ-Al₂O₃ and heated for water evaporation and to make a sludge. The sludges were dried at 120°C for 2 h and, then, calcined at 400°C for 4 h for the CuO phase formation.

2.2.2. Catalyst characterization

After calcination, the catalysts were analyzed using ICP-OES, XRD, BET, and TEM to determine their characteristics. The CuO loading amounts on γ-Al₂O₃ were analyzed by Varian VISTA-MPX inductively coupled plasma-optical emission spectrometry (ICP-OES) instrument. The XRD patterns of catalysts were obtained with X’Pert Philips type: 3040/60 X-ray diffractometer with monochromatized Cu/Kα radiation. The surface area, pore volume, and average pore sizes of catalysts that are effective parameters in catalytic performance were measured by BELSORP-mini II, MicrotracBEL Company, Japan. For this purpose, samples were degassed at 200°C for 4 h under 50 mTorr vacuum, and the parameters were determined. Transmission electron microscopy, TEM. (Philips CM20, 100kV, equipped with a NARON energy dispersive spectrometer with germanium detector) was used to illustrate the presence of particles in the bulk of nano-porous support. Samples for TEM micrographs were treated by ultrasonic dispersion in ethanol. The suspensions were dropped onto a carbon-coated copper grid.

2.2.3. The experiment procedure

To determine the order of the reaction based on Relation (1) and Eq. (2), in the absence and presence of CuO/γ-Al₂O₃ catalysts, the concentration of one reactant was much less than that of others. The reaction was performed at 25°C and atmospheric pressure. Specified volumes of reaction mixture were sampled at specific time reactions, and the remaining potassium permanganate was detected by the UV-VIS spectrometer at a wavelength of 526 nm. Experiments done for calculating Eₚ were carried out by modifying the temperature and detecting the remaining potassium permanganate at different specific reaction times. To find a probable linear relationship between time and concentration, diagrams of [A]⁻¹, [A]⁻ₓ, and ln[A] versus time are plotted.
6K MnO 4 + 9H 2 SO 4 + 5(CH 3 ) 2 CO → 3K 2 SO 4 +6MnSO 4 + 5CH 3 COOH + 5HCOOH +9H 2 O. \[ \text{Rate} = k[K\text{MnO}_4]^{m}[H_2\text{SO}_4]^{n}[(\text{CH}_3)_2\text{CO}]^{l} \]
\[ [\text{K}_2\text{SO}_4]^{1}[\text{MnSO}_4]^{2}[\text{CH}_3\text{C(OH)O}]^{2}[\text{HCOOH}]^{3}. \]

Activation energies of the reactions were calculated based on Arrhenius equation (Eq. (3)), which depicts the interdependence of temperature and rate constant. It has been empirically observed that if the temperature range is in a narrow range, the logarithm of the rate constant with changes in $T^{-1}$ linearly changes and the line slope is negative. In this term, if the logarithm of the rate constant is equal to $T^{-1}$, then $E_a$ has no dependence on $T$. The factor $A$ is the number of collisions per unit time and volume unit, yet not for all collisions. The factor holds for those collisions that are in the right direction and have enough energy to reach the peak. If the constant of the reaction rate follows the Arrhenius equation, it can be calculated based on other parameters of Arrhenius equation by measuring the reaction rate constant at different temperatures.

\[ \frac{d\ln k}{dT} = \frac{E_a}{RT^2}, \quad k = Ae^{(-E_a/RT)}. \] (3)

3. Results and discussion

3.1. Catalyst characterization

The ICP-OES was used to determine CuO amounts that were impregnated on γ-AI2O3. Results are reported in Table 1. As shown in the table, the values of impregnated metals are very close to the expected ones.

Table 1. The results of ICP-OES analysis of calcined catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Catalyst name</th>
<th>Expected values (wt%)</th>
<th>ICP-OES values (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-AI2O3</td>
<td>CuO-0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuO/γ-AI2O3-2.5wt%</td>
<td>CuO-2.5</td>
<td>2.5</td>
<td>2.46</td>
</tr>
<tr>
<td>CuO/γ-AI2O3-5wt%</td>
<td>CuO-5</td>
<td>5</td>
<td>4.93</td>
</tr>
<tr>
<td>CuO/γ-AI2O3-10wt%</td>
<td>CuO-10</td>
<td>10</td>
<td>9.88</td>
</tr>
</tbody>
</table>

Figure 1 shows TEM micrographs of γ-AI2O3 (a) and CuO/γ-AI2O3 (b) with 10 wt% of CuO as a catalyst with the best performance. The figure clearly shows the nano-porous structure of γ-AI2O3 and approves the favorable incorporation of CuO particles with nano sizes and porous support.

The XRD patterns of γ-AI2O3 and CuO/γ-AI2O3 with different CuO amounts are shown in Figure 2. Peaks at 2θ = 35.5, 38.7, 49.1 and peaks at 2θ = 37.4, 45.9, 61.6, and 66.6 are related to CuO and γ-AI2O3, respectively.

The surface characterization results of all catalysts are reported in Table 2. Results of BET surface area ($S_{BET}$) showed that, in all cases, the addition of metal oxide to γ-AI2O3 reduced the $S_{BET}$ of the catalysts. Pore volume and average pore diameter also decreased with the increasing CuO loading. Pore blockage by loaded CuO is responsible for this increase.
3.2. Order of the reaction for reactants and products

To find the order of the reaction for KMnO₄, a solution was prepared using acetone, KMnO₄ and H₂SO₄ with concentrations of 0.206, 0.00486, and 0.36 M, respectively. The KMnO₄ concentration was determined in time periods. Data were collected and diagrams were plotted. Results showed that there was a linear relationship between the reaction time and the logarithm of KMnO₄ concentration. Therefore, the obtained order of the reaction for potassium permanganate was one. For acetone, a solution was prepared using acetone, KMnO₄ and H₂SO₄ with concentrations of 0.0264, 0.0101, and 0.36 M, respectively. There was also a linear relationship between reaction time and the logarithm of acetone concentration. Therefore, the obtained order of the reaction for acetone was also one. Figure 3 shows the relationship between KMnO₄ and acetone concentrations over time.

For H₂SO₄, 10 solutions with H₂SO₄ concentrations of 0.36, 0.50, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, and 2.50 with the constant concentration of acetone and potassium permanganate were prepared. Results showed that there was a linear relationship between the concentration of H₂SO₄ and reaction rate. Therefore, the obtained order of reaction for H₂SO₄ was one. Figure 4 shows diagrams of the order of the reaction for H₂SO₄.

To determine the order of the reaction for products, solutions with constant concentrations of acetone (0.206 mole.L⁻¹), KMnO₄ (0.005 mole.L⁻¹), and H₂SO₄ (1.00 mole.L⁻¹) and different MnSO₄ concentrations were prepared as the reaction medium. The remaining KMnO₄ was detected at the same reaction times and results are shown in Table 1. It was observed that there was no relationship between MnSO₄ concentration and reaction rate. To illustrate the dependence of the reaction rate on K₂SO₄, acetic acid, and formic acid concentrations, similar experiments were designed and, thus, similar results were obtained. Therefore, the reaction rate law becomes as follows:

\[
Rate = k[KMnO₄][H₂SO₄]^{1/2}(CH₃)₂CO^{1/2}.
\]

3.3. Activation energy of the non-catalytic reaction

Ten same solutions as reaction media were prepared with acetone and KMnO₄ and H₂SO₄ concentrations of 0.206, 0.005, and 1.00 mole.L⁻¹, respectively. Reaction was carried out at ten different temperatures, and the remaining KMnO₄ was detected at different time reactions. The initial rate and rate constant were calculated according to the initial concentrations and reaction rate law in the time range at different temperatures. Diagram of ln k versus inverse temperature was plotted (Figure 5), and -Ea.R⁻¹ and -ln A were evaluated according to the line equation, as shown in Table 3.
3.4. Effect of CuO/γ-Al₂O₃ on Arrhenius parameters

To determine the effect of prepared catalysts on Arrhenius parameters, the same experiments shown in Section 3.3 were designed and performed in the presence of CuO-0, CuO-2.5, CuO-5, and CuO-10. Table 4 shows the Arrhenius parameters of the reaction in the presence of catalysts. Figure 6 also shows the linear relationship between -ln k and inverse temperature for all catalysts. Figure 7 compares the activation energies for reaction in the absence and presence of CuO/γ-Al₂O₃.

According to the results, reaction in the presence of γ-Al₂O₃ (CuO-0) had slightly higher activation energy than non-catalytic one. It can be related to the fact that γ-Al₂O₃ has no notable catalytic effect on the reaction of acetone acidic oxidation with K₂MnO₄, like many other reactions. Actually, γ-Al₂O₃ is used as catalyst support because of amphoteric and inert behavior in the reaction medium and the high surface area for metal or metal oxide distribution [19]. However, the reaction had slightly greater activation energy in the presence of γ-Al₂O₃ than non-catalytic reaction, which can be attributed to the homogeneity of the reaction medium in the non-catalytic one. The γ-Al₂O₃ creates a heterogeneous medium for reaction and can limit the mass transfer of reactants during the reaction. Therefore, higher activation energy is

Figure 4. The rate of reaction versus initial H₂SO₄ concentration for the first (a) 25, (b) 50, (c) 75, and (d) 100 minutes.

Figure 5. Linear function of -ln k vs T⁻¹ confirms that the constant of the reaction rate in the absence of heterogeneous catalysts follows the Arrhenius equation.

Table 3. Arrhenius equation parameters extracted from -ln k vs T⁻¹ diagram for reaction in the absence of heterogeneous catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Eₐ / R</th>
<th>Eₐ (kJ)</th>
<th>ln A</th>
<th>A (L•mol⁻¹•s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-0</td>
<td>6832.7</td>
<td>56.807</td>
<td>13.427</td>
<td>678017</td>
</tr>
<tr>
<td>CuO-2.5</td>
<td>6492.5</td>
<td>53.978</td>
<td>12.492</td>
<td>266199</td>
</tr>
<tr>
<td>CuO-5</td>
<td>6023</td>
<td>50.075</td>
<td>11.441</td>
<td>90681</td>
</tr>
<tr>
<td>CuO-10</td>
<td>5626.7</td>
<td>46.777</td>
<td>10.630</td>
<td>40945</td>
</tr>
</tbody>
</table>

Table 4. Arrhenius equation parameters extracted from -ln k vs 1/ T⁻¹ diagram.
Figure 6. The linear relationship between $-\ln k$ and inverse temperature for (a) CuO-0, (b) CuO-2.5, (c) CuO-5, and (d) CuO-10.

Figure 7. The activation energies for reaction in the absence and presence of different concentrations CuO on the catalyst.

required for the reaction progress. With the addition of CuO concentration to $\gamma$-$\text{Al}_2\text{O}_3$, the activation energy started to decrease. It is related to the catalytic effect of CuO on acidic oxidation of acetone in the presence of KMnO$_4$. Figure 8 shows the suggested mechanisms for acidic acetone oxidation with KMnO$_4$ on CuO nano-catalyst. According to similar studies, two mechanisms can be suggested. Since the reaction mechanism of ketones oxidation contains enol creation as intermediates, the intermediate is 2-hydroxypropene in case of acetone oxidation, and it appears that CuO facilitates the C=O bond adsorption on the catalyst surface and makes enols more stable (Figure 8(a)). Therefore, the formation of the activated complex requires less energy than that in the non-catalytic process. On the other hand, it has been reported that CuO has catalytic effect on oxygenates (alcohols and ethers) production from syngas or sugar precursors [20]. The effect is associated with the tendency of CuO to C-O group adsorption. Therefore, C-O group of enols also can be adsorbed on CuO surface, which can be another reason for enol stability in the presence of this catalyst. More stable intermediate needs less activation energy. The description of another mechanism is based on MnO$_4^-$ adsorption on CuO surface. Since MnO$_4^-$ has negative charge, it can interact with half-filled orbital of CuO. More CuO sites on the catalyst surface cause more interactions with MnO$_4^-$ and, subsequently, more enol oxidation (Figure 8(b)). Therefore, the tendency of MnO$_4^-$ to be adsorbed on CuO surface decreases the activation energy.

4. Conclusion

A kinetic study of acidic oxidation of acetone with KMnO$_4$ in the absence and presence of CuO supported on a nano-porous structure of $\gamma$-$\text{Al}_2\text{O}_3$ was carried out. There were linear relationships between the reaction time and the logarithms of acetone and KMnO$_4$ concentrations and, also, between the concentration of $\text{H}_2\text{SO}_4$ and the reaction rate. Therefore, the reaction order for all of them was measured to be one. There was no relationship between the product concentrations and the rate of the reaction. Results showed a
significant catalytic effect of CuO in this reaction. It was demonstrated that the 10 wt% increase of CuO in catalyst formula decreased 17.5% of activation energy of the reaction, which corresponded to the tendency of CuO to the adsorption of species with C=C and C-O functional groups. As the enols are intermediates in the ketone oxidation mechanism, these adsorptions make 2-hydroxypropene more stable on the catalyst surface. The stability of intermediates causes lower activation energy requirement. The adsorption of MnO$_4^-$ on CuO surface because of the interaction between the negative charge and half-filled orbital of CuO and, subsequently, the oxidation of enols can be another way for acetone oxidation. Therefore, the CuO/γ-Al$_2$O$_3$ nano-catalyst, which is an inexpensive material, can be good candidate for a heterogeneous catalyst for the acidic oxidation of acetone with KMnO$_4$.

References


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Biographies

Mohammad Taha Badri received a BSc degree from Shahid Rajaee University and a MS degree in Physical Chemistry from Kharazmi University in Tehran. He is a PhD student at Kishan University. His research field is about statistical mechanics and the study of thermodynamic quantities. The calculation of internal energy is based on the Ising model on a two-layer square lattice as a sample of his research work. Currently, his subject matters of interest cover the chemical kinetics and obtaining kinetic parameters and determining the mechanism.

Mohammad Barati is a faculty member of Kishan University who works in the field of Applied Chemistry. Most of his research topics cover the field of gaseous, liquid, and solid fuels produced from biore-sources. Biodiesel production from algae and other oily biomass in supercritical conditions is also included. Water, methanol, hexane, and acetone in supercritical conditions are used for biomass conversion to biofuels in the Lab. Nanocomposites for bio applications are his other field of research. Chemicals from medicinal herbs are considered for applying to the controlled drug delivery systems, especially polymer nanocomposites. Recent studies have also researched the production of biodiesel from algae and other oily biomass under supercritical conditions. His PhD thesis is focused on the production of hydrogen gas from biomass feedstock using catalytic sub and supercritical water gasification. Ni, Ru, Cu, and K are the metals he is working on. His MSc thesis is focused on inhibiting the steel electrochemical corrosion with polymer nanocomposite
coatings. The polymer matrix contains polyaniline as an electroactive polymer and Zn metal nanoparticles applied as an additive.

**Sayyed Hossein Rasa** is a faculty member of Kashan University who works in the field of Physical Chemistry. Most of his research topics cover the field of thermodynamics and kinetics. A study of two-phase systems, theoretical and empirical analysis of liquid-liquid systems of liquid systems, kinetic studies, and the provision of a mechanism such as the kinetic study of sulfite ion oxidation, enzymatic reactions, hydroquinone oxidation and reactive oxygen species in several systems using simulation are a few examples of his research work. Recent studies have also researched the synthesis and properties of nanostructures.