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Development of High-Surface-Area Alumina-Supported Catalysts for the Generation of Hydrogen from $NaBH_4$

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$NaBH_4$'ten Hidrojen Üretimi için Yüksek Yüzey Alanlı Alümina Destekli Katalizörlerin Geliştirilmesi

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Abstract

Hydrogen as a valuable energy carrier plays a significant role in renewable energy technologies to reduce the greenhouse gas emission into the atmosphere. However, natural hydrogen gas does not exist in the universe and should be gained from hydrogen-containing compounds. In this regard, metal hydrides are excellent candidates for producing hydrogen gas. Among complex metal hydrides, sodium borohydride ($NaBH_4$) possesses its advantages due to its enhanced hydrogen storage capacity and low cost. In the present study, hydrogen gas was generated through the catalytic hydrolysis of $NaBH_4$. In this regard, high-surface-area alumina-supported Ni/Al_2O_3, $NiCo/Al_2O_3$, and $Ru-NiCo/Al_2O_3$ catalysts have been prepared via wash coating method and tested in a continuous flow reactor. The results indicate that the $Ru-NiCo/Al_2O_3$ catalyst with a specific surface area of 154.40 $m^2 \cdot g^{-1}$ showed the highest initial catalytic activity of 0.031 $mmol \cdot s^{-1} \cdot g^{-1}$ but with a rapid loss in its activity. Compared to that, despite a lower initial catalytic activity in the presence of the $NiCo/Al_2O_3$ catalyst, the hydrogen generation kept rising during the reaction, and 225 mL H_2 was produced after 100 min. Therefore, the $NiCo/Al_2O_3$ catalyst with a surface area of 165.84 $m^2 \cdot g^{-1}$ can be proposed as a promising alternative.

Keywords: *Sodium borohydride; Hydrolysis; Hydrogen; Alumina; Catalyst*

Öz

Değerli bir enerji taşıyıcısı olan hidrojen, yenilenebilir enerji teknolojilerinde atmosfere sera gazı emisyonunun azaltılmasında önemli bir rol oynamaktadır. Ancak hidrojen gazı doğada mevcut olmayıp hidrojen içeren bileşiklerden elde edilmesi gerekmektedir. Metal hidrürler hidrojen gazı üretimi için mükemmel adaylardır. Karmaşık metal hidrürler arasında sodyum borhidrür ($NaBH_4$), gelişmiş hidrojen depolama kapasitesi ve düşük maliyeti gibi çeşitli avantajlara sahiptir. Bu çalışmada katalitik hidroliz yoluyla $NaBH_4$'ten hidrojen gazı üretilmektedir. Bu amaçla yıkayarak kaplama yöntemi ile yüksek yüzey alanına sahip alümina destekli Ni/Al_2O_3, $NiCo/Al_2O_3$ ve $Ru-NiCo/Al_2O_3$ yapılı katalizörler hazırlanmış olup bu katalizörler sürekli akışlı reaktörde test edilmiştir. Elde edilen sonuçlara göre yüzey alanı 154.40 $m^2 \cdot g^{-1}$ olan $Ru-NiCo/Al_2O_3$ yapılı katalizör başlangıçta 0.031 $mmol \cdot s^{-1} \cdot g^{-1}$ değerinde en yüksek katalitik aktiviteye sahip olup reaksiyon boyunca aktivitesinde hızlı bir azalma gözlemlenmiştir. $NiCo/Al_2O_3$ yapılı katalizörün varlığında ise başlangıçta daha düşük bir katalitik aktivite görülmesine rağmen reaksiyon boyunca hidrojen üretimi hızla artmaya devam etmiş olup 100 dk. sonra 225 ml H_2 gazı üretilmiştir. Bu nedenle 165.84 $m^2 \cdot g^{-1}$ yüzey alanına sahip $NiCo/Al_2O_3$ yapılı katalizör alternatif olarak önerilebilir.

Anahtar Kelimeler: *Sodyum borhidrür; Hidroliz; Hidrojen; Alümina; Katalizör*

1. Introduction

Air pollution with the following issue “climate change” is one of the most important issues for societies. Using fossil fuels as energy sources harms air quality. Through the combustion of fossil fuels, the amount of atmospheric carbon dioxide (CO_2) is increased. The increase in the CO_2 amount causes the formation of CO_2 layer around the earth resulting in global warming (Baykara et al. 2022). Hence, the utilization of alternative energy sources is essential to reduce CO_2 emissions. In this respect, hydrogen is a valuable energy carrier, and its reaction with the air produces just water. On the one hand, the usage of hydrogen as an energy carrier can mostly cover the energy demand, on the other hand, it reduces CO_2 emissions because of its carbon-free nature (Baykara et al. 2018). Compared to the storage of fossil fuels, the storage of hydrogen gas is challenging and still needs to be improved (Zhu et al. 2023). In this regard, metal hydrides are good candidates to store hydrogen, conveniently. They are classified as binary, intermetallic, and complex hydrides. This type of material has the potential to desorb the pre-absorbed hydrogen atoms forming the hydrogen gas. Binary metal hydrides in a nominal chemical formula of MH_x consist of a main group or transition metal and hydrogen (Luo et al. 2020). AB_xY_x represents intermetallic metal hydrides, herein, A and B are for hydrating and non-hydrating metals, respectively (Schneemann et al. 2018). Complex hydrides shown as MEMx include alkaline metal cations and hydrogen-

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containing anions such as alanates (AlH_4^-) and borohydrates (BH_4^-) and possess the highest hydrogen storage capacity (Schneemann et al. 2018). Hydrolysis of complex metal hydrides is a convenient method to release hydrogen at ambient temperature. $LiBH_4$, $NaBH_4$ and $Mg(BH_4)_2$ possess high hydrogen storage capacity and are suitable for obtaining hydrogen via the hydrolysis process (Zhu et al. 2023, Laversenne et al. 2008)). In the presence of these metal hydrides, hydrogen obtained has a high purity required for real-time proton membrane fuel cell applications. $LiBH_4$ possesses the highest hydrogen storage capacity with 13.9 wt%, however, due to its enhanced cost, it is hard to use for large-scale applications. $Mg(BH_4)_2$ with its hydrogen capacity of 12.8 wt% is another candidate for hydrolysis processes, but a large amount of heat is released during the reaction. In addition, toxic B_2H_6 is produced as a byproduct that makes the process unfavorable (Solovev et al. 2018).

Regarding its lower price and non-toxic byproduct during hydrolysis, $NaBH_4$ gained more attraction to release hydrogen at ambient temperature. Several studies have been conducted to enhance the hydrogen evolution rate through catalytic hydrolysis (Balkanli and Figen 2019, Özkar and Zahmakiran 2005, Xu et al. 2024, Zhu et al. 2023). In the presence of noble metals, high catalytic activity has been reported (Patel and Miotello 2015), however, the higher cost of noble metals is a significant reason for developing of alternative catalysts with transition metals. Additionally, unsupported catalysts suffer from the agglomeration of its particles which leads to a decrease in catalytic activity. Hence, the utilization of support materials is inevitable (Fernandes et al. 2009). Several studies have been focused on the implementation of noble metals such as Ru, Pt, Pd, and Rh on the carbon nanotubes (CNTs) or cobalt oxide (Co_3O_4) supports (Bozkurt et al. 2019, Uzundurukan and Devrim 2019, Zhang et al. 2021). Catalysts which include non-noble metals such as Co, Ni, Fe, and Cu exhibit relatively good performance in hydrolysis of $NaBH_4$ (Filiz and Figen 2019, Wang et al. 2021). Furthermore, their lower cost compared to the noble-metal-included catalysts widens their application in this process.

Regarding the necessity of support materials in catalyst development for the hydrolysis of $NaBH_4$, high-surface-area alumina (Al_2O_3) pellets were used in this study. Alumina pellets were coated with Ni-Co alloy and doped with Ru to be tested in hydrolysis of $NaBH_4$. The as-prepared catalysts have been characterized by BET, ICP-MS, and XRD analyses, and their catalytic performances were tested in a continuous reactor under the flow of $NaBH_4$ solution.

2. Materials and Methods

2.1 Synthesis of catalysts

In this study, three different Al_2O_3-supported catalysts were prepared via the wash coating method listed in Table 1. The synthesis procedure consists of three steps. For the preparation of 1M precursor solutions, the appropriate amount of metal salts ($NiN_2O_6{\cdot}6H_2O$, Alfa Aeser, $Co(NO_3)_2{\cdot}6H_2O$, Carlo Erba and $RuCl_3{\cdot}xH_2O$), Merck) were dissolved in deionized water, and citric acid was added as chelate agent ($n_{\text{nitric acid}}$:$n_{\text{metal cation}}$=1.5). The pH of each solution was adjusted to 7 with ammonia solution. In the second step, Al_2O_3 pellets (Alfa Aesar, high surface catalyst support) were washed in the precursor solutions several times and then oven-dried at 225 °C. In the last step, they have been calcined at 700 °C for 2h. For the synthesis of Ru-NiCo/Al_2O_3 catalysts, Al_2O_3 pellets were firstly washed in 1M precursor solution including nickel- and cobalt salts and calcined at 700 °C for 2 h. NiCo/Al_2O_3 pellets obtained after the first calcination step were washed in 0.05 M precursor solution consisting of Ru salt. After this step, pellets were recalcined at 500 °C for 2h.

2.2 Characterization of catalysts

The crystalline phases of all samples were determined by XRD analyses. XRD measurements were conducted by a Philips Panalytical EMPYREAN X-ray diffractometer (XRD) in a diffraction angle range of 10° to 90° with CuKα radiation. Brunauer–Emmett–Teller (BET) isotherm technique was used to determine the specific surface area of all samples. BET measurements were carried out by nitrogen adsorption using Micromeritcs Gemini VII BET Instrument. Before BET measurements, each sample was pretreated at 300 °C for 12h to remove the humidity from the sample. The metal contents in each sample were determined by Agilent Technologies 7700x inductively coupled plasma mass spectrometry (ICP-MS). Prior to measurements, samples were prepared for analysis in ETHOS EASY MILESTONE microwave acid digestion system at 210 °C.

2.3 Catalytic hydrolysis of $NaBH_4$

The catalytic hydrolysis of $NaBH_4$ was carried out in an integrated continuous system as shown in Figure 1. To prevent self-hydrolysis of $NaBH_4$ at ambient temperature (Schlesinger et al. 1953), firstly, an 0.5 M alkaline solution of $NaBH_4$ (c_{NaBH_4}: c_{NaOH}=1:1) was prepared, and the solution was fed to the reactor (filled with 1.7 g catalyst) by a peristaltic pump with the flow rate of 3 ml·min^{-1}. The amount of generated hydrogen gas was determined by the water displacement method. All reactions were carried out at room temperature. Before testing the

catalytic performance of the catalysts, they were reduced in 0.075 M $NaBH_4$-solution.

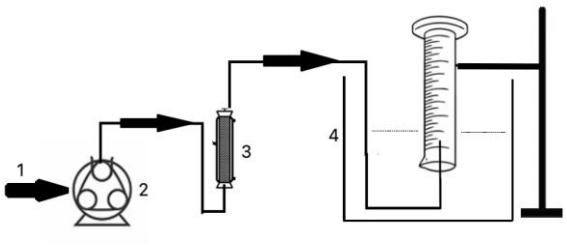

Figure 1. The scheme of the catalytic performance system (1: inlet solution, 2: peristaltic pump, 3: fix-bed reactor, 4: gas collection (water displacement method))

3. Results and Discussions

3.1. Characterization of catalysts

Pristine alumina pellets possess a high surface area of 212.48 $m^2 \cdot g^{-1}$. In Table 1, the BET surface areas of Ni/Al_2O_3, $NiCo/Al_2O_3$, and $Ru\text{-}NiCo/Al_2O_3$ catalysts were listed, and a decrease in the specific surface area has been noticed. These results revealed that the alumina pellets have been successfully coated with the relevant metal oxide structure. In addition, the $NiCo/Al_2O_3$ catalyst has the highest, and because of the additional coating procedure, the catalyst $Ru\text{-}NiCo/Al_2O_3$ possess the lowest specific surface area, as expected. ICP-MS analyses have been conducted to determine the metal contents in each catalyst. $NiCo/Al_2O_3$ and $Ru\text{-}NiCo/Al_2O_3$ catalysts have similar Co and Ni content, however, in $Ru\text{-}NiCo/Al_2O_3$ catalyst, the presence of Ru has been detected which shows that the coating with RuO_2 has been accomplished. The crystal phases of all catalysts were determined by XRD analyses, and XRD patterns are shown in Figure 2. The diffraction pattern of pristine alumina displays significant peaks at 2θ of 37.12°, 39.49°, 45.06°, and 67.52°. The Ni/Al_2O_3 catalyst possesses peaks at 2θ of 37.11°, 45.14°, 59.81°, and 65.75°, which are assigned to the crystal phase of $NiAl_2O_4$. Furthermore, the presence of the $NiAl_2O_4$ phase indicates that the Ni^{2+} cations were successfully incorporated into the alumina structure. The XRD pattern of the $NiCo/Al_2O_3$ catalyst shows the characteristic peaks for the Co_2NiO_4 crystal phase at 2θ of 37.32°, 60.18° and 66.16°. Herein, these results confirm the deposition of Co_2NiO_4 on the alumina. The $Ru\text{-}NiCo/Al_2O_3$ catalyst differs from the $NiCo/Al_2O_3$ through RuO coating, and the presence of RuO has been proved at 2θ of 28.30° and 54.45°.

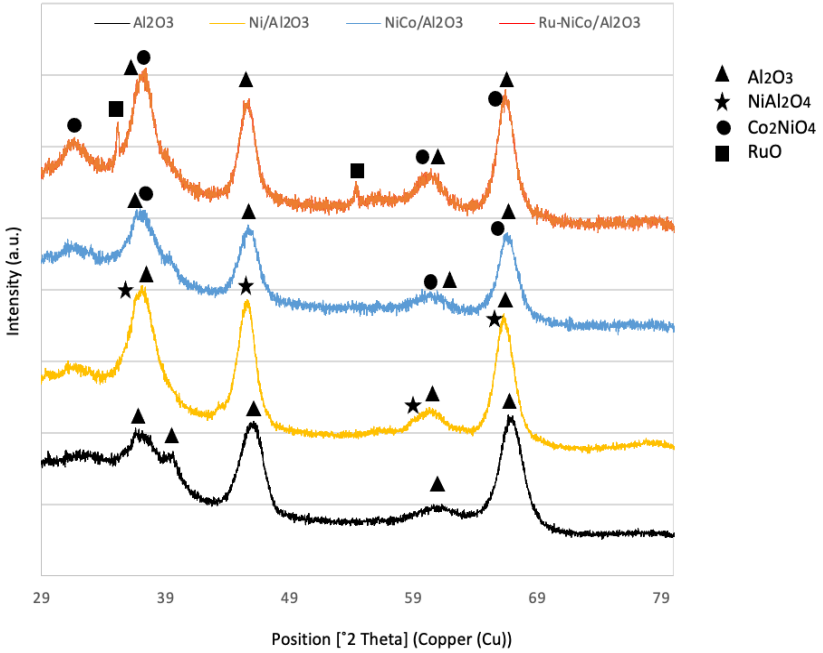

Figure 2. XRD patterns of all synthesized catalysts.

Table 1. Synthesized catalysts with their crystal phases by XRD, metal contents by ICP-MS and specific surface areas by BET

Code for catalysts	Crystal phases by XRD (Reference Code)	Metal contents by ICP-MS				BET ($m^2 \cdot g^{-1}$)
		Ru (wt %)	Co (wt %)	Ni (wt %)	Al (wt %)	
Ni/Al_2O_3	$NiAl_2O_4$ (01-078-6954) Al_2O_3 (00-056-1186)	-	-	8.20 ± 0.16	31.54 ± 2.1	165.44
$NiCo/Al_2O_3$	Co_2NiO_4 (04-018-4105) Al_2O_3 (00-056-1186)	-	4.16 ± 0.22	2.86 ± 0.05	32.55 ± 2.2	165.84
$Ru\text{-}NiCo/Al_2O_3$	RuO_2 (00-040-1290) Co_2NiO_4 (04-018-4105) Al_2O_3 (00-056-1186)	0.02 ± 0.0024	3.96 ± 0.21	2.89 ± 0.06	31.32 ± 2.1	154.40

3.2. Catalytic hydrolysis of $NaBH_4$

The hydrogen generation through $NaBH_4$ hydrolysis takes place through the following reaction (Equation (1)) (Liu and Li 2009). In this process, 0.5 M $NaBH_4$ solution was fed to the reactor continuously, and hydrogen generation was measured by the water displacement method.

$$NaBH_4\ (aq) + 2H_2O \rightarrow NaBO_2\ (aq) + 4H_2(g) \qquad (1)$$

Firstly, the catalytic performance of the pristine alumina was tested to understand whether the alumina pellets have a catalytic effect on the hydrolysis reaction. As a result, in the presence of pristine alumina, no hydrogen generation was observed. The three synthesized different catalysts have been tested in this continuous flow reactor at the same reaction parameters. Among these catalysts, the Ni/Al_2O_3 sample exhibited poor hydrogen generation which shows that the monometallic Ni coating did not improve the catalytic performance of alumina. Additionally, regarding the XRD results, it can be concluded that $NiAl_2O_4$ species are not active phases to dissociate $NaBH_4$.

On the other hand, the $NiCo/Al_2O_3$ catalyst showed a promising catalytic activity as demonstrated in Figure 3a and 3b. In the presence of this type of catalyst, the initial hydrogen generation rate was slow, but it increased continuously. The behavior of this catalyst can be attributed to the presence of inactivated catalyst species that are activated after self-reduction with the generation of H_2. After a 2h reaction, the H_2 generation rate rises to 0.0014 $mmol \cdot s^{-1} \cdot g^{-1}$. As a result, it can be said that the Co_2NiO_4 crystal phase acts as an active species for the dissociation of $NaBH_4$ molecules.

The addition of RuO into the catalyst structure has a significant improvement on the performance of $NiCo/Al_2O_3$ catalyst as seen in Figure 3c and 3d. In the presence of the $Ru\text{-}NiCo/Al_2O_3$ catalyst, the hydrolysis reaction starts with a reaction rate of 0.031 $mmol \cdot s^{-1} \cdot g^{-1}$, but the reaction rate decreases rapidly and the hydrogen generation rate sinks to 0.005 $mmol \cdot s^{-1} \cdot g^{-1}$. The behavior of the catalyst can be assigned to the deactivation of Ru species through the accumulation of Na-based compounds on the catalyst surface (Arzac et al. 2012).

Table 2 gives an insight into the performances of various catalysts from the literature comparable with results from the present study. Here, it can be concluded that the alumina-supported catalysts in powder form exhibited higher H_2 generation due to its higher amount of active metal sites on the catalyst surface (Xu et al. 2007). However, in the presence of a catalyst supported on ceramic foam (Balkanlı and Figen 2019) or cylindrical pellets (Su et al. 2012), H_2 generation is significantly lower than in the presence of the powder catalyst. In this study, despite the lower concentration of $NaBH_4$ solution and lower amount of noble metal (Ru) in the catalyst structure, a maximum H_2 generation rate of 50.4 $ml \cdot min^{-1} \cdot g^{-1}$ was achieved. In addition, it is expected that with an increase in the concentration of $NaBH_4$ solution achievement of higher H_2 generation compared to those stated in the literature is possible.

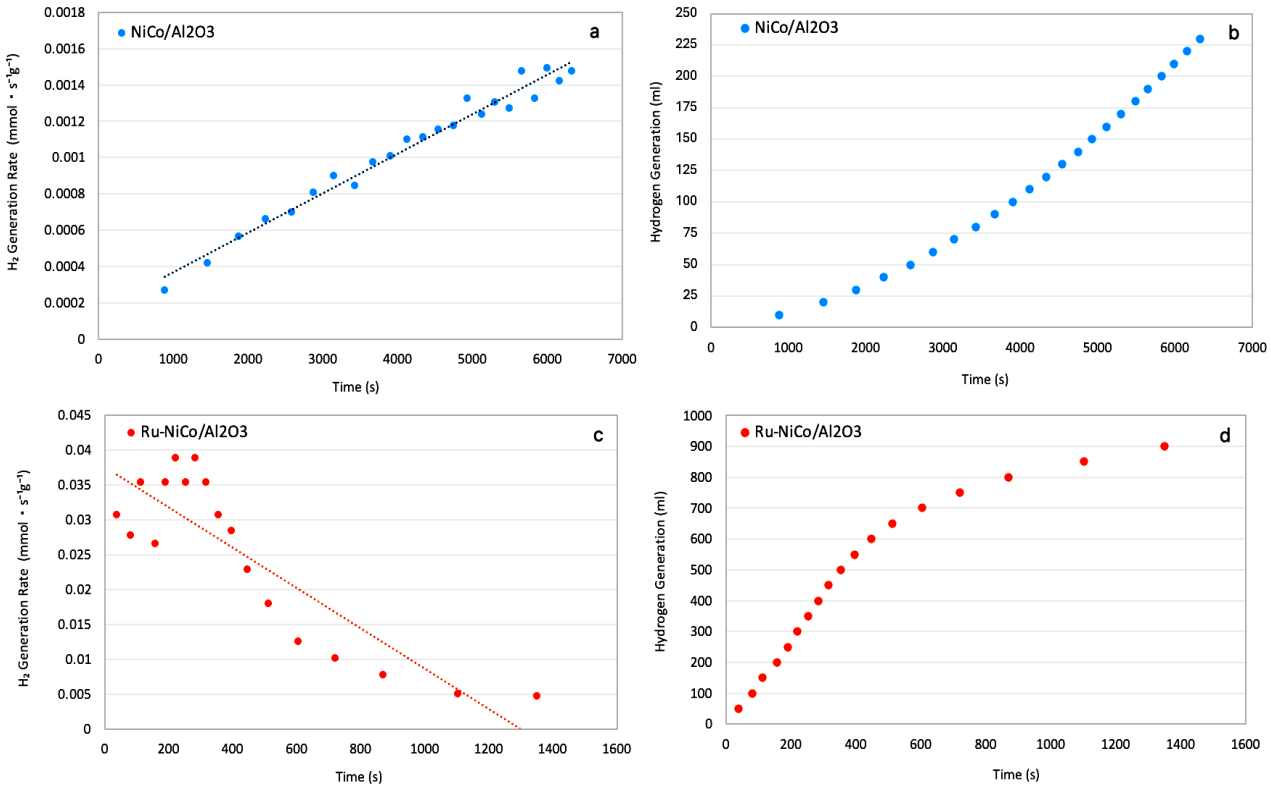

Figure 3. Hydrogen generation from $NaBH_4$ in the presence of $NiCo/Al_2O_3$ and $Ru\text{-}NiCo/Al_2O_3$ catalysts at 25 °C.

Table 2. Comparison of the results from the present study with those in the literature

Catalyst composition	Support form	T (°C)	$NaBH_4$ solution	Max. H_2 generation	Ref.
0.05 wt% Pd-4.7 wt% LiCo/SiC-based ceramic foam	Ceramic foam	25	$cNaBH_4$: cNaOH=1:1	4.76 ml·min^{-1}	Balkanli and Figen 2019
5 wt% Ru/Al_2O_3	Pellet	25	10 wt% $NaBH_4$-1 wt% NaOH	65.5 ml·min^{-1}·g^{-1}	Su et al. 2012
2 wt% Pt/Al_2O_3	Powder	30	10 wt% $NaBH_4$-5 wt% NaOH	8510 ml·min^{-1}·g^{-1}	Xu et al. 2007
7 wt% NiCo/Al_2O_3	Pellet	25	2 wt% $NaBH_4$-2 wt% NaOH	2.2 ml·min^{-1}·g^{-1}	Present study
0.02 wt% Ru-7 wt % NiCo/Al_2O_3	Pellet	25	2 wt% $NaBH_4$-2 wt% NaOH	50.4 ml·min^{-1}·g^{-1}	Present study

4. Conclusions

In summary, the high-surface area alumina pellets have been proposed as an effective support material for the catalysts in the hydrolysis reaction of $NaBH_4$. Alumina samples loaded with metal oxides were successfully prepared via the wash coating method. Results revealed that Co_2NiO_4 species form active centers for the dissociation of $NaBH_4$ molecules. Consequently, the Ru-NiCo/Al_2O_3 catalyst exhibited the highest initial hydrogen generation rate, however, the NiCo/Al_2O_3 catalyst can be proposed as a promising alternative due to its increasing catalytic performance during the reaction.

Declaration of Ethical Standards
The authors declare that they comply with all ethical standards.

Declaration of Competing Interest
The authors have no conflicts of interest to declare regarding the content of this article.

Data Availability
All data generated or analyzed during this study are included in this published article.

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