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NO_x conversion efficiency of an SCR system with V_2O_5-WO_3/TiO_2 catalyst and C_2H_5OH reductant: An experimental study

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Abstract: Internal combustion engines (ICEs) have long been the dominant power source in the transportation sector due to their high power-to-weight ratio. However, their widespread use poses significant environmental challenges, primarily due to the emission of harmful gases. To mitigate these emissions, stringent regulations necessitate the development of advanced after-treatment systems. In this study, a SCR (Selective Catalytic Reduction) system integrated with a diesel engine was investigated using V_2O_5-WO_3/TiO_2 as the catalyst and C_2H_5OH as the reductant. Engine tests were conducted under three different load conditions -no load (0 kW), 2 kW, and 4 kW- within an exhaust temperature range of 150-240 °C. NO_x conversion efficiency was evaluated with respect to engine load and temperature variations. Additionally, catalyst characterization was performed using Energy-Dispersive X-ray Spectroscopy (EDS), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET), and X-ray Diffraction (XRD) analyses. The results indicate that increasing engine load and exhaust gas temperature enhances , likely due to the higher hydrocarbon (HC) content in the exhaust at increased load levels and improved catalytic activity at elevated temperatures. The highest of 93.28% was achieved at 4 kW and 240°C.

Keywords: diesel engine; emission; NO_x; selective catalytic reduction.

1. Introduction

Internal combustion engines (ICEs) have been the primary power source for the transportation sector for decades but they pose significant challenges to environmental sustainability. Despite their dominance, largely due to their high power-to-weight ratio, one of the most critical issues associated with these engines is the release of harmful gases as byproducts of combustion. These emissions are regulated through stringent emission standards that compel manufacturers to keep them within permissible limits.

The combustion of fossil fuels plays a major role in environmental degradation, releasing pollutants such as carbon dioxide (CO_2), carbon monoxide (CO), hydrocarbon (HC), oxides of nitrogen (NO_x), particulate matter (PM) and other harmful gases [1,2]. Among all these emissions, NO_x is a significant emission produced by ICEs that has harmful impacts on both human health and the environment. Reducing NO_x emissions is therefore of critical importance [3]. Therefore, strict regulations and various reduction methods are being implemented to mitigate their adverse effects.

NO_x emissions can be reduced through effective methods like Exhaust Gas Recirculation (EGR), Lean NO_x Trap (LNT), Selective Catalytic Reduction (SCR), or by using water-emulsified fuels without engine modification [4]. SCR is one of the most critical technologies for reducing NO_x emissions as it introduces a reductant into the exhaust stream where it reacts with NO_x in the presence of a catalyst to form harmless products. SCR systems are classified by the reductant used. As the most popular and commercialized one, Urea-SCR systems are designed with the target of reducing NO_x emissions by injecting AdBlue (a solution of 32.5% urea and 67.5% deionized water) as reductant into the exhaust gases. Urea ($CO(NH_2)_2$) is subjected to thermal decomposition, producing gaseous ammonia (NH_3) and isocyanic acid (HNCO) at higher exhaust temperature levels. NH_3 produced from $CO(NH_2)_2$ as a precursor acts as the active reductant and reacts with NO_x to produce harmless nitrogen (N_2) and water (H_2O). AdBlue is preferred over pure ammonia because it is safer to store and less toxic, making it more suitable for passenger ve-

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hicles. On the other hand, the V_2O_5-WO_3/TiO_2 catalyst is used in commercialized Adblue systems as a catalyst [5,6]. Unfortunately, NH_3 negatively impacts both the environment and human health, causing toxicity, corrosion, undesirable odor, eye irritation, and respiratory issues. To address these challenges, researchers have directed their efforts toward both the development of catalysts and also the investigation of alternative reductants. [7].

Besides NH_3, various reducing gases like HCs, CO, and hydrogen (H_2) are being studied as potential SCR reductants for the removal of NO_x from the exhaust stream [8]. HC examples include methane (CH_4), iso-propanol (C_3H_8O), octane (C_8H_{18}), and pentane (C_5H_{12}) [9]. With HCs as reductants in SCR systems, an effective solution is provided to problems related to NH_3, such as NH_3 slip, the need for large urea tanks, and the complexity and cost of the injection system [10].

Upon reviewing the literature, it has been observed that HCs are widely used as reductants in various studies. Keskin [11] investigated the NO_x conversion performance of the SCR system with Ce/TiO_2 and Au-doped Ce/TiO_2 catalysts in real exhaust conditions. Low temperature characteristics of the catalysts were evaluated under 200-300 °C temperature intervals. The results indicated that Ce/TiO_2 catalysts were more effective at reducing NO_x than Au-Ce/TiO_2 catalysts. The addition of Au decreased the catalyst's surface properties, leading to reduced activity in the Au-Ce/TiO_2 catalysts. Ahmad et al. [12] studied the low exhaust gas temperature performance of an SCR system utilizing ethanol (C_2H_5OH)/H_2O blends with different ratios (100% C_2H_5OH (E), 96% C_2H_5OH + 4% H_2O (E4W), 92% C_2H_5OH + 8% H_2O (E8W)) as reductants. The results were also evaluated with respect to two different space velocity (SV) values (20000 h^{-1}, and 40000 h^{-1}). Increased engine load caused to slight rise in NO_x conversion rates. %68 as the highest NO_x conversion rate was obtained with the use of 100% C_2H_5OH as reductant. Furthermore, it was determined that adding H_2O to C_2H_5OH negatively impacts NO_x conversion rates. Özarslan [13] utilized an Ag-Ni-TiO_2/Cordierite catalyst in a C_2H_5OH-SCR system for the purpose of NO_x reduction in a compression ignition engine. NO_x reduction measurements were performed within the temperature range of 190 to 270 °C, at intervals of 20 °C. The tests were conducted with engine loads of 1 kW and 3 kW, and a SV of 30000 h^{-1}. It was shown that the Ag-Ni-TiO_2/Cordierite catalyst, using C_2H_5OH as a reductant, achieved 93.8% efficiency of NO_x conversion () at 270 °C and 3 kW. Kass et al. [14] aimed to reduce NO_x emissions from a diesel engine using a C_2H_5OH-SCR system. NO_x reductions of 90% and 80% were achieved at SVs of 21000 h^{-1} and 57000 h^{-1}, respectively, within a catalyst temperature range of 360 - 400 °C. The study revealed that C_2H_5OH was quickly converted to acetaldehyde by the silver-loaded alumina catalyst. However, significant amounts of acetaldehyde bypassed the catalyst at an SV of 57,000 h^{-1}. Gu et al. [15] assessed the H_2 addition effects on via HC-SCR system with different reductants at low temperature values. In this study, H_2 has been employed in HC-SCR systems to improve NO_x conversion efficiencies, especially at low temperatures between 245°C and 315°C. The tests were conducted at temperatures below 315°C using a 2.5 wt.% Ag/Al_2O_3 catalyst. Propene (C_3H_6), heptane (C_7H_{16}), and dodecane ($C_{12}H_{26}$) were employed as reductants in the tests to assess the impact of various chemical structures and chain lengths. C_7H_{16} showed the highest of 43% at 315°C without H_2. However, with the addition of H_2, $C_{12}H_{26}$ achieved the greatest efficiency, reaching 58% at the same temperature. In the engine experiments, it was found that using diesel fuel as the reductant led to a maximum of 79% at 315°C and 76% at 245°C. Dong et al. [16] investigated the NO_x reduction performance of a C_2H_5OH -based SCR system using Ag/Al_2O_3 catalysts in both engine bench and real-road exhaust conditions. High NO_x conversion (up to 90%) was observed between 350 - 450 °C under controlled test bench conditions, whereas in real-road bus demonstrations, conversion efficiency dropped below 15%. The results highlighted that sulfur poisoning and catalyst thermal inertia significantly affected catalyst performance. Additionally, the Ag/Al_2O_3 catalyst reduced soluble organic fractions in PM emissions but showed minimal effect on dry soot and variable effects on sulfate formation depending on temperature. Kruczyński et al. [17] evaluated the NO_x reduction performance of metal-based catalysts (Cu, Ag, Au) supported on Al_2O_3–SiO_2 carriers using C_3H_6 as the reducing agent under real diesel exhaust conditions. Catalysts were evaluated for NO, NO_2, and HC conversion, as well as CO and N_2O formation. All catalysts achieved nearly 100% NO_2 and C_3H_6 conversion, but NO conversion was highest with Ag/Al_2O_3–SiO_2 (81%) at around 480 °C. The Ag-based catalyst also showed the lowest N_2O formation compared to Au and Cu variants. The study concluded that although metals on acidic supports can be effective, their full application in low-temperature NO_x control remains limited.

In this study, engine tests were conducted on a SCR system coupled with a diesel engine using V_2O_5-WO_3/TiO_2 as the catalyst and C_2H_5OH as the reductant. were determined by calculating the NO_x reduction rates under three different engine load conditions as no load (0 kW), 2 kW, and 4 kW within an exhaust temperature range of 150-240°C. Catalyst characterization was also achieved via Energy-Dispersive X-ray Spectroscopy (EDS), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET), and X-ray diffraction (XRD) analyses.

2. Materials and Methods

The engine tests were conducted in the Engine Test Laboratory while the catalyst preparation processes were carried out in the Fuel Analysis Laboratory, both located within the Automotive Engineering Department of Çukurova University. In addition, the catalyst

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characterization tests were performed in the Central Research Laboratory of Çukurova University.

2.1. Preparation of Catalyst

In the SCR system used for NO_x reduction purpose, V_2O_5-WO_3/TiO_2 was employed as the catalyst and C_2H_5OH was used as the reducing agent.

The SCR catalyst was synthesized through the conventional wet impregnation method, following a previously reported study by Keskin et al. [18] with certain modifications. The cordierite was used as the main carrier structure in catalyst production. Initially, a pre-treatment was applied using a solution containing 250 g of oxalic acid and 500 mL of distilled water to enhance the surface area providing extra binding sites for catalytic materials. This treatment was carried out using a heated magnetic stirrer at a temperature range of 95-100°C for about 4 hours. Subsequently, a washing step was performed with distilled water until the pH reached approximately 7 which corresponds to a neutral condition. In the next step, a drying process was carried out at 120 °C using a furnace. Finally, specimens were exposed to the calcination process at 550 °C for 2 hours to get rid of impurities.

V_2O_5-WO_3/TiO_2 catalyst includes V_2O_5, WO_3, and TiO_2 with molar ratios of 1.62, 1, and 45.41, respectively [19], and the preparation of the catalyst began by mixing the materials in these molar ratios and corresponding weights in 300 mL of distilled water using an ultrasonic stirrer for 15 minutes. Then, the mixture was transferred to a heater, and the stirring process continued until the water contained in the mixture evaporated. The resulting mud-like structure was dried at 120°C for 1 hour, then subjected to calcination at 500°C for 1 hour using a muffle furnace. The obtained structure was ground into a powder. The powder catalyst was mixed with 10% of its weight in colloidal silica and stirred for 1 hour in 300 mL of water using a magnetic stirrer to improve binding between materials. Then, the cordierite structure was immersed in this mixture to ensure it was fully wet. Next, drying was applied in an oven at 120°C for 1 hour. The impregnation subsequent drying process was repeated three times consecutively. At last, the cordierite coated with catalyst material was prepared through calcination at 500°C for 3 hours.

The entire process can be summarized in three main stages: cordierite pre-treatment, production of powdered catalyst, and catalyst-coated cordierite production.

2.2. Characterization of Catalyst

The chemical characterization and the surface morphologies of the catalysts were analyzed using EDS and SEM techniques, respectively, with an FEI brand Quanta 650 FEG SEM device. Additionally, the measurement of the catalysts' surface area was based on the BET theory via N_2 gas adsorption analysis using a Sorptometer 1042 instrument. On the other hand, the crystallographic properties were evaluated using XRD analysis. This analysis was performed with the PANalytical Empyrean XRD device.

2.3. Test Rig and Experiments

Load and emission tests were done in 2 cylinders, water-cooled compression ignition engine. The technical specifications of the test engine are summarized in **▶Table 1**. The test set-up was schematized in the following **▶Figure 1**. In tests, diesel was utilized as fuel and values were evaluated using V_2O_5-WO_3/TiO_2 catalyst and C_2H_5OH as a reductant under engine loads of 0 kW, 2

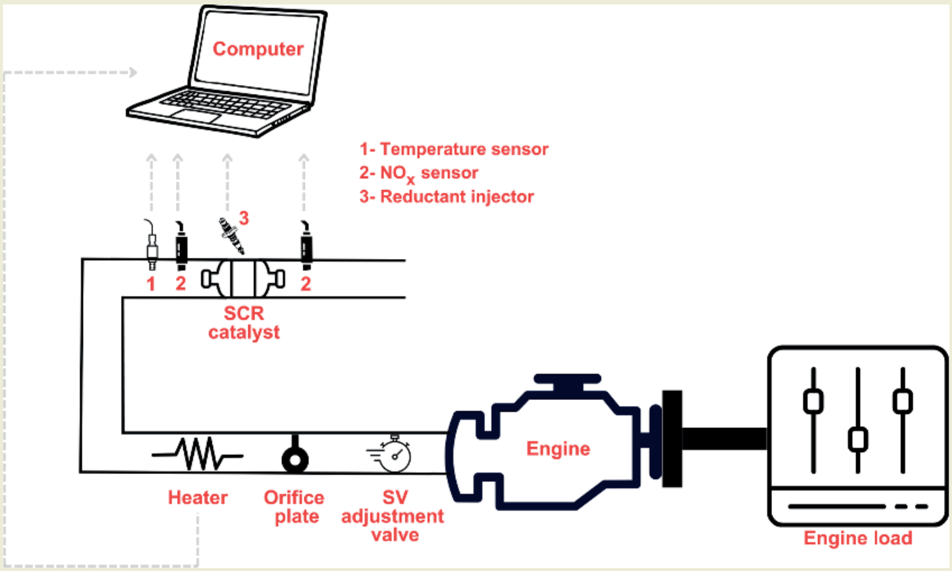


Figure 1. Experimental test rig

kW, and 4 kW. These load values were obtained from a 10 kW electrically controlled loading unit based on current and voltage measurements. As seen in ▶**Figure 1**, the exhaust flow rate required for SV determination (the ratio of exhaust flow rate to the volume of catalyst) is adjusted via an orifice, while the exhaust temperature is regulated using a heater in the exhaust line. The tests were also conducted at temperatures from 150 °C to 240 °C with 10 °C increments and an SV value of 40000 h^{-1}. A K-type thermocouple is installed immediately before the SCR to measure the exhaust temperature. Additionally, Continental UniNO_x sensors are placed both before and after the SCR to determine calculated with the following formula:

$$\eta_{NO_x} = \frac{\left(NO_{x_{in}} - NO_{x_{out}}\right)}{NO_{x_{in}}}\, x\; 100 \tag{1}$$

Table 1. Engine specifications

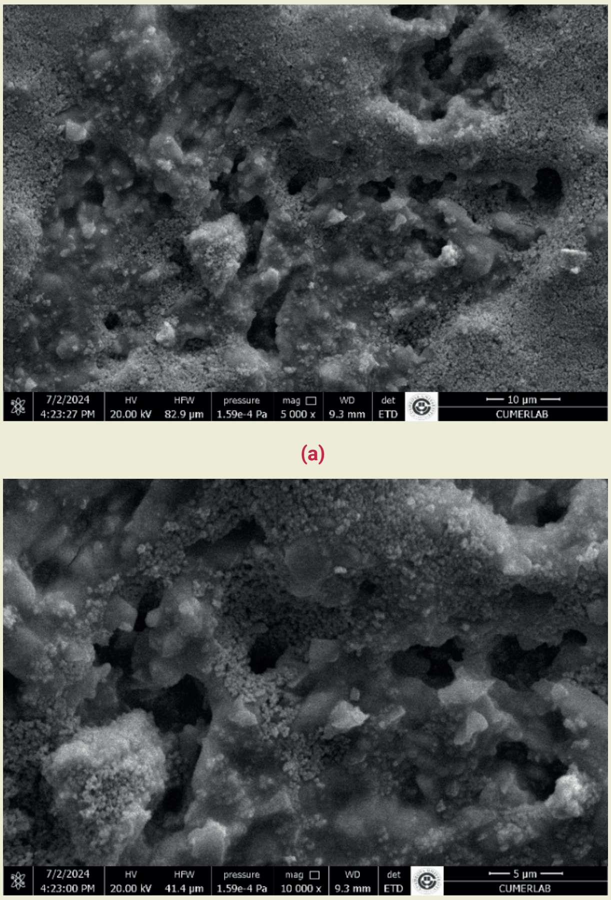
Brand / Model	AKSA / A2CRX08
Number of cylinders	2
Engine speed	3000 rpm
Cylinder volume	830 cm^3
Bore / Stroke	80 / 79 mm
Compression ratio	23/1
Cooling	Water-cooled

3. Results and Discussions

3.1. Catalyst Characterization Results

SEM-EDS analysis was conducted to evaluate the micromorphology and surface structure of the catalyst, revealing that the surfaces were coated with catalytic elements. ▶**Figure 2** illustrates the surface morphology of the catalyst coated cordierite structure with 5000x/10000x magnifications. The porous structure of cordierite can easily be seen from the images. The catalyst material is distributed within an irregular structure of cordierite.

The elemental overlay was determined by EDS analysis as shown in ▶**Figure 3** and the distribution of elements contained in the catalyst can be seen. Total EDS imaging identified two predominant colors: yellow and turquoise, representing Si and Ti, respectively. Elemental distribution analysis determined the proportions of Si, Al, O, Mg, Ti, W, and V as 34%, 8%, 13%, 4%, 33%, 2%, and 7%, respectively.



(a)

(b)

Figure 2. SEM results of V_2O_5-WO_3/TiO_2 catalyst/cordierite structure (a) 5000x (b) 10000x

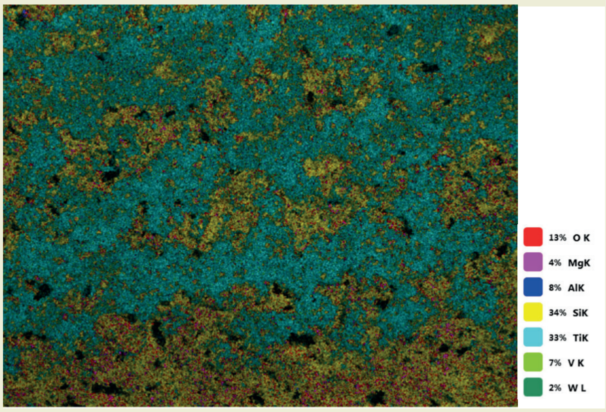


Figure 3. Elemental overlay of V_2O_5-WO_3/TiO_2 catalyst/cordierite structure through EDS analysis

XRD analysis was used to characterize the catalysts, exploring the crystallization and distribution of catalytic elements on the cordierite surface. As a result of the XRD analysis, it was determined that cordierite has an orthorhombic crystal structure, anatase and vanadium have a tetragonal crystal structure, and tungsten has a monoclinic crystal structure. As can be seen in ▶**Figure 4**, each chemical used in catalyst production has distinct characteristic peaks at specific angles. In the pattern, the characteristic diffraction peaks of cordierite were determined at 10.33, 18.01, 21.63, 26.27, 28.34, 29.35, 33.79, and 54.15° (Ref. Code: 98-007-5635), consistent with earlier studies [20, 21]. The characteristic peaks of anatase were observed at 25.22, 36.87, 38.43, and 47.97 (Ref. Code: 98-000-9853). Similar peaks were also observed in previous studies [22, 23]. The peaks corresponding to vanadium and tungsten were detected at 36.87°, 39.44°, 54.99°, 64.32°, and 69.59°

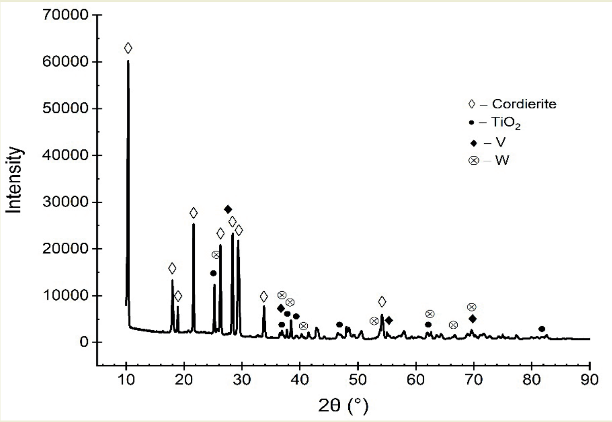


Figure 4. XRD results of V_2O_5-WO_3/TiO_2 catalyst/cordierite structure

(Ref. Code: 98-023-7337), and at 25.77°, 36.87°, 37.72°, 41.47°, 57.87°, and 69.59° (Ref. Code: 98-008-0829), respectively. These peaks exhibit relatively low diffraction intensities, indicating that the active metal species are highly dispersed on the catalyst surface [24, 25].

BET surface area is generally crucial for catalyst performance, as a larger surface area increases active sites, enhances component dispersion, and promotes reactant adsorption, thereby improving catalytic activity. BET analysis revealed that the surface area of the catalyst was found as 43.58 m^2/g, while the cordierite surface area was nearly 0.5 m^2/g. The approximately 87 times increase in active surface area significantly enhances catalytic activity.

3.2. NO_x Conversion Efficiency Results

The of the catalyst was evaluated with respect to varying engine load and temperature as illustrated in ▶**Figure 5**. In tests, the 0 kW case was compared with 2 kW and 4 kW load conditions. The tests were repeated with exhaust gas temperatures ranging from 150 °C to 240 °C rising in increments of 10 °C. It is obvious that an increase in engine load and exhaust gas temperature cause to obtain higher . As the engine load increases, HC content in the exhaust gases also rises. Due to their reducing properties, HCs contribute to the NO_x conversion process that improve [6,26]. Besides that, the increase in exhaust gas temperature clearly demonstrates a positive effect on . This may possibly be explained by the fact that higher exhaust temperatures enhance catalytic activity, leading to improved conversion efficiency [10]. Within the 150-240 °C temperature range, average values of 87.98%, 90.4%, and 91.41% were achieved under no-load, 2 kW, and 4 kW conditions, respectively. The average values at 2 kW and 4 kW loads resulted in a 2.75% and 3.9% improvement in compared to the 0 kW condition. The highest was achieved at 240 °C compared to lower temperature values under all load conditions. Furthermore, the highest of 93.28% was observed at 4 kW and an exhaust temperature of 240°C.

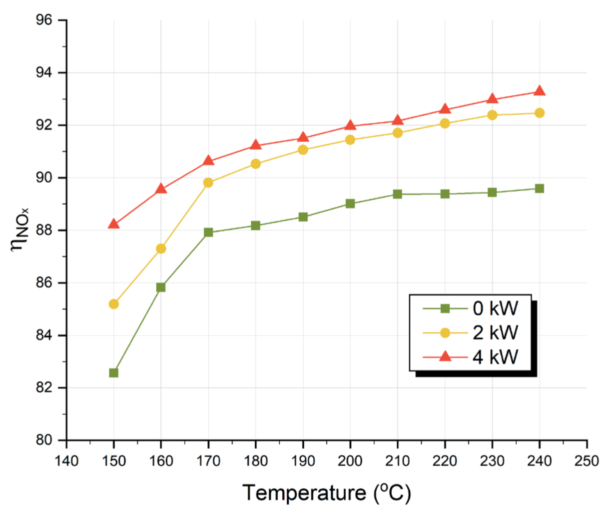


Figure 5. versus temperature at various engine loads

4. Conclusions

At the conclusion of the study, the following findings were made:

- SEM-EDS analysis confirmed the successful coating of the catalyst on the cordierite surface.
- Elemental distribution identified Si, Ti, Al, O, Mg, W, and V as the main components.
- XRD analysis revealed that cordierite has an orthorhombic crystal structure, anatase and vanadium have a tetragonal structure, and tungsten has a monoclinic structure.
- BET analysis showed a significant increase in surface area from 0.5 m^2/g (cordierite) to 43.58 m^2/g (catalyst), enhancing catalytic activity.
- Increasing engine load and exhaust gas temperature improved .
- The highest (93.28%) was achieved at 4 kW load and 240°C conditions.

Research ethics

Not applicable.

Author contributions

The author solely conducted all stages of this research.

Competing interests

The author state(s) no conflict of interest.

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Data availability

Not applicable.

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