

Importance of Vanadium-Catalyzed Oxidation of SO₂ to SO₃ in Two-Stroke Marine Diesel Engines

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S Supporting Information

ABSTRACT: Low-speed marine diesel engines are mostly operated on heavy fuel oils, which have a high content of sulfur and ash, including trace amounts of vanadium, nickel, and aluminum. In particular, vanadium oxides could catalyze in-cylinder oxidation of SO₂ to SO₃, promoting the formation of sulfuric acid and enhancing problems of corrosion. In the present work, the kinetics of the catalyzed oxidation was studied in a fixed-bed reactor at atmospheric pressure. Vanadium oxide nanoparticles were synthesized by spray flame pyrolysis, i.e., by a mechanism similar to the mechanism leading to the formation of the catalytic species within the engine. Experiments with different particle compositions (vanadium/sodium ratio) and temperatures (300–800 °C) show that both the temperature and sodium content have a major impact on the oxidation rate. Kinetic parameters for the catalyzed reaction are determined, and the proposed kinetic model fits well with the experimental data. The impact of the catalytic reaction is studied with a phenomenological zero-dimensional (0D) engine model, where fuel oxidation and SO_x formation is modeled with a comprehensive gas-phase reaction mechanism. Results indicate that the oxidation of SO₂ to SO₃ in the cylinder is dominated by gas-phase reactions and that the vanadium-catalyzed reaction is at most a very minor pathway.

INTRODUCTION

In comparison to other ways of transport, maritime transport and shipping benefit from low CO₂ emissions, even though emissions of NO_x and SO_x may be a concern. Two-stroke marine diesel engines used for low-speed vessels can operate on heavy fuel oils, which are the most economic option among fuels but typically contain large amounts of sulfur (2.5–3.5 wt %). During combustion, sulfur is quickly oxidized to SO₂, with a small fraction oxidized further to SO₃. The presence of SO₃ may lead to the formation of sulfuric acid (H₂SO₄), which can cause corrosion if the temperature locally drops below the sulfuric acid dew point (cold corrosion).^{1,2} To improve the efficiency and future development of the engines, an understanding of the SO₃ formation mechanism is required.

The formation of SO₃ in the cylinder of a large two-stroke marine diesel engine burning heavy fuel oil was studied by Cordtz et al. with a phenomenological zero-dimensional (0D) model.² Oxidation of SO₂ to SO₃ can take place through a sequence of gas-phase reactions, which are reasonably well-established.^{3,4} However, fuel oil contains trace amounts of vanadium that cannot be easily removed from the oil. Particles emitted from two-stroke marine diesel engines on modern container ships have been reported to belong to two size ranges: 5–8 and 30–100 nm.⁵ The 5–8 nm nanoparticles, which dominate the total number of particles, are composed mainly of V, Ni, and S. Vanadium oxide (V₂O₅) is known to catalyze SO₂ oxidation¹ and, thus, may facilitate the formation of SO₃ in the cylinder.

It has been reported that vanadium becomes more reactive when doped with alkali elements, such as potassium, cesium, or

sodium.^{1,6} Sodium is typically present in considerable quantities in the engine cylinder, originated partly from seawater contamination⁷ and partly from the fuel oil. Reported mass ratios of V/Na in the engine exhaust are in fairly good agreement, with values of 7.9 in the exhaust gas ash particles of a large-scale medium-speed diesel engine⁸ and 6.3 in the particulate matter from a large ship diesel engine.⁹ A report from the International Bunker Industry Association (IBIA) indicates that the V/Na ratio in the marine engine would be in the range of 7–10 or higher, depending upon the centrifuge system that removes water.

In this context, the objective of this work is to investigate the relative importance of homo- and heterogeneous (catalyzed by vanadium oxides) oxidation of SO₂ into SO₃ through experiments and kinetic modeling. Representative vanadium aerosols, produced by flame spray pyrolysis, are used in fixed-bed reactor experiments to determine the rate of the catalytic reaction as a function of the particle composition (V/Na ratio), SO₂ concentration, and temperature. The contribution of the catalyzed oxidation of SO₂ is then determined on the basis of computations with the phenomenological model of Cordtz et al.²

EXPERIMENTAL SECTION

The vanadium particles used in the present study are produced in a flame spray pyrolysis setup,^{10,11} where oxide nanoparticles are formed

Received: March 18, 2016

Revised: June 4, 2016

76 by spraying a combustible solution of organometallic salts into a flame.
77 The setup is described in detail by Høj et al.¹² In the flame,
78 catalytically active oxide nanoparticles are produced by a mechanism
79 similar to the mechanism leading to the formation of the catalytic
80 species within an engine.¹³ The combustible solution is composed of
81 organometallic precursors [vanadium(III) acetylacetonate and sodium
82 2-ethylhexanoate] at a total metal concentration of 0.125 M dissolved
83 in methanol. The solution is fed at a rate of 3 mL min⁻¹, dispersed by a
84 5 NL min⁻¹ flow of O₂, and ignited by an annular 1:3 (mol/mol)
85 CH₄/O₂ flame.

86 The flame pyrolysis allows the vanadium aerosols to be formed
87 under conditions that resemble those of an engine. The aerosol size
88 range (11–21 nm) is similar to the values reported for marine diesel
89 engines (5–8 nm). The particle diameter d_p was calculated assuming
90 spherical particles: $d_p = 6/(SSA \cdot \rho)$, where ρ is the density of the
91 particles (taking into account the content and densities of V₂O₅ and
92 Na₂O in the particles) and SSA is the specific surface area, determined
93 by the Brunauer–Emmett–Teller (BET) surface analysis. Table 1
94 summarizes these values. The present experiments were conducted
95 with V/Na mass ratios of 4, 7.9, and 15, in addition to reference
96 experiments made with pure vanadium.

Table 1. Catalyst Particle Properties

V/Na ^a	d_p (nm)	SSA (m ² /g)
4	20.9	91.2
7.9	21.2	87.6
15	11.9	153.0
100% V	11.5	155.1

^aOn a mass basis.

97 The kinetics of SO₂ oxidation over vanadium oxides is studied in a
98 fixed-bed reactor at atmospheric pressure. Details of the experimental
99 setup and procedures can be found elsewhere.¹⁴ The reactor is a fixed-
100 bed quartz reactor, with solids placed on a porous quartz plate in an
101 isothermal zone. Reactant gases are introduced separately in the
102 reactor and mixed just above the porous plate. The reactor is placed in
103 a three-zone electrically heated oven, operated in the 300–800 °C
104 temperature range. The reactor temperature is measured under inert
105 conditions with a type-K thermocouple. A total of 0.25 g of the
106 synthesized aerosols is mixed with an equal amount of silica particles
107 (150–200 μm) to form a fixed bed with good heat dispersion. In the
108 bed, it is conceivable that some further aggregation of the vanadium
109 clusters may occur, resulting in larger particles. Furthermore, at higher
110 temperatures, the vanadium–sodium compounds may melt (melting
111 points are around 550–700 °C). The dispersion of the synthesized
112 particles with quartz particles can help to avoid a large pressure drop.
113 A total flow rate of 157 mL min⁻¹ (1 atm and 25 °C) is used, with a
114 composition of 1380 ppm of SO₂, 14% O₂, and 2.6% H₂O, all diluted
115 in N₂. The amount of oxygen is in large excess compared to SO₂ to
116 obtain pseudo-first-order reaction conditions^{6,14} and representative of
117 the exhaust gases of marine diesel engines.⁸

118 The oxidation of SO₂ is exothermic, but as a result of the high
119 dilution under the present experimental conditions, the heat release
120 can be neglected. Water vapor is present in significant amounts in the
121 combustion products and may conceivably have an impact on the
122 catalyzed reaction. For this reason, the stream, including N₂ and O₂,
123 was saturated with water vapor by passing the gas through an
124 evaporator at room temperature. Upon dilution with N₂ to satisfy the
125 flow rate needed in the analyzer (~1000 mL min⁻¹), the product gas
126 from the reactor was led to a continuous UV-NGA2000 MLT4
127 analyzer (Rosemount Analytical) to quantify the SO₂ concentration.

128 ■ RESULTS AND DISCUSSION

129 **Vanadium-Catalyzed SO₂ Oxidation.** A series of experi-
130 ments is conducted in the fixed-bed reactor for the different V/
131 Na compositions (Table 1), varying the temperature and the
132 SO₂ inlet concentration. Figure 1 shows results of the

conversion of SO₂ as a function of the aerosol composition 133
and temperature. 134

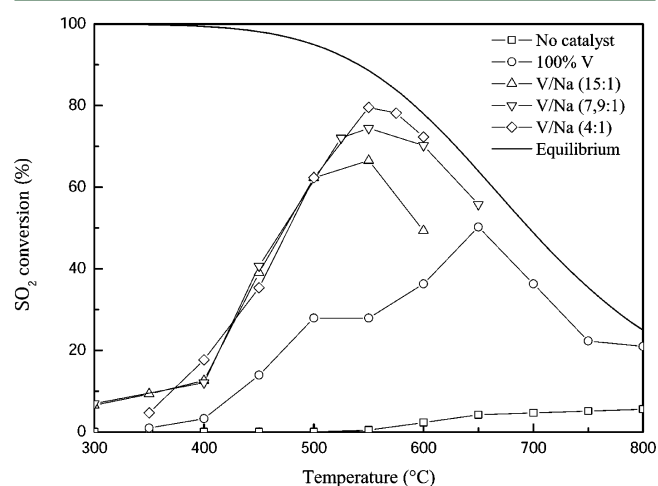


Figure 1. Effect of the catalyst composition and temperature on the oxidation of SO₂ in the fixed-bed reactor. Results are shown for experiments with an empty reactor, with pure vanadium, and with particles with V/Na ratios in the range of 4–15 (mass based). Flow rate, 157.4 mL min⁻¹ (25 °C and 1 atm), with 1376 ppm of SO₂, 14% O₂, 2.6% H₂O, and balanced with N₂.

Without catalyst (empty reactor), the SO₂ conversion is very 135
limited, especially below 550 °C; this is in line with results 136
reported by Jørgensen et al.¹⁴ The introduction of vanadium 137
aerosols in the fixed bed leads to a significant oxidation of SO₂ 138
above 350 °C. Catalyst particles doped with sodium exhibit an 139
even higher reactivity, with the maximum conversion increasing 140
with the sodium content. The SO₂ conversion peaks at 550 °C; 141
above this temperature, the conversion is limited because the 142
reaction approaches chemical equilibrium. The importance of 143
sodium in the catalyst is in agreement with findings from 144
sulfuric acid production, where catalysts with a mass ratio of V/
Na = 0.75 are used.¹⁵ 145

The difference between thermal equilibrium and exper- 147
imental data at higher temperatures may be attributed to 148
experimental uncertainties. These include possible aggregation 149
and/or melting of particles and changing the reaction 150
conditions during the course of an experiment. However, 151
similar observations have been reported from sulfuric acid 152
production, where SO₂ emissions from acid plants were slightly 153
above equilibrium values.¹⁶ It has been reported that 154
commercial sulfuric acid catalysts suffer a sudden loss in 155
activity at 420–450 °C that is attributed to the precipitation of 156
crystalline compounds of vanadium (V^{III} and V^{IV}).¹⁵ This loss is 157
a reversible process, and the catalytic activity is regained upon 158
heating the catalyst bed up to 500 °C, showing a hysteresis 159
behavior. 160

Figure 2 shows the influence of the SO₂ concentration. 161
Below the temperature where the conversion peaks, a higher 162
conversion is obtained with a lower concentration of SO₂. 163
Above the peak temperature, the conversion is the same for the 164
two SO₂ levels. It is not possible from the present work to 165
determine a reaction order in SO₂, because the amount of data 166
is limited and differences may be partly attributed to 167
experimental uncertainties. Results from the literature¹⁷ suggest 168
that the reaction is first-order in SO₂. 169

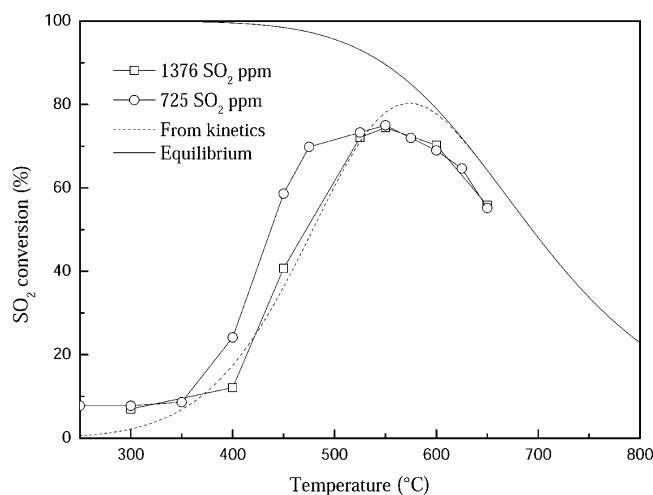


Figure 2. Conversion of SO₂ for two different initial concentrations of SO₂ and the same catalyst (V/Na = 7.9). A comparison between experimental results and predictions with the kinetic model is also shown.

170 **Kinetic Model.** The experimental results (Figure 1) were
171 used to establish the rate equation for the catalytic reaction. We
172 assume the reaction to be first-order in SO₂.¹⁷

$$173 \quad -r_{\text{SO}_2} = kP_{\text{SO}_2}(1 - \beta) \quad (1)$$

174 Here, k is described by an Arrhenius expression with a pre-
175 exponential factor A and an activation energy E_a . The rate is
176 assumed to be independent of the oxygen concentration. As
177 mentioned, O₂ is in large excess and has been reported to be
178 zero-order in similar experiments at 400 °C with vanadium
179 catalysts.⁶ The $(1 - \beta)$ term accounts for the decrease in the
180 rate as the reaction approaches equilibrium, with β related to
181 the equilibrium constant K_c and the concentration of the
182 molecules, $\beta = P_{\text{SO}_3}/K_c P_{\text{SO}_2} P_{\text{O}_2}^{0.5}$. If the concentrations of SO₂
183 and SO₃ reach the equilibrium values, β will be equal to 1 and
184 the reaction rate will be 0.

185 Nonlinear regression was made to determine the kinetic
186 parameters A and E_a for each catalyst composition; the values
187 obtained are listed in Table 2. A comparison between the

Table 2. Kinetic Parameters

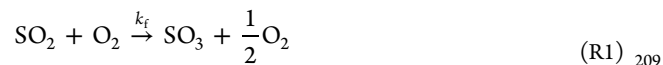
V/Na ^a	E_a (kJ/mol)	A (mol s ⁻¹ g ⁻¹ bar ⁻¹)
4	69.5	20.6
7.9	67.3	14.5
15	57.8	3.0
100% V	47.9	0.2

^aOn a mass basis.

188 experimental and calculated results for the particles with a V/
189 Na ratio of 7.9 is shown in Figure 2. The measured activation
190 energies are not directly comparable to values from the
191 literature because the present work constitutes the first study of
192 the oxidation of SO₂ with flame-generated particles. Similar
193 supported vanadium catalysts made by impregnation techni-
194 ques have shown activation energies around 85 kJ mol⁻¹,⁶
195 approximately 25% higher compared to the values obtained in
196 the present work. The difference is attributed to variations in
197 morphology and catalyst support. A comparison to reported
198 turnover frequencies for commercial vanadium catalysts of

different composition¹⁸ indicates that our catalysts (V/Na = 4
and 100% vanadium) are in the lower end of the range.

The rate equation is used to evaluate the importance rate of
vanadium-catalyzed SO₃ formation compared to the rate of SO₃
formation by homogeneous oxidation in a two-stroke diesel
engine. For the homogeneous oxidation rate, calculations were
conducted with the detailed chemical kinetic model of
Hindiyarti et al.,⁴ using a 0D model described in the next
section. The catalyzed reaction was introduced in the
mechanism as a pseudo-first-order reaction.



$$-r_{\text{SO}_2} = k'[\text{SO}_2]^1[\text{O}_2]^0 = 2.1 \times 10^{-3} \exp\left(\frac{-8050}{T}\right)[\text{SO}_2] \quad (2)$$

The rate constant k' is based on the kinetic parameters for
particles with a V/Na ratio of 7.9 (see Table 2). This ratio
corresponds to the reported V/Na ratio in engines, as discussed
above. To obtain the first-order rate constant, conditions
representative of the cylinder were chosen, with the fuel
consumption rate, exhaust flow, and fuel vanadium content
(100 mg/kg of fuel) drawn from the literature.⁹ Details of the
calculations can be seen in the Supporting Information.

Engine Simulation. The phenomenological 0D model of
Cordtz et al.² is adopted here to simulate a large two-stroke
marine diesel engine operating at a low power output at a speed
of 80 rpm. A detailed gas-phase reaction mechanism⁴ is applied
and integrated with MATLAB and Cantera^{19,20} to describe SO_x
formation in the burned gas.

Figure 3 shows a sketch of a two-stroke diesel engine
cylinder. The piston position determines the volume of the

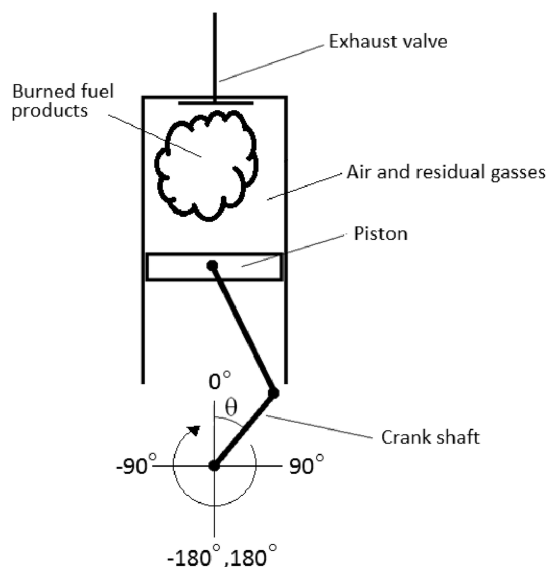


Figure 3. Sketch of a two-stroke engine cylinder.

trapped gas that is coupled to the angular position of the crank
shaft (θ). The two-stroke cycle involves a compression stroke
($\theta < 0^\circ$) and an expansion stroke ($\theta \geq 0^\circ$). The position at $\theta =$
 0° is termed the piston top dead center (TDC). Close to TDC,
fuel is injected into the hot compressed fresh gas that consists
mostly of air but includes residual gases, i.e., combustion
products from the prior cycle. As the fuel burns (diffusion-

234 controlled combustion), thermal work/power is transferred to
 235 the rotating crank shaft. Late in the expansion stroke, the
 236 exhaust valve opens (EVO) and the cylinder gas products are
 237 replaced by fresh scavenging air at 30 °C. The air is provided
 238 via scavenging ports in the bottom of the cylinder (not shown
 239 in the figure) and flows upward through the cylinder. The
 240 exhaust valve closes shortly after the crank shaft has passed the
 241 bottom dead center at $\theta = 180^\circ$, where a new cycle begins.

242 In the 0D engine model, the burned fuel is separated in
 243 multiple, slightly lean, and homogeneous gas zones. The
 244 computed mean temperature and the overall SO₃ concentration
 245 of the burned gas for a wide range of the pre-exponential factor
 246 of reaction R1 are plotted in Figure 4. SO₃ is thermodynamically

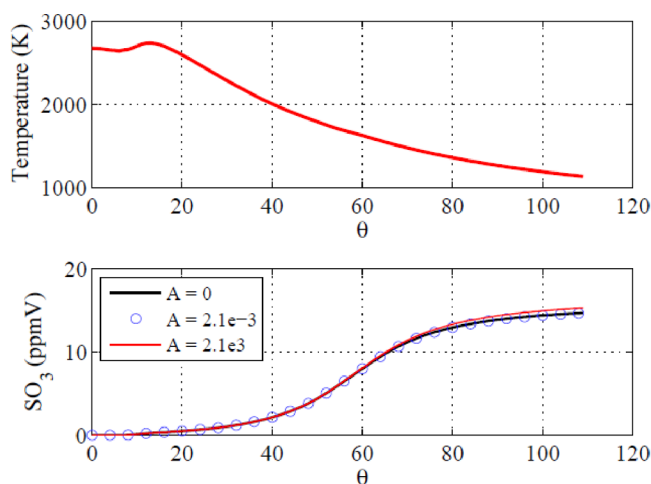


Figure 4. Mean temperature and overall SO₃ concentration of the burned gas during combustion and expansion until the exhaust valve opens. The figure shows the effect of a factor of 1000 change in the pre-exponential factor *A* for the catalytic vanadium reaction (reaction R1).

247 cally restricted at combustion temperatures but forms during
 248 the expansion stroke primarily through reactions of SO₂ with
 249 the radical pool.² Reaction R1 is comparably slow, and the
 250 catalytic effect is negligible, unless the pre-exponential factor is
 251 increased by 3 orders of magnitude.

252 The fraction of residual gases (in the fresh gas) is around 3%
 253 (m/m). If the air and residual gas are computationally
 254 separated during the cycle, the temperature of the residual
 255 gas (that holds SO₂ of the prior cycle) peaks above 2000 K
 256 during combustion, as illustrated in Figure 5. The temperature
 257 trace is determined from the cylinder pressure and isentropic
 258 correlation.

$$259 \quad \frac{T_{\theta+1}}{T_{\theta}} = \left(\frac{p_{\theta+1}}{p_{\theta}} \right) \quad (3)$$

260 Here, the mean cylinder gas temperature and species
 261 composition at EVO of the prior cycle are set as initial
 262 conditions. As indicated in Figure 5, SO₃ formation in the
 263 residual gas is thermodynamically restricted at the highest
 264 temperatures and the rate of reaction R1 is too slow to
 265 contribute to SO₃ formation.

266 If the fresh charge air and residual gas are fully mixed during
 267 the cycle, the mixture temperature peaks at ~1000 K, as shown
 268 in Figure 6. Below 1000 K, SO₃ is thermodynamically preferred
 269 over SO₂.²¹ Still, reaction R1 is too slow to form considerable

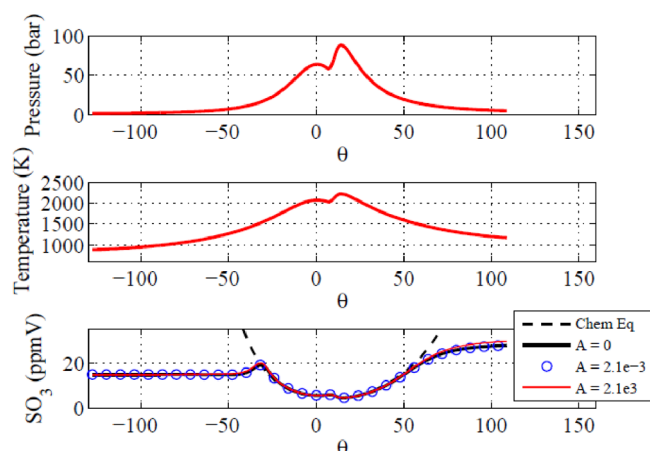


Figure 5. Cylinder gas pressure, residual gas temperature, and catalytic SO₃ formation in the residual gas over the engine cycle. The figure shows the effect of a factor of 1000 change in the pre-exponential factor *A* for the catalytic vanadium reaction (reaction R1).

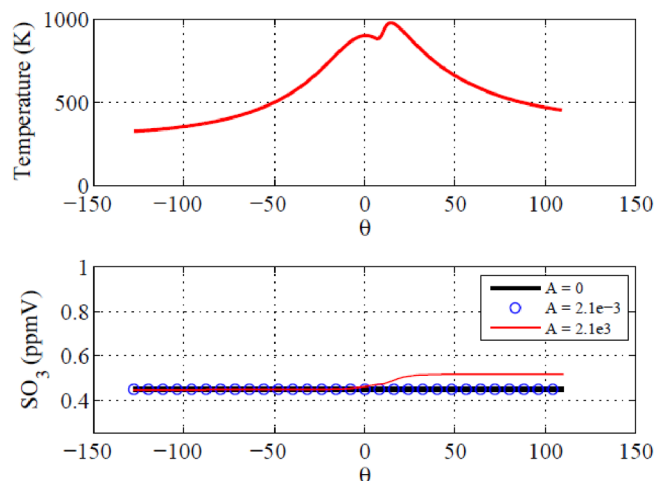


Figure 6. Fresh gas temperature and catalytic SO₃ formation in the fresh gas over the engine cycle. The figure shows the effect of a factor of 1000 change in the pre-exponential factor *A* for the catalytic vanadium reaction (reaction R1).

amounts of SO₃, unless the pre-exponential factor is increased
 by 3 orders of magnitude.

CONCLUSION

The present work is the first study on the importance of catalytic species in the formation of sulfur oxides in engines. The SO₂ oxidation catalyzed by vanadium aerosols was studied in a fixed-bed reactor at atmospheric pressure. The aerosols were formed in a flame pyrolyzer and represent particles formed from combustion of heavy fuel oil in a marine two-stroke diesel engine. The rate of the catalyzed reaction was determined in a fixed bed as a function of the catalyst composition (V/Na ratio), temperature, and SO₂ concentration. Experiments showed that both the temperature and sodium content had a major impact on the oxidation rate. Kinetic parameters for the catalyzed reaction were determined using a proposed kinetic model. To simulate fuel oxidation and SO_x formation inside a two-stroke marine diesel engine, a detailed gas-phase reaction mechanism was combined with a step describing the catalyzed reaction and used with a phenomenological 0D model. Results indicate that the

290 proposed catalytic vanadium reaction is slow compared to the
291 gas-phase reactions and it is unlikely that vanadium contributes
292 significantly to SO₃ formation.

293 ■ ASSOCIATED CONTENT

294 ● Supporting Information

295 The Supporting Information is available free of charge on the
296 ACS Publications website at DOI: [10.1021/acs.energy-](https://doi.org/10.1021/acs.energy-fuels.6b00638)
297 [fuels.6b00638](https://doi.org/10.1021/acs.energy-fuels.6b00638).

298 Estimation of the vanadium-catalyzed oxidation rate
299 constant for engine conditions (PDF)

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303 Notes

304 The authors declare no competing financial interest.

305 ■ ACKNOWLEDGMENTS

306 The authors from the University of Zaragoza acknowledge the
307 Aragón government and European Social Fund [Thermochem-
308 ical Processes Group (GPT)] and MINECO and FEDER
309 (Project CTQ2015-65226-R) for financial support. The authors
310 from DTU acknowledge financial support from the Danish
311 Strategic Research Council.

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