

Vanadium catalyzed oxidation of SO₂ to SO₃. Application in two-stroke marine diesel engines

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INTRODUCTION

Denmark is one of the world's foremost shipping nations, leading in cargo transport, tanker shipping, refrigerated cargo, and offshore. Maritime transport and shipping benefit from low CO₂ emissions and low noise levels but emissions of NO_x and SO_x are, however, generated. Formation of SO₃ may lead to sulfuric acid (H₂SO₄), which can cause corrosion if the temperature locally drops below the sulfuric acid dew point (cold corrosion) [1]. In order to improve the efficiency and future development of the engines, a study of SO₃ formation is required.

Marine diesel engines used for low-speed vessels, particularly two-stroke machines, can run on heavy fuel oils, which often contain large amounts of sulfur. During combustion the sulfur is quickly oxidized to SO₂ and a small fraction of it is further oxidized to SO₃. For the moment, it is known that the oxidation of SO₂ to SO₃ takes place through a sequence of gas-phase reactions which are comparatively well established [2]. However, fuel oils contain trace amounts of vanadium that cannot be removed easily from the oil. Vanadium oxide (V₂O₅) is known to catalyze SO₂ oxidation and may facilitate formation of SO₃ in the cylinder. The aim of this work is to elucidate the importance of the catalytic oxidation of SO₂ to SO₃ in marine diesel engines.

EXPERIMENTS AND KINETIC MODEL

The relative importance of homogeneous and heterogeneous (catalyzed by vanadium oxides) oxidation of SO₂ into SO₃ was evaluated through experiments and kinetic modeling. The kinetics of SO₂ oxidation over vanadium oxides were studied in a fixed bed reactor at atmospheric pressure. The vanadium aerosols were produced in a flame spray pyrolysis setup that enabled the formation of oxide nano-particles by spraying a combustible solution of organo-metallic salts into a flame. With this setup, catalytically active oxides can be produced by a mechanism similar to the one leading to formation of the catalytic species within the engine. Different vanadium-sodium particle compositions were chosen (Table1), in accordance to the composition of the exhaust gases of a medium-speed marine diesel engine [3].

The experimental results (Figure 1) were used to establish the rate equation for the catalytic reaction, using non-linear regression to a simple rate expression (the parameters obtained are listed in Table1):

$$-r_{SO_2} = k \cdot P_{SO_2} \cdot (1 - \beta)$$

CONCLUSIONS

The oxidation of SO_2 to SO_3 in a quartz fixed bed reactor with different vanadium-sodium particles composition was studied in the temperature range 300-600°C. Experiments were conducted with 0,25g of particles in the fixed bed, a total flow rate of 160 mL/min, and a composition of 1400 ppm of SO_2 and 10% O_2 in N_2 . The model proposed fits properly the experimental data. The homogeneous oxidation was simulated with Chemkin-II and then compared with the heterogeneous oxidation using the kinetic parameters previously determined. The homogeneous way dominates the oxidation of SO_2 in our comparison (Figure 2). These are the first studies in this topic, as far as we know.

Table 1: catalyst particles data

Catalyst [m/m]	Area [m ² /g]	Ea [kJ/mol]	A [mol/(s·g·bar)]
V/Na: 4/1	91,2	69,53	20,6
V/Na: 8/1	87,6	67,3	14,48
V/Na: 15/1	153,0	57,84	2,96
V 100%	155,1	47,91	0,17

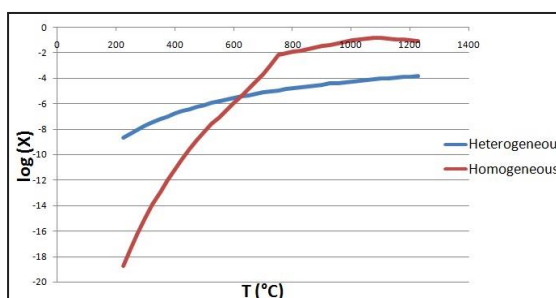


Figure 2: SO_2 conversion (X) for both ways of oxidation

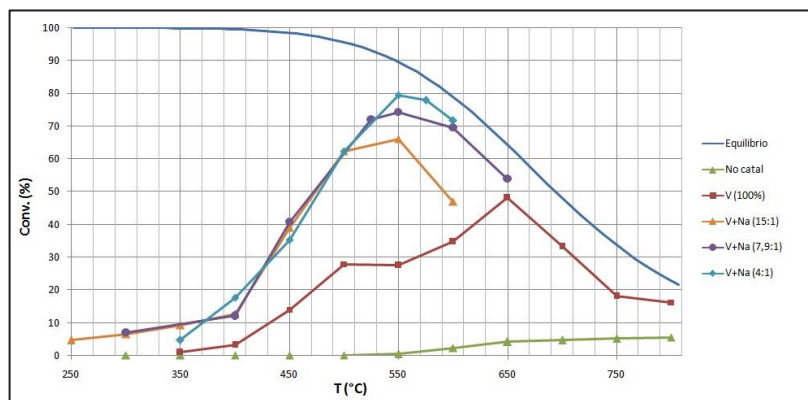


Figure 1: SO_2 conversion over vanadium-sodium catalysts at different temperatures

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