Methane slip abatement by hydrogen addition

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The regeneration of sulfur poisoned catalyst by hydrogen in gas engine was studied. Laboratory experiments were also performed to examine sulfur regeneration by hydrogen containing gas mixtures. A bimetallic palladium-platinum catalyst with alumina support was used in the experiments.

According to the literature review, the hydrogen treatment of the exhaust gas often enhanced the methane conversion, but no exact mechanism behind the effect was found. To study the role of hydrogen in sulfur regeneration for a methane oxidation catalyst (MOC), laboratory and engine test bench experiments were conducted.

Laboratory examinations. Different regeneration mixtures were examined in the laboratory. Bimetallic Pd-Pt MOC samples were poisoned by sulfur using 25 ppm SO_2 in the feed gas. After poisoning, samples were regenerated using hydrogen containing mixtures at 550°C and the SO_2 and H_2S formation was detected during the regeneration. After regeneration, the light-off curves of the samples were compared to the corresponding curves measured for the fresh and S-poisoned catalysts.

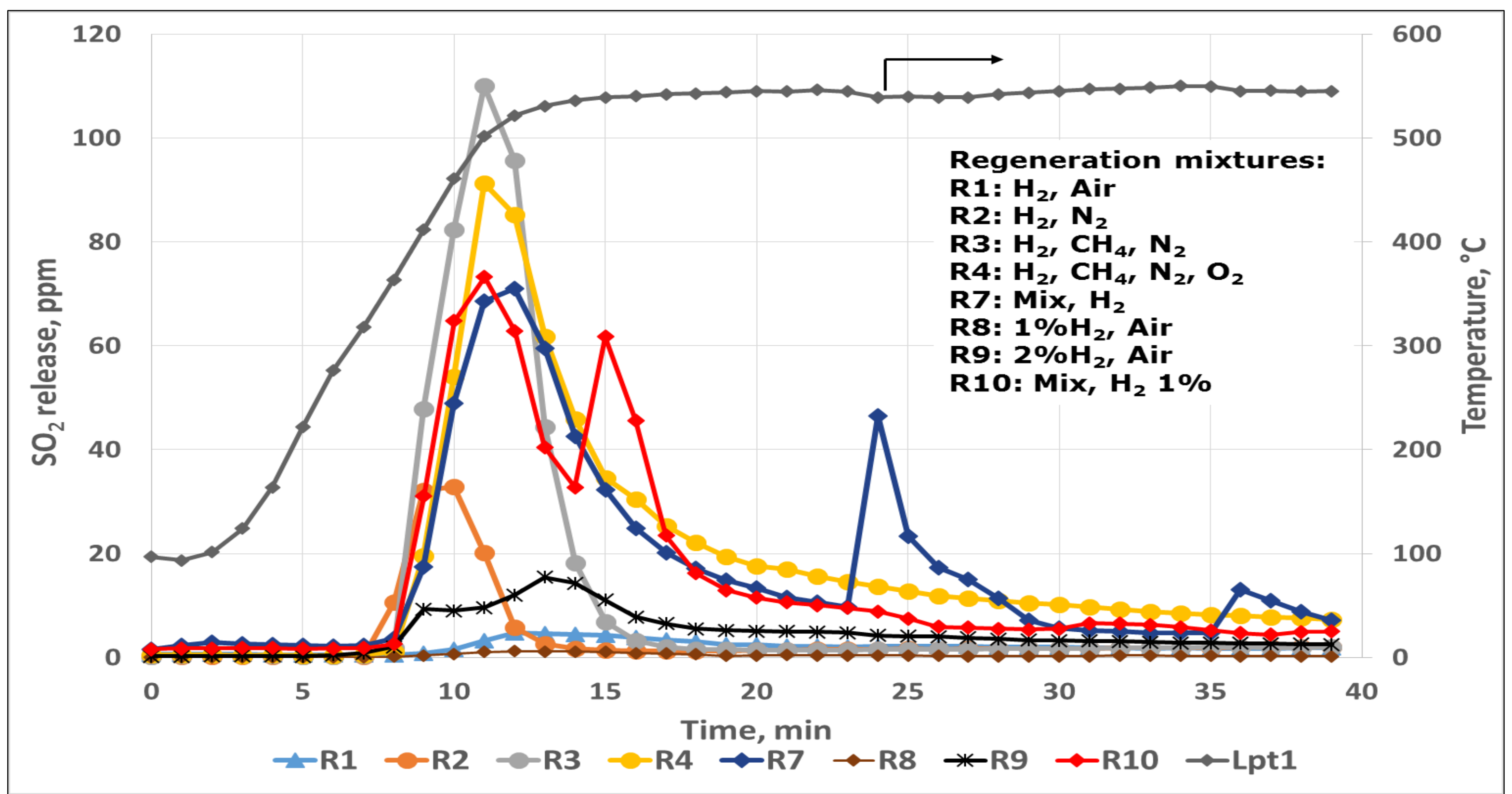

Fig. 1. SO_2 release curves during the regeneration by different mixtures; Mix = simulated exhaust gas; H_2 amount in R1 and R2 = 4000 ppm, in R3 and R4 = 1000 ppm; temperature curve added from one experiment.

Based on the regeneration examinations SO_2 release order was: R3>R4>R10=R7>R2>R9 and R1 and R8 mixtures seemed not to release SO_2 at all, Fig. 1. It seems that when using hydrogen alone as a reductant the amount should be quite high to regenerate sulfur, but together with other reductants like methane SO_2 release is higher. H_2S was also measured during the regeneration and it was found that mixtures R2 and R3 released H_2S (for R2 sulfur was released mainly by H_2S). These mixtures don't contain oxygen and are very reductive and therefore releases lot of sulfur out, but lot of it by smelly H_2S.

Different regeneration methods improved the light-off performance of the S-poisoned sample, Fig. 2. The best performance was achieved by the mixtures R2 and R3 which also released best sulfur out of the sample. The light-off curves for these samples were only slightly worse than corresponding curve for the fresh catalyst sample.

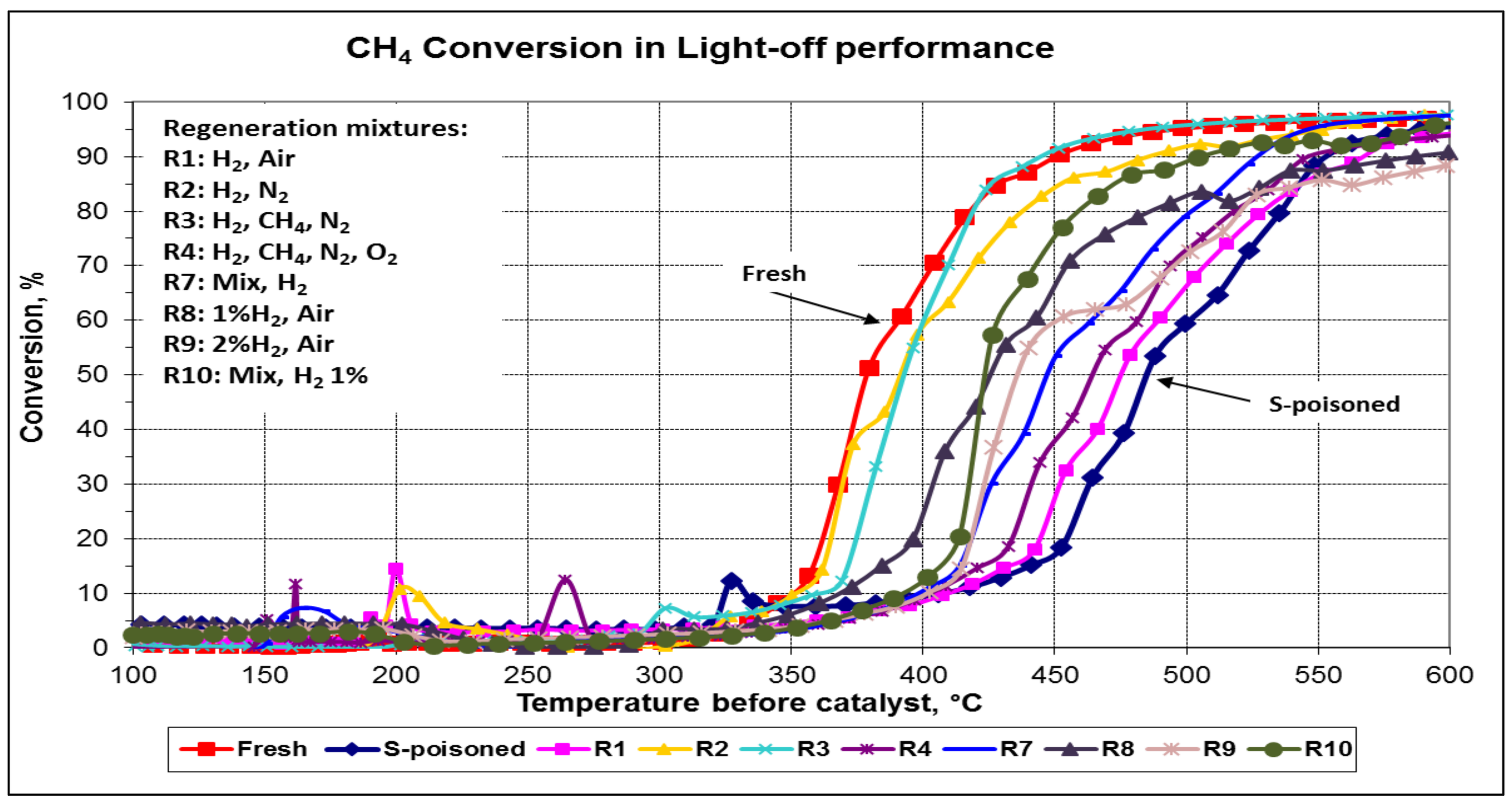

Fig. 2. Methane (CH_4) light-off curves for the differently regenerated samples compared to the corresponding curves for the fresh and S-poisoned samples.

Engine examinations. The hydrogen regeneration was tested in various concentrations at 380 °C in gas engine's exhaust flow. Hydrogen amounts introduced to exhaust gas before the MOC were selected based on the laboratory examinations. The temperature was too low for the methane conversion as shown in Fig. 3. The conversion was low throughout the whole experiment and therefore it was difficult to draw conclusions about if the regeneration improved the methane conversion. The experiments will be continued at a higher exhaust temperature. The engine experiments were performed at VTT, Espoo.

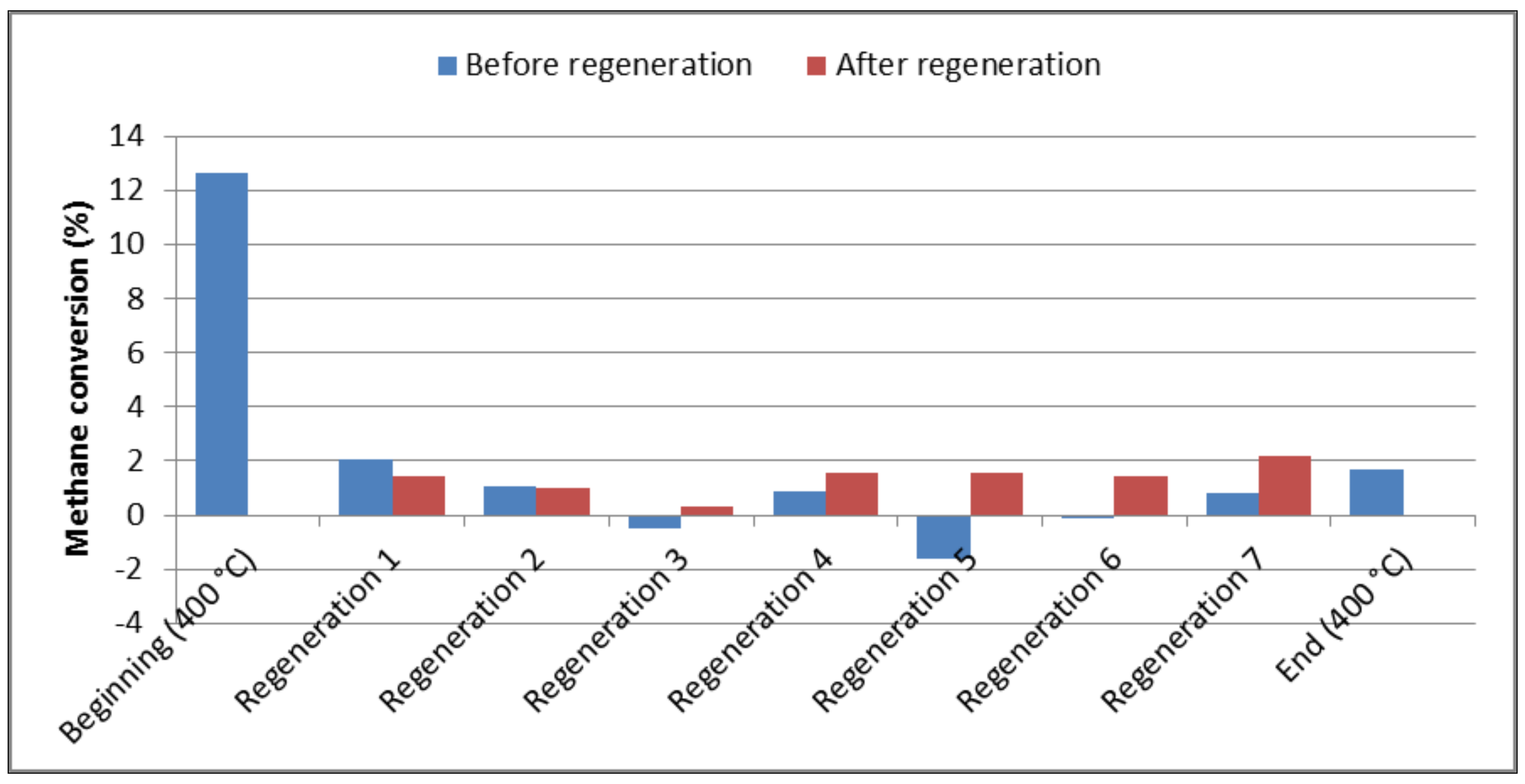

Fig 3. Average methane conversions during the experiment at 380 °C.