Utilization of sulfur contaminated methanol rich VOC emissions

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Introduction

Volatile organic compound (VOC) emissions are released from various industrial sources causing harmful effects on the environment and human health. One interesting route to avoid harmful impacts is to utilize the emissions. Significant amounts of methanol (MeOH) rich VOC emissions are emitted from the chemical pulp mills. These emissions are contaminated with reduced sulfur compounds for example methanethiol (MT), and therefore utilized in energy production leading to increased CO_2 emissions. Instead, sulfur contaminated methanol could be used in formaldehyde production [1, 2]. In this case, a catalytic process converts methanol and part of the reduced sulfur compounds, such as methanethiol, into formaldehyde according to the following reactions:

$$CH_3OH + ½\,O_2 \rightarrow HCHO + H_2O$$
$$CH_3SH + 2O_2 \rightarrow HCHO + SO_2 + H_2O$$

Based on our previous studies [3], it was shown that the vanadia-alumina (V-Al) catalyst is efficient in formaldehyde production from a mixture of MeOH and MT. However, the V-Al catalyst deactivates easily in the presence of sulfur. The main aim of this study was to improve the sulfur-resistance of the V-Al catalyst by using silica, gadolinia or hafnia promoted alumina supports.

Materials and Methods

Support preparation: Modified alumina supports, with target compositions of 80 wt-% for alumina and 20 wt-% for additives, were prepared by the sol-gel method based on the procedure described by Yoldas [4]. The utilized additives were hafnia, gadolinia, and silica.

Vanadia impregnation: The 1.5 wt-% vanadia catalysts were prepared by a wet impregnation method. Each calcined binary oxide was impregnated with vanadyl acetylacetonate $VO(acac)_2$, dissolved in methanol, at room temperature for 20 h. Dried samples were calcined at 600 °C for 4 h. Catalysts are represented as V-Al, V-SiAl, V-HfAl and V-GdAl.

Poisoning treatment: The poisoning treatment was performed at 400 °C for 5 h under a gas mixture containing 100 ppm SO_2, 10% H_2O, 10% air, and balance N_2.

Oxidation experiments: The activity of fresh and poisoned samples were investigated in the production of formaldehyde from a mixture of methanol (MeOH 500 ppm) and methanethiol (MT 500 ppm). The temperature range of experiments was 100-600 °C.

References
1. Burgess, T.L., Gibson, A.G., Furstein, S.J. and Wachs I.E. (2002) Environmental Progress 21, 137–141.
2. Wachs, I.E. (1999) United States patent 5907066 May 25
3. Laitinen, T., Ojala, S., Cousin, R., Koivikko, N., Poupin, C., El Assal, Z., Aho, A., and Keiski, R.L. (2020) J. Ind. Eng. Chem. 83, 375–386.
4. Yoldas, B.E. (1975) Am. Ceram. Soc. Bull. 54, 289–90.
5. Christodoulakis, A., Machli, M., Lemonidou, A.A., Boghosian, S. (2004) J. Catal. 222, 293–306.
6. Uy, D., Dubkov,A., Graham, G.W. and Weber, W.H. (2000) Catalysis Letters 68, 25–32.
7. Gao, S. Wang, P., Yu, F., Wang, H. and Wu, Z. (2016) Catal. Sci. Technol., 6, 8148

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Results

Table 1. Specific surface area of the fresh and poisoned catalysts, optimal formaldehyde production temperatures, temperature when conversion of methanethiol is 100% and methanol conversions at maximum formaldehyde production temperature.

Sample	Specific surface area [$m^2\,g^{-1}$]		Optimal temperature (°C)		Temperature (°C) (conversion of MT 100%)		MeOH conversion (%)	
	Fresh	Poisoned	Fresh	Poisoned	Fresh	Poisoned	Fresh	Poisoned
V-Al	237	227	445	420	325	350	91	92
V-HfAl	172	160	455	440	350	355	90	85
V-GdAl	170	169	500	495	330	380	92	92
V-SiAl	335	277	455	435	290	340	91	91

Table 2. Composition of fresh catalysts and calculated VOx surface densities.

Sample	Concentration [wt-%]			VOx surface density [VOx nm^{-2}]
	Al_2O_3	Additive	V_2O_5	
V-Al	98	-	1.8	0.5
V-HfAl	76	20	1.5	0.6
V-GdAl	80	17	1.4	0.6
V-SiAl	78	20	1.8	0.4

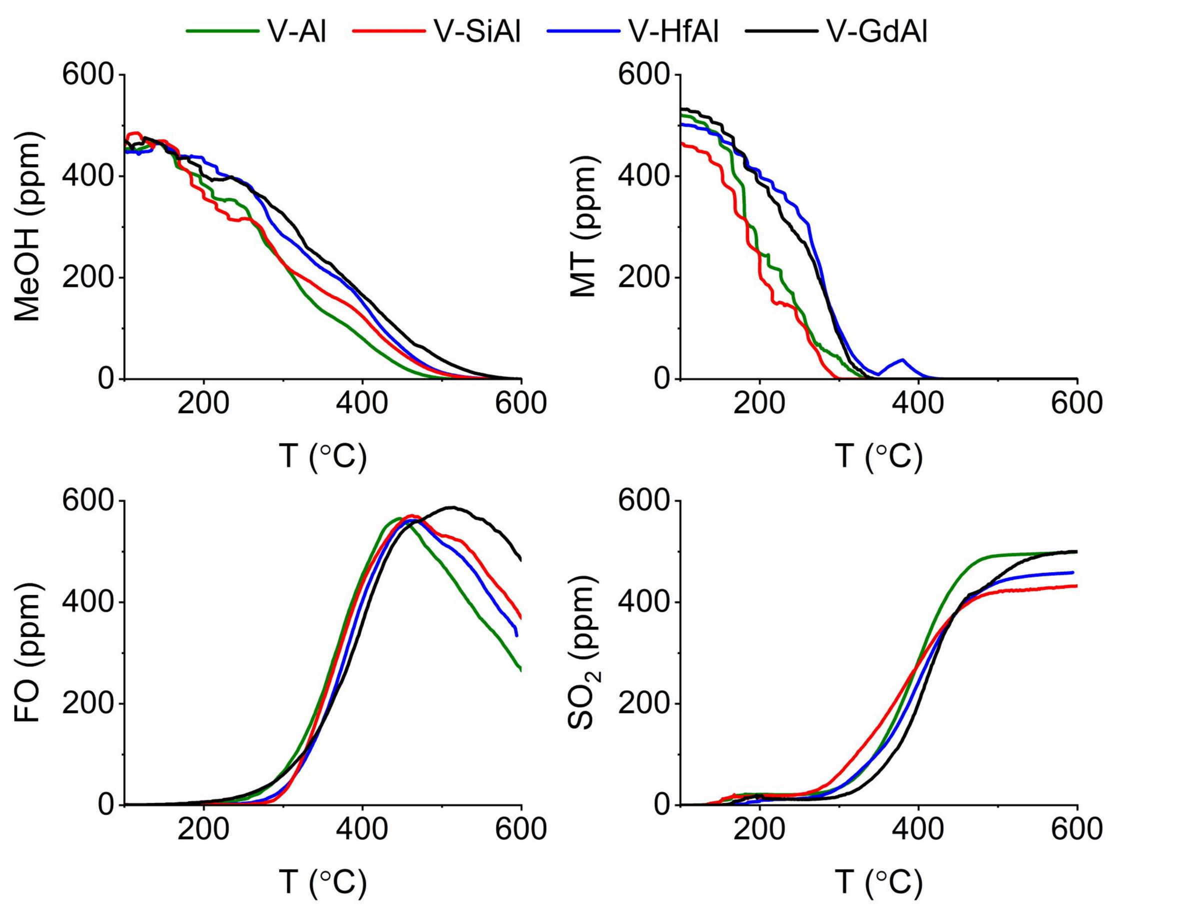

Figure 1. Oxidation of the methanethiol (500 ppm) and methanol (500 ppm) mixture: concentration of reactants and products over the fresh vanadia catalysts.

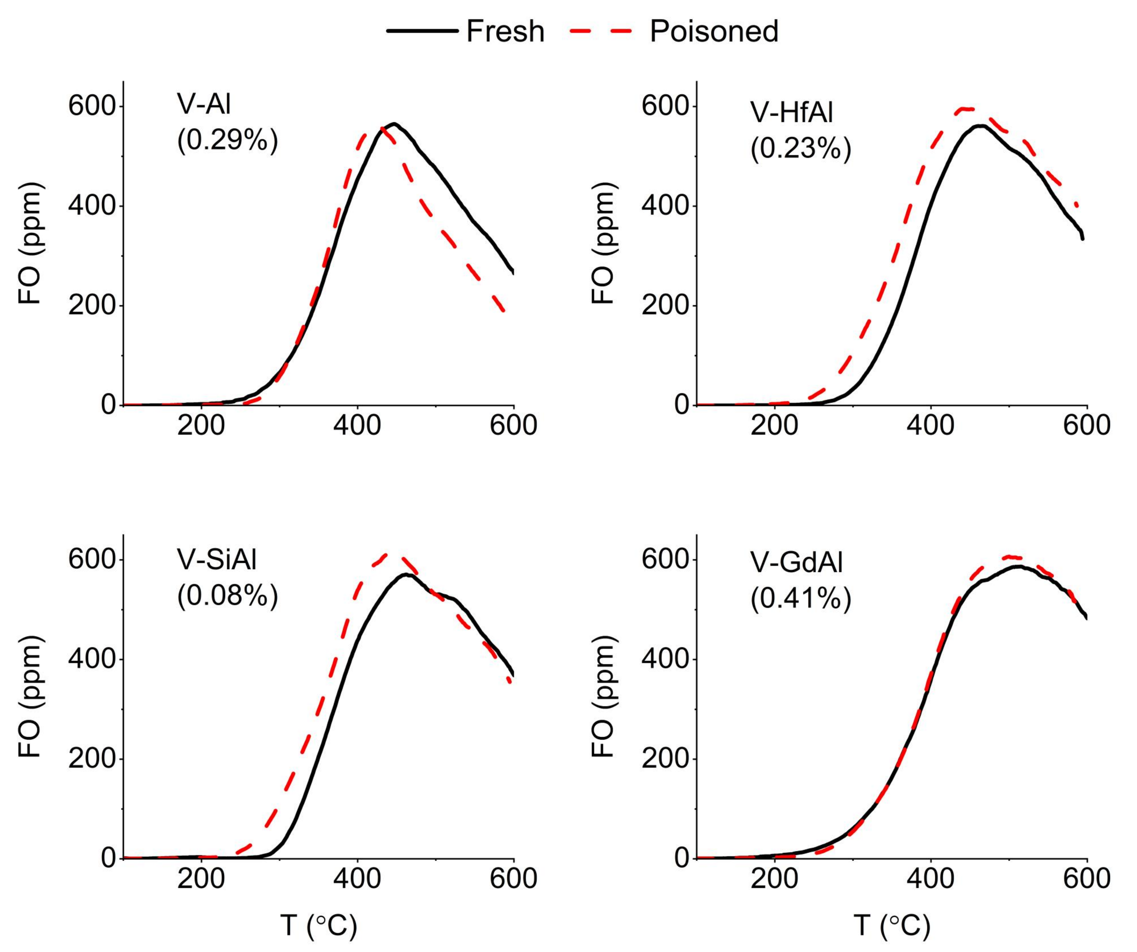

Figure 2. Formaldehyde concentration vs. temperature over the vanadia catalysts (sulfur contents of the poisoned samples are shown in brackets).

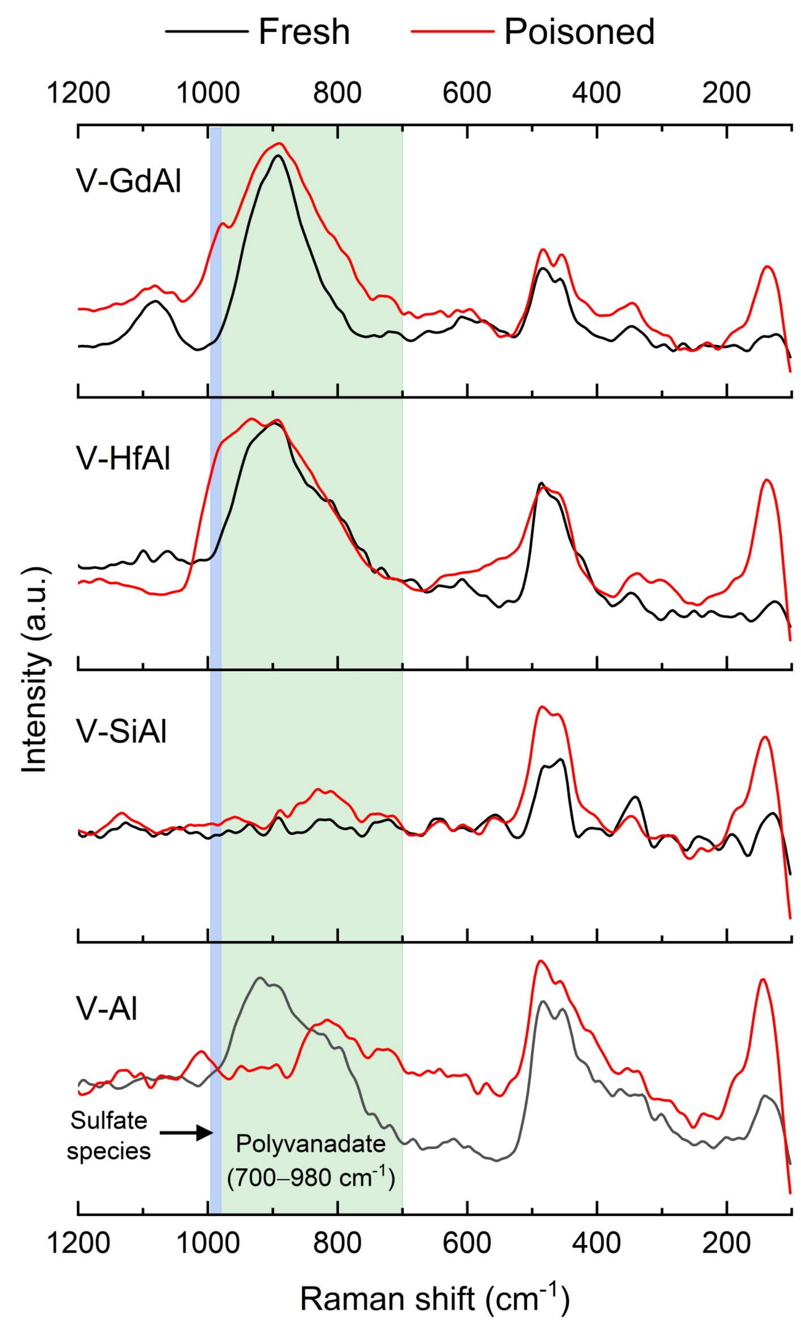

Figure 3. Raman spectra of the fresh and poisoned catalysts [5-7].

Conclusions

- The poisoned V-SiAl accumulated the lowest amount of sulfur.
- The poisoning treatment slightly improved the catalytic activity of all the samples.
- Poisoning leads to a decrease in specific surface area values from 1 to 17%.
- Formaldehyde yield was increased by 2–4% and the optimum reaction temperature decreased by 5–25 °C after the poisoning treatment.
- Raman measurements proved the good dispersion of vanadia, and only polyvanadate species were tentatively observed in the prepared samples excluding the V-SiAl sample. This was expected due to the low surface VOx density.
- The V-SiAl sample showed the highest sulfur-resistance and activity in the formaldehyde production from the mixture of MeOH and MM.

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