

Sulfation Study of Vanadia Catalyst by In Situ FTIR

Xiaoyu Guo, Aaron Nackos, Calvin H. Bartholomew, Larry L. Baxter, William C. Hecker

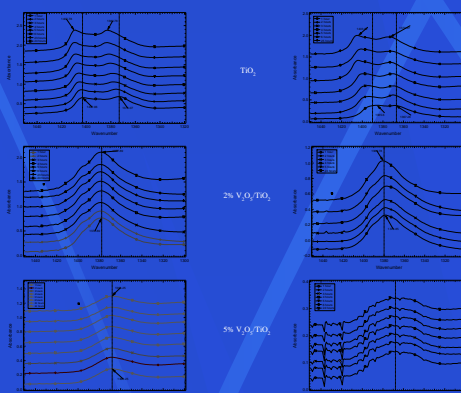
Objectives

- Understand formation mechanism of sulfate species on both the support, TiO_2 , and the catalyst, $\text{V}_2\text{O}_5/\text{TiO}_2$.
- Understand how sulfate species affect adsorption and reaction on vanadium oxide species on the catalyst surface.
- Determine the effects of moisture, vanadia content, and time on sulfation.

FTIR Spectra of 24 h Sulfation Test

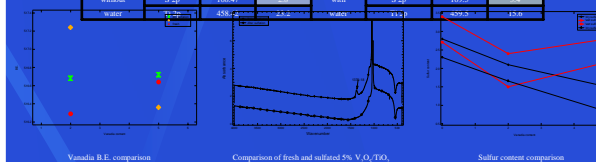
Dry Conditions

Moist Conditions



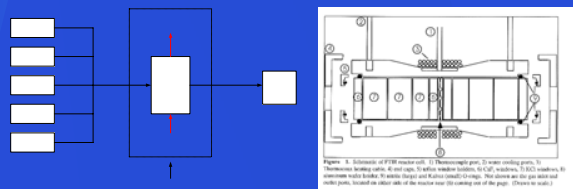
XPS Analysis Results

Sample	Element	B.E.	Atom %	Sample	Element	B.E.	Atom %
5% V	C 1s	285	24.2	5% V	C 1s	285	8.3
Sulfation	O 1s	533.99	56	Sulfation	O 1s	533.30	65.8
without	S 2p	168.46	7.8	without	S 2p	168.55	0.9
water	Ti 2p	458.19	16.5	water	Ti 2p	458.14	20.2
	V 2p3/2	516.72	8.3		V 2p3/2	516.68	3.3
2% V	C 1s	285	8.3	2% V	C 1s	285	10.1
Sulfation	O 1s	533.74	67.7	Sulfation	O 1s	530.63	65.2
without	S 2p	168.97	2.1	without	S 2p	169.25	2.4
water	Ti 2p	458.16	20.9	water	Ti 2p	458.72	20.2
	V 2p3/2	516.36	1.9		V 2p3/2	517.24	2.1
Titanium	C 1s	285	8.7	Titanium	C 1s	285	10.2
	O 1s	529.48	66.4		O 1s	530.48	70.7
Sulfation	S 2p	168.47	2.8	Sulfation	S 2p	169.5	4.8
without	V 2p3/2	458.16	1.9	without	V 2p3/2	459.8	4.8

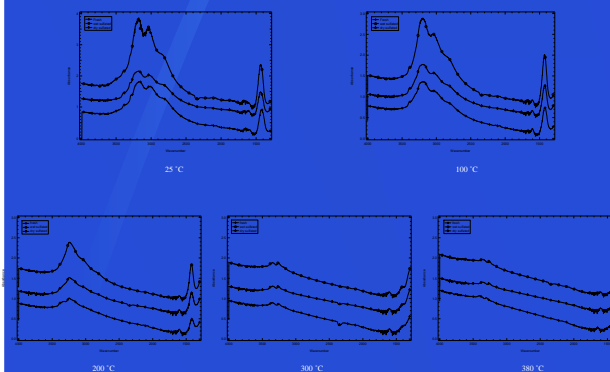


Experimental Design

- Sulfation gas: 3000 ppm SO_2 , 5% O_2 , He balance, dry or moist gas
- Temperature: 380 °C
- Pressure: 1 atm
- Duration of experiment: 6 hours preliminary test; 24 hours full test
- Sample: TiO_2 , 2% $\text{V}_2\text{O}_5/\text{TiO}_2$, 5% $\text{V}_2\text{O}_5/\text{TiO}_2$
- FTIR equipment: Nicolet 730
- XPS equipment: SSX-100ESCA



NH_3 adsorption on 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ at different temperatures



Conclusion

- $\text{S}=\text{O}$ (1375 cm^{-1} on the FTIR spectrum) intensity decreases with increasing vanadia content on the catalyst surface
- Surface sulfate species do not form in vanadia sites but in titania sites.
- XPS analysis results are consistent with FTIR results
 - Sulfate content decreases with increasing vanadia content on $\text{V}_2\text{O}_5/\text{TiO}_2$ surface
 - Vanadia is in 5+ oxidation state before and after sulfation, no vanadyl (V^{4+}) sulfate formed during sulfation.
- Water assists sulfation
- Sulfation intensify NH_3 adsorption

Future Work

- Combine FTIR study with temperature-programmed desorption and MS to analyze quantities of species adsorbed/desorbed.
- Investigate contaminants (Ca, K, and Na) effects on $\text{V}_2\text{O}_5/\text{TiO}_2$ properties: sulfation, NH_3 adsorption, activity, etc.