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"The Utility of $FeVO_4$ in Combination with Stabilized Titanias for Mobile SCR Application"

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Brilliance inspired by titanium

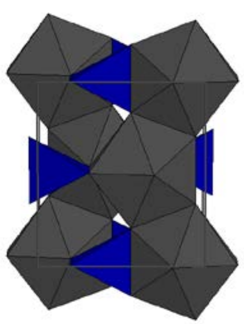
Background

- Cristal have introduced stabilized titanias for vanadia-based mobile source SCR applications
  - Chapman, D. et al., *SAE Int. J. Fuels Lubr.*, 3(1):643-653, 2010
  - US 2011/0027154A1; US 2011/0138789A1
    - ***The new materials exhibit an attractive combination of activity and stability***
- Treibacher have introduced transition metal vanadates as raw materials for SCR applications
  - US 2011/015073A1
  - SAE 2011-01-1331
    - ***FeVO4 is not listed as hazardous by GHS (other vanadia precursors are)***

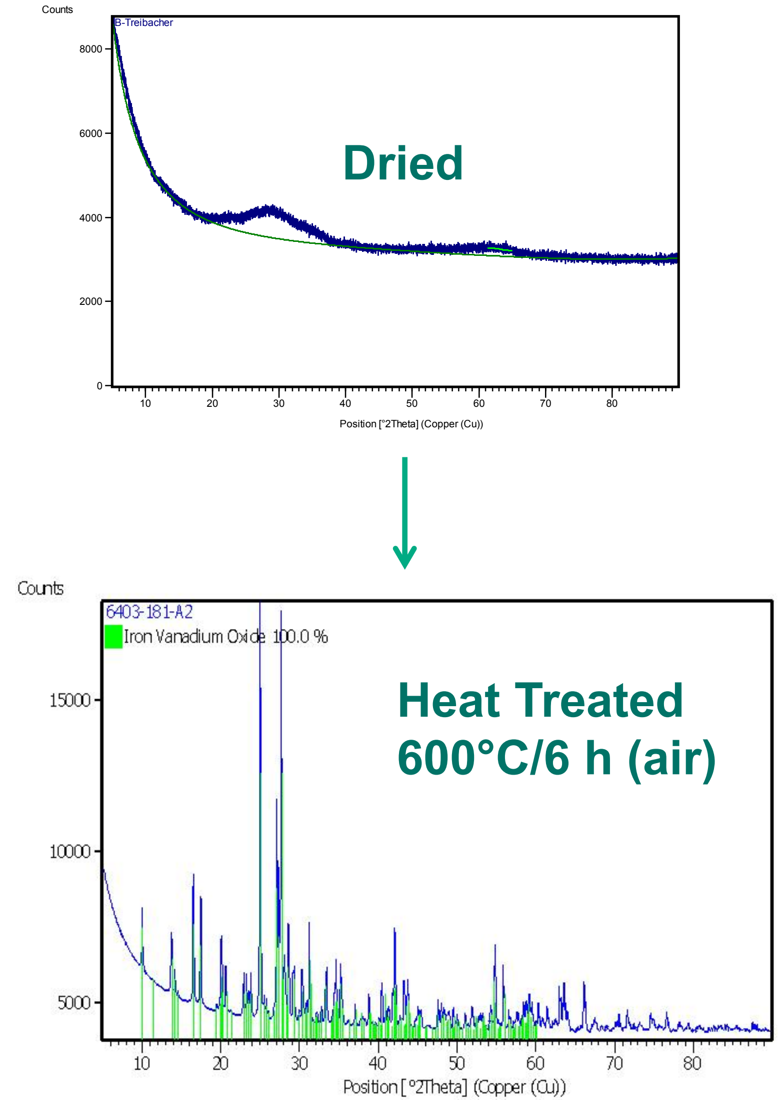
- Objective: evaluate stabilized titanias in combination with $FeVO_4$

Structure of $FeVO_4$

- Two samples provided
  - Dried, calcined
- Dried material is amorphous
- Calcined material is crystalline $FeVO_4$
  - Triclinic: P1
  - Fe^{3+}, V^{5+} valence
  - VO_4 tetrahedral
    - Not considered active form of V for SCR



XRD Powder Patterns



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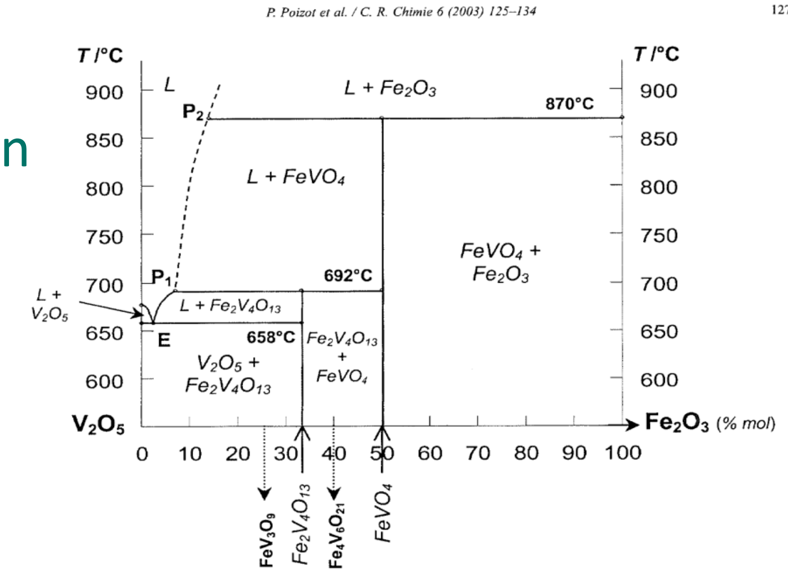
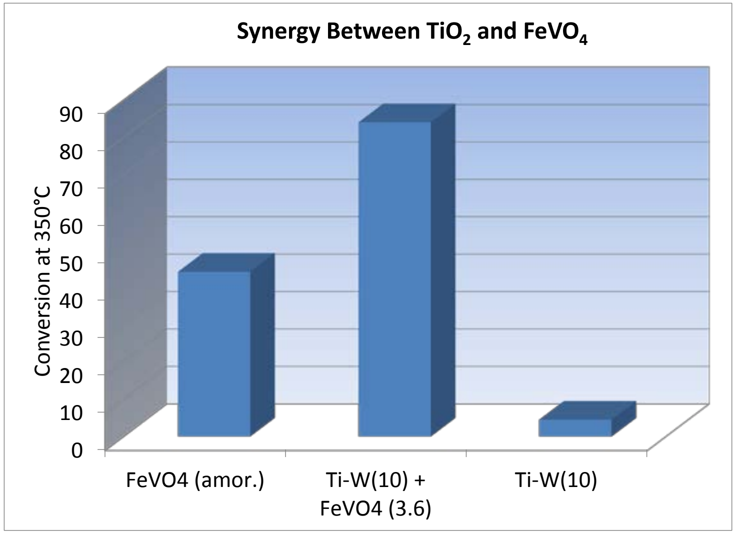
Phase and SCR Behavior of $FeVO_4$ -Synergy with TiO_2

- $FeVO_4$ incongruent m.p. 870°C
- At T < 692°C and excess V, solid solution
- D.T.A. for pure $FeVO_4$- no features < 800°C
- D.T.A. for $FeVO_4$ + TiO_2: no unusual features < 800°C
- Pure materials not very active for SCR
- $FeVO_4$ + TiO_2 (physical mix plus heat) is very active for SCR
- Amorphous $FeVO_4$ is more active than crystalline form



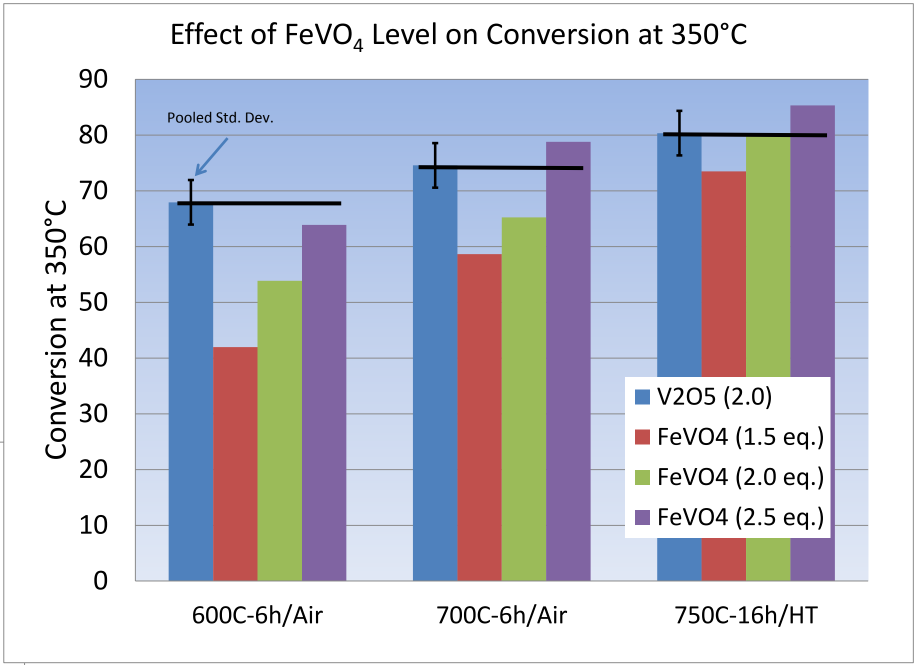


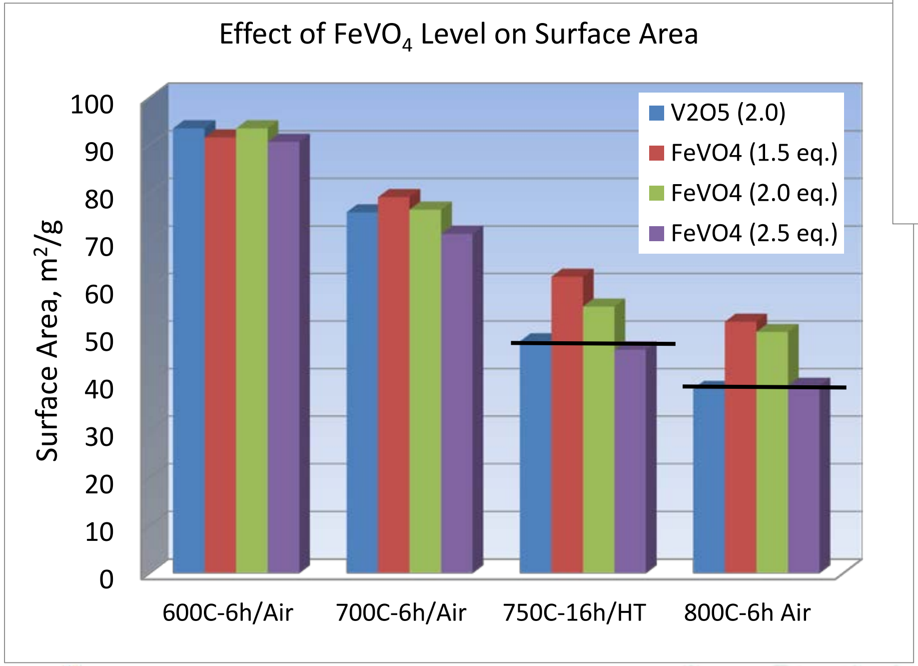
Equivalent Concentrations

wt%		
V_2O_5	V	$FeVO_4$
1.5	0.8	2.8
2.0	1.1	3.8
2.5	1.4	4.7

Screening Studies
$FeVO_4$ Level and Thermal History

- *Commercial Ti-Si(10)-W(9)*
- Amorphous $FeVO_4$
  - Powders slurried, sonicated, dried and heat-treated
  - "$FeVO_4$ (2.0 eq.)" corresponds to 2.0 wt% V_2O_5
- DeNOx 650 L/(h*g); 500 ppm NO, α = 1.0

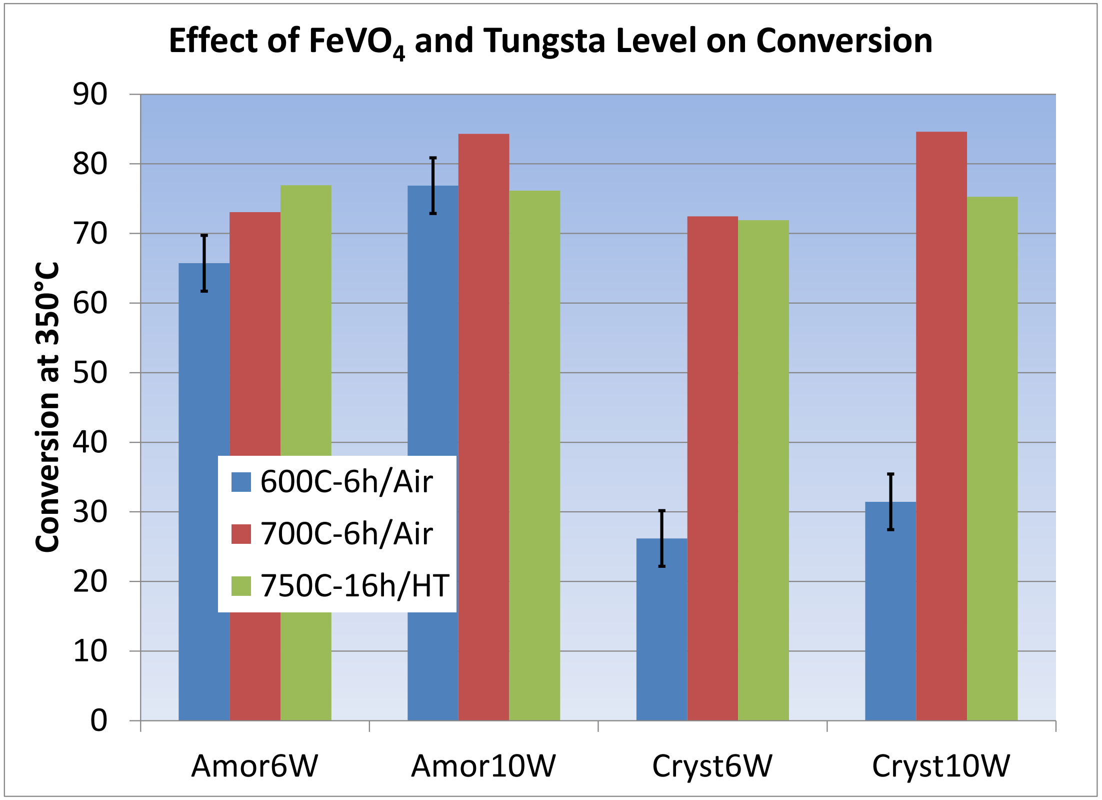




- Similar performance
  - *Activity and stability benefit for $FeVO_4$ after severe aging*

Screening Studies
$FeVO_4$ Source, Tungsta Level and Thermal History

- *Developmental Ti-Si(4.5)*
- Amorphous or crystalline $FeVO_4$
  - Powders slurried, sonicated, dried and heat-treated
  - 3.2 wt% FeVO4 (1.7 eq.)
- DeNOx 650 L/(h*g); 500 ppm NO, α = 1.0



- *Amorphous $FeVO_4$ gives highest activity at lowest activation T*
- *Higher tungsta gives higher activity*

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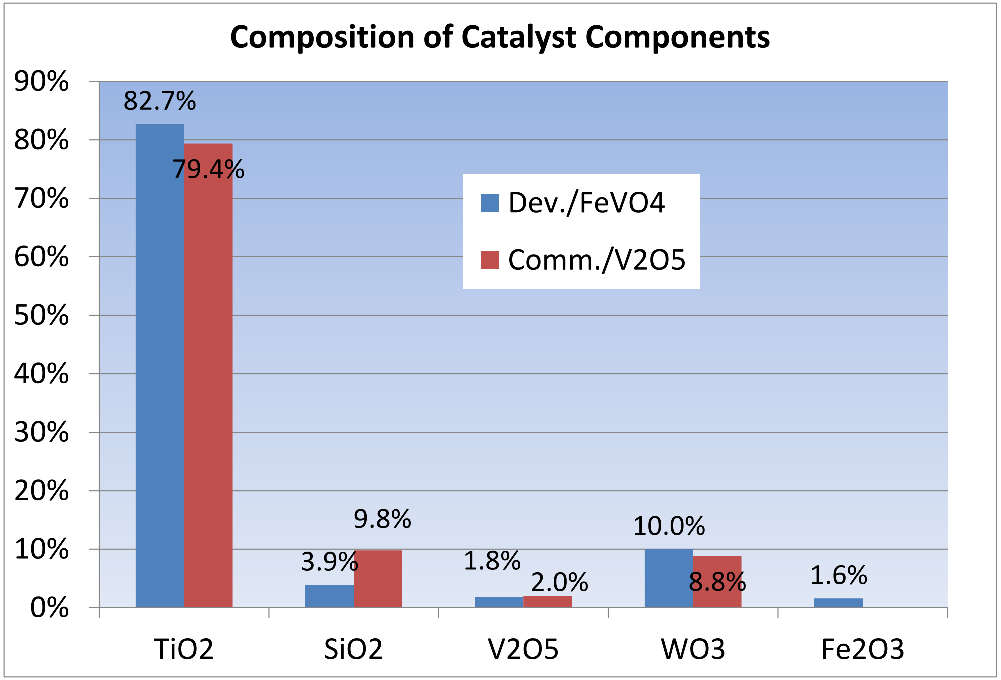
IRMA Study
Catalytic Evaluation of Wash-coated Parts

- *Test: Dev. Ti-Si(4.5) + WO_3 + $FeVO_4$*
  - Nominal 3.4% $FeVO_4$
- *Ref: Comm. Ti-Si(10)-9(W) + V_2O_5*
  - Nominal 2.0% V_2O_5
- 80% Catalyst, 20% binder
  - Nominal 150 g/L loading
  - 2" l. x 1" dia. cores
- Fast SCR (NO, NO_2 = 200 ppm; NH_3 = 400 ppm)
- Std. SCR (NO = NH_3 = 400 ppm)
- GHSV = 30,000 h^{-1}
- Fresh: Calcined 500°C
- Age: 700°C, 10 h, 10% H_2O



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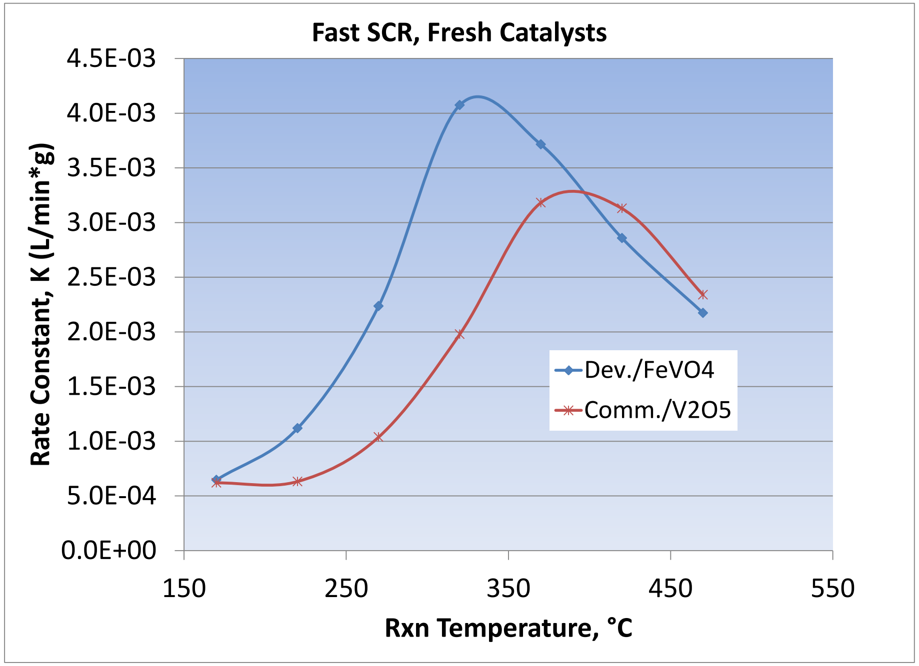
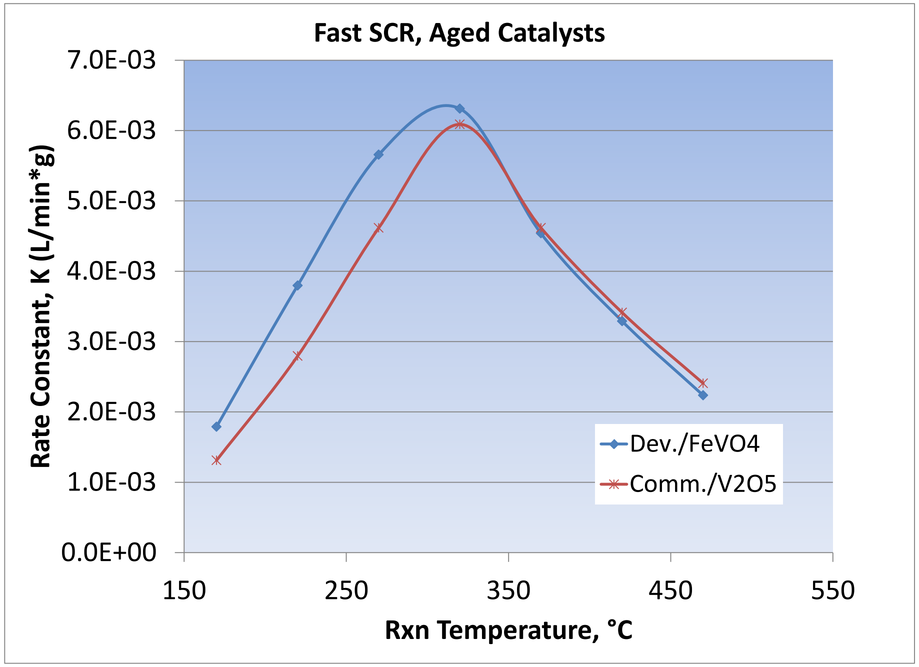
IRMA Study
Fast SCR

- Rate constants calculated from conversion:

K = -((total flow*NO conc)/cat mass))*LN(1-conv/100)





- In fast SCR, Dev./$FeVO_4$ has higher activity at low temperature fresh and aged

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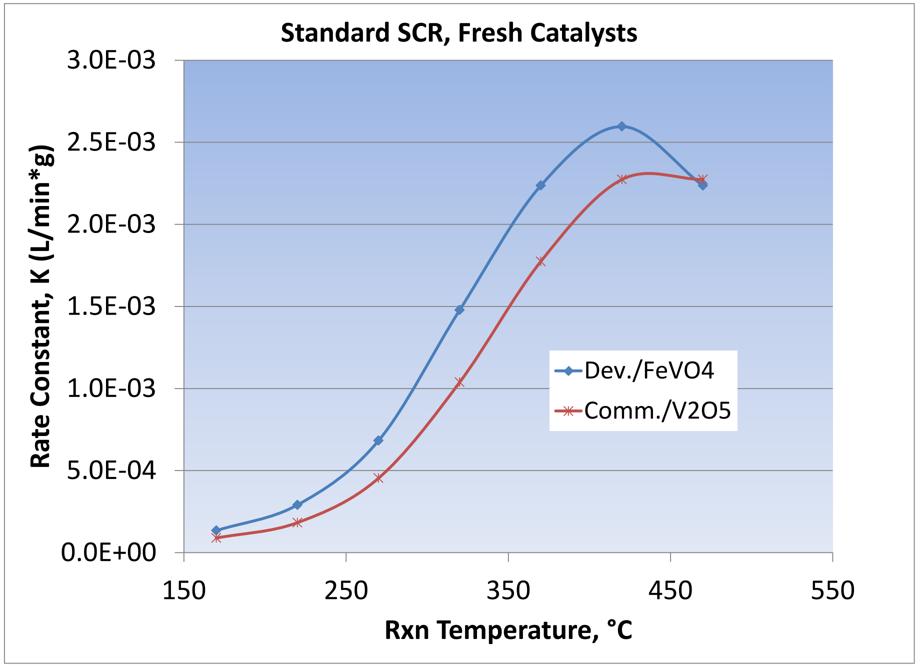
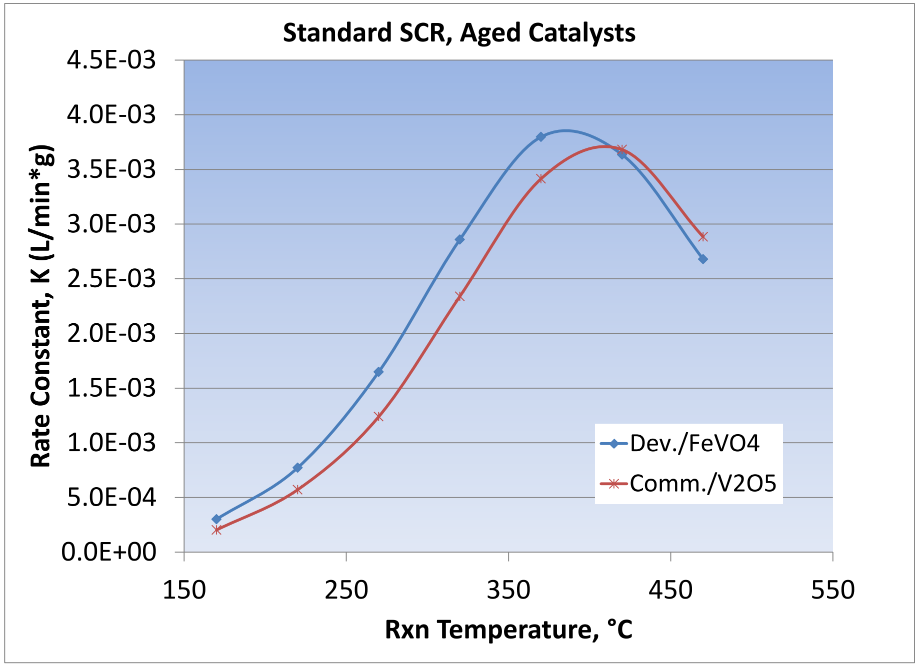
IRMA Study
Standard SCR

- Rate constants calculated from conversion:

K = -((total flow*NO conc)/cat mass))*LN(1-conv./100)





- In std. SCR, Dev./$FeVO_4$ has higher activity at low temperature fresh and aged

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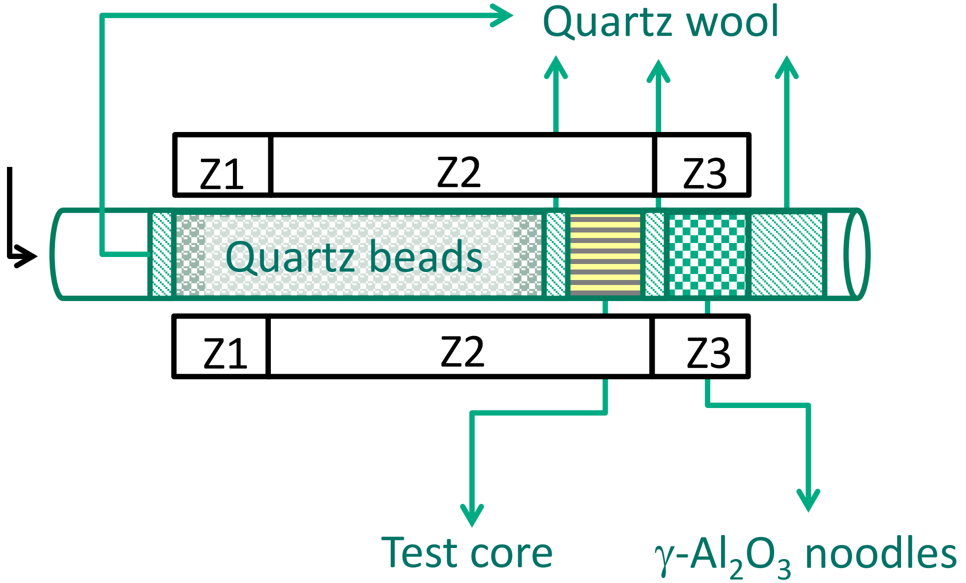
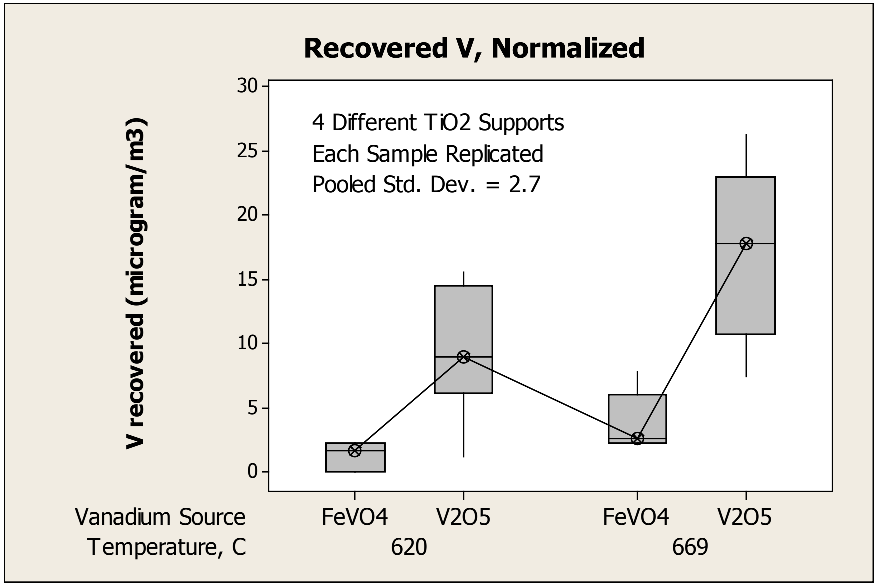
Vanadium Volatility

- 3-zone clamshell furnace
- 1” or 2” l core at end of Z2
- 4.5 g γ-Al_2O_3 1/8” extrudates
- Gas: 5% O_2, H_2O bal. N_2
- 7.5 L/m, 18 h, GHSV ~35,000 h^{-1} (1” core)
- Analysis:
  - Digest Al_2O_3 and downstream Quartz Wool
  - ICP-OES quantification
  - < 1 ppm detection limit
  - Blank < 0.3 $\mu g/m^3$
- Reference V_2O_5 and test $FeVO_4$ cores from IRMA study
  - < 1 $\mu g/m^3$ V at 620°C





- Clear trend for lower volatile V with $FeVO_4$ as source

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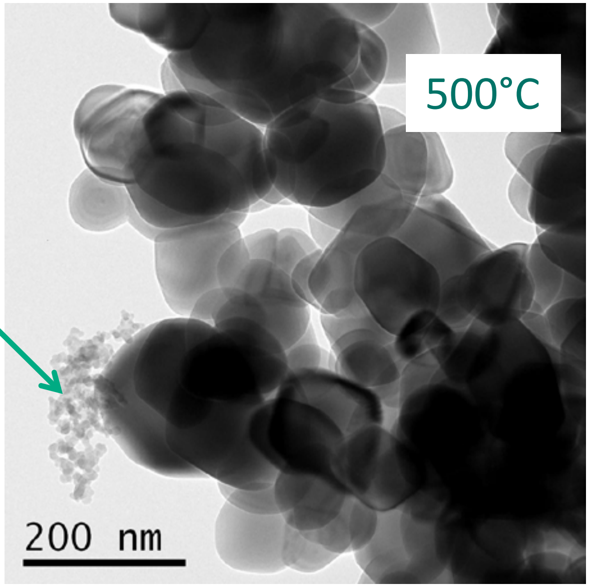
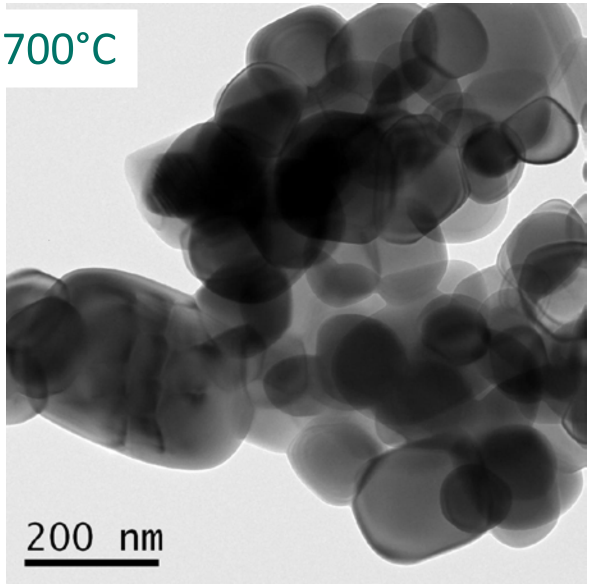
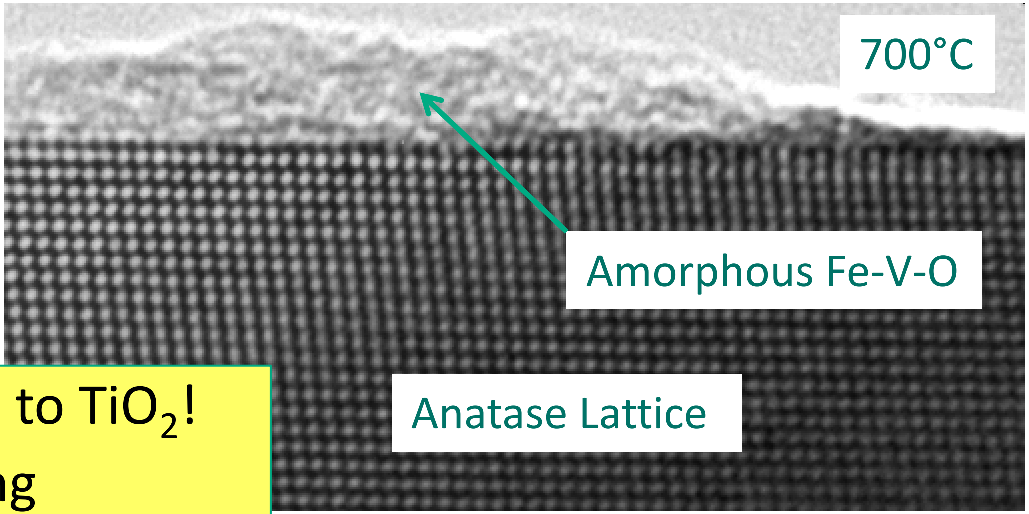
Microscopy (I)- Powder Mixes

- SEM/EDS and TEM/EDS on $TiO_2/FeVO_4$
  - Calcined 500°C/6 h
  - Calcined 700°C/6 h



$FeVO_4$





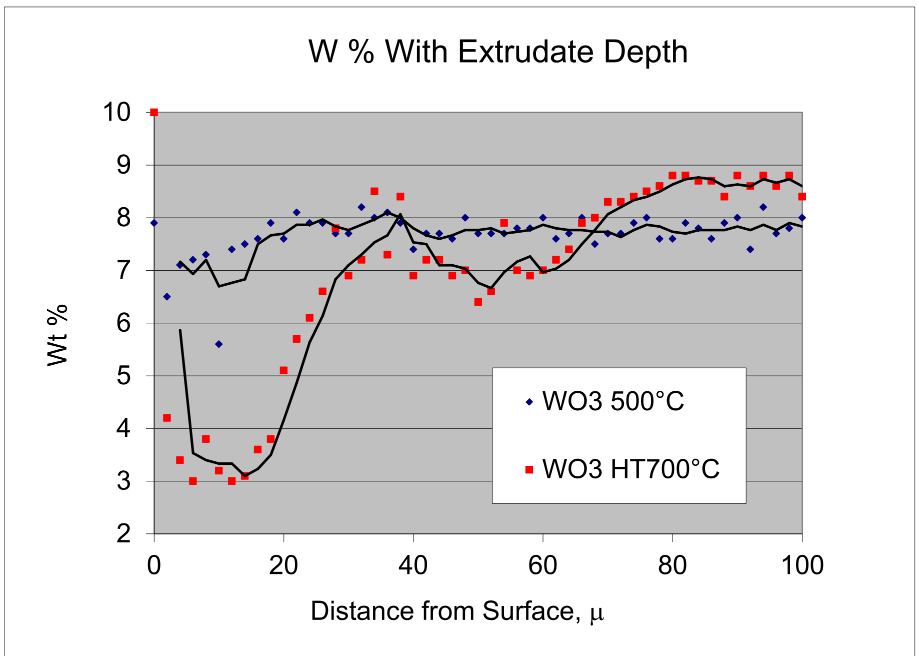
- Sub-liquidus Fe, V migration to TiO_2!
- Heterogeneous TiO_2 sintering

XRD and Microscopy (II)

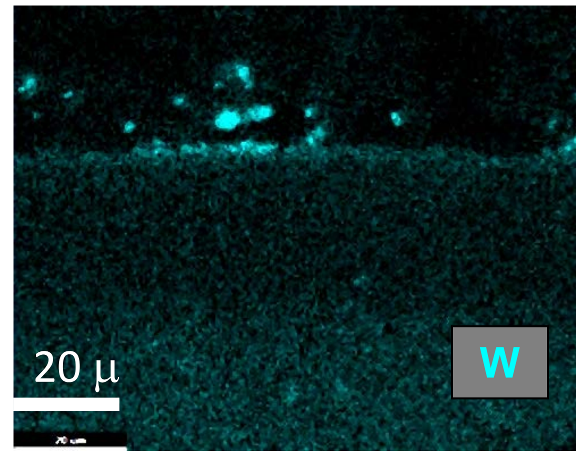
- XRD on $TiO_2/FeVO_4$
  - Calcined 700°C/6 h
  - Hydrothermal age 750°C/16 h
- SEM/EDS on TiO_2-WO_3(10) extrudates coated with $FeVO_4$ shell
  - Calcined 500°C/6 h
  - Hydrothermal age 700°C/16 h

XRD Rietveld Analysis

Tungsta Level	Age Condition	Fe_2O_3	Fe_2WO_6
6% WO3	700°C-6h/Air	Y	N
	750°C-16h/HT	Y	N
10% WO3	700°C-6h/Air	Y	N
	750°C-16h/HT	N	Y



HT 700°C



- After high temperature age
  - Evidence for V, Fe migration <100 μ into extrudate
  - Evidence of W migration to $FeVO_4$

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Conclusions

- For intimate mixtures of $FeVO_4$ and TiO_2 that are heated at high temperature (~700°C and above)
  - $FeVO_4$ separation into constituent phases
  - V (and some Fe) migration onto TiO_2 surface
  - Fe-rich phase crystallization to Fe_2O_3 or Fe_2WO_6
- Tungsta appears to migrate to and interact with $FeVO_4$
- Fe(III) believed to be mostly a harmless spectator

- ***Vanadia volatility is suppressed***
- ***Developmental Ti-Si(4.5) support with 10% WO_3 and ~3.4% $FeVO_4$ shows excellent stability, activity and selectivity***
  - ***At least as good as commercial TiO_2-V catalyst of comparable V concentration***

Thank you!