Thermolysis Characterization of Urea-SCR

Howard L. Fang and Herbert F. DaCosta

Cummins Inc.

DEER Workshop

August 25-29, 2002

San Diego, CA

PROBLEMS: (1) Deposit formation in the exhaust pipe prior to catalyst (2) Stoichiometric imbalance in urea consumption

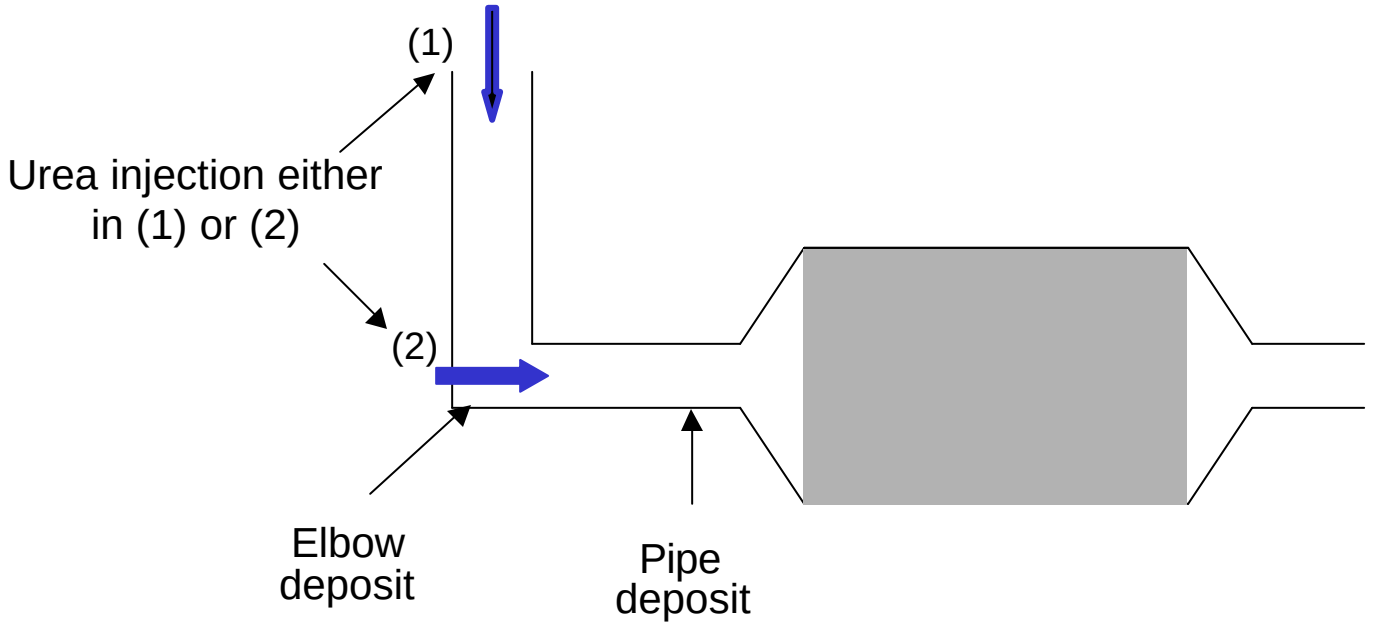
- Beige and dark brown deposits are accumulated within the pipe depending upon heating history and spraying quality

  What are these decomposed products?

  Are they responsible for excess urea consumption?

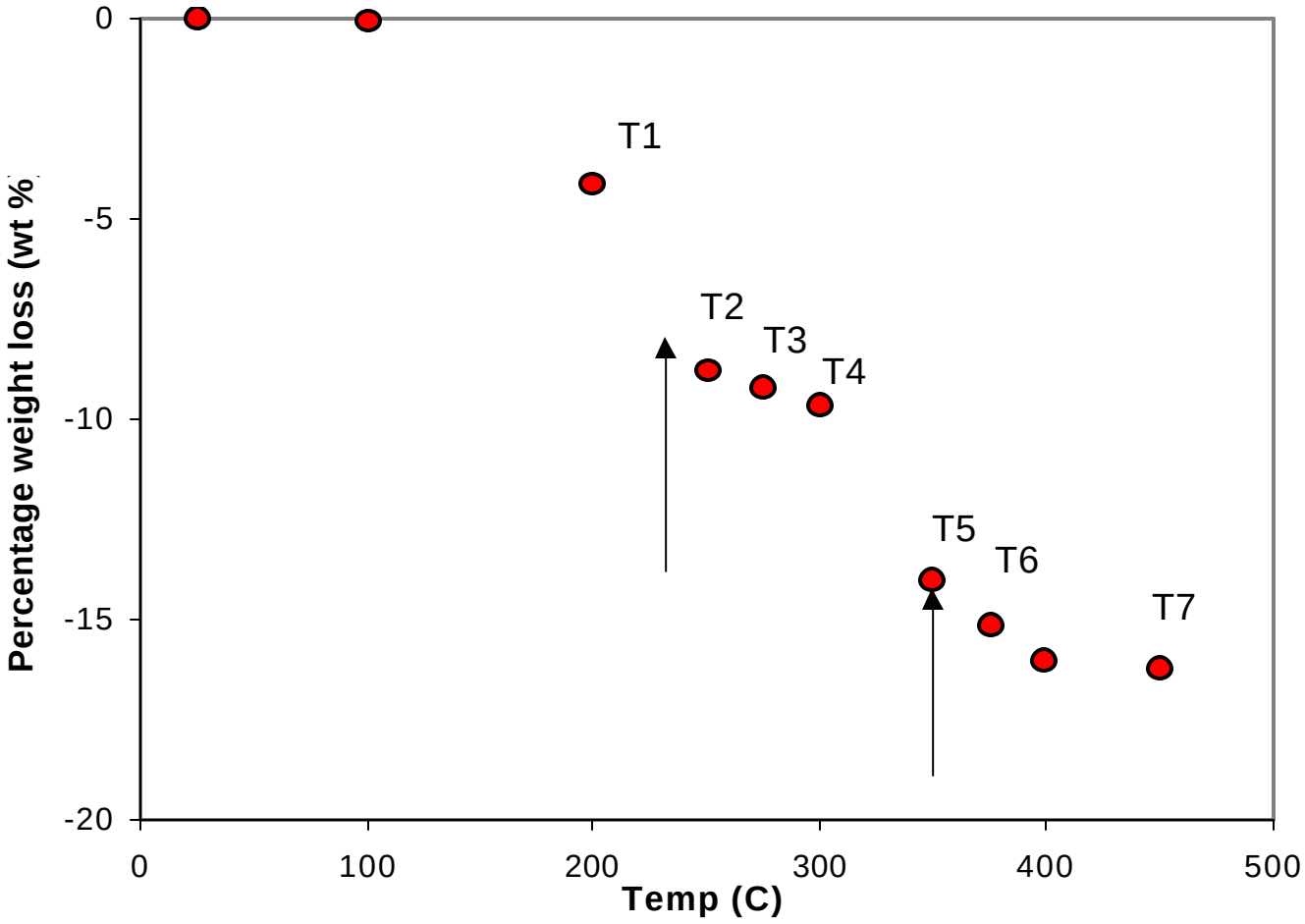
  What are their impacts on catalytic performance? system design aspects?

- DRIFTS and DSC/TGA were applied to identify the decomposed components



Thermal Decomposition of Urea

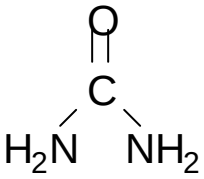
- Decomposition was conducted under stepwise mode at individual desired temperatures
- Urea thermal decomposition contains two stages:
  (1) stage I at 220 -250°C, to form pale beige color deposit
  (2) stage II at 340 -380°C, to form dark beige color deposit
- The final product at 450°C (T7) is a dark brown powder

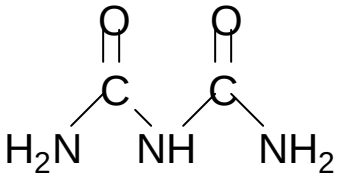


Identification of Decomposed Products at Various Stages Using IR

Group A:

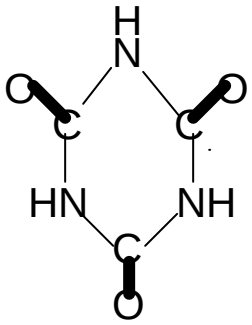
A mixture of urea and biuret

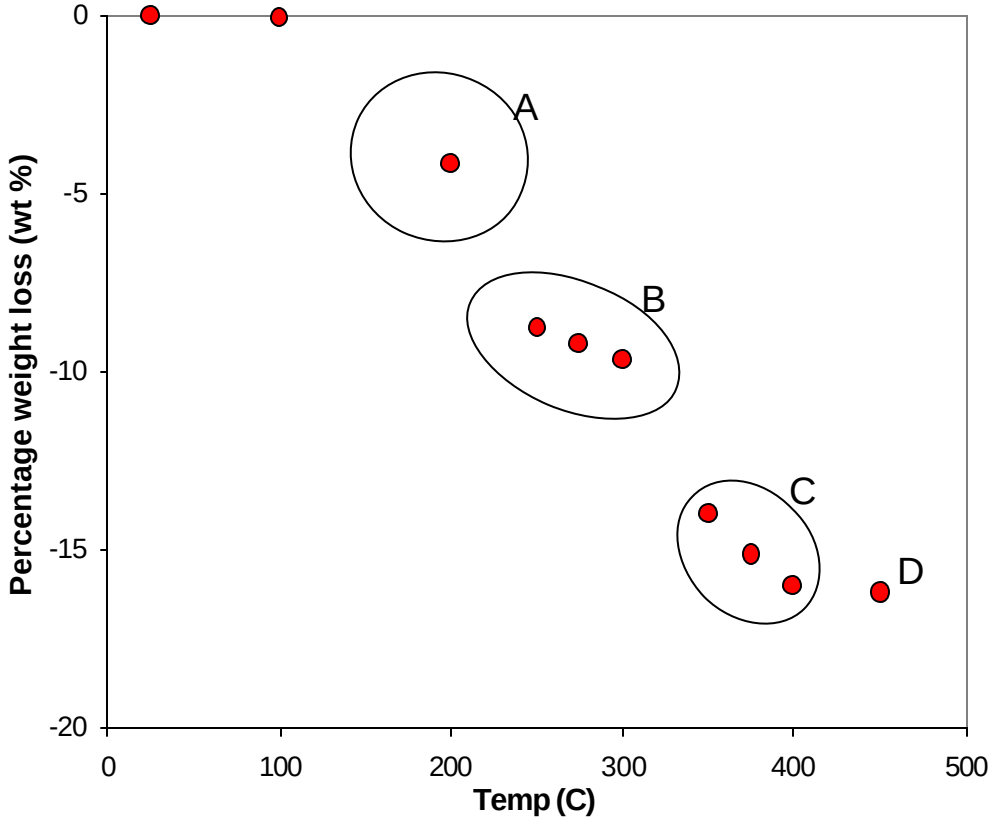




Group B:

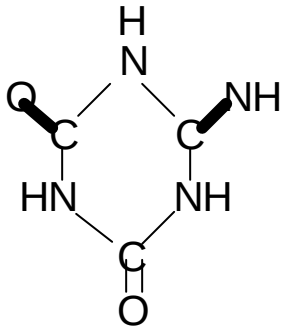
The main component is cyanuric acid

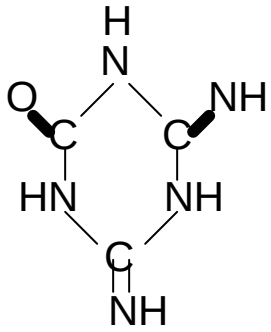




Group C:

Major components are ammeline and ammelide





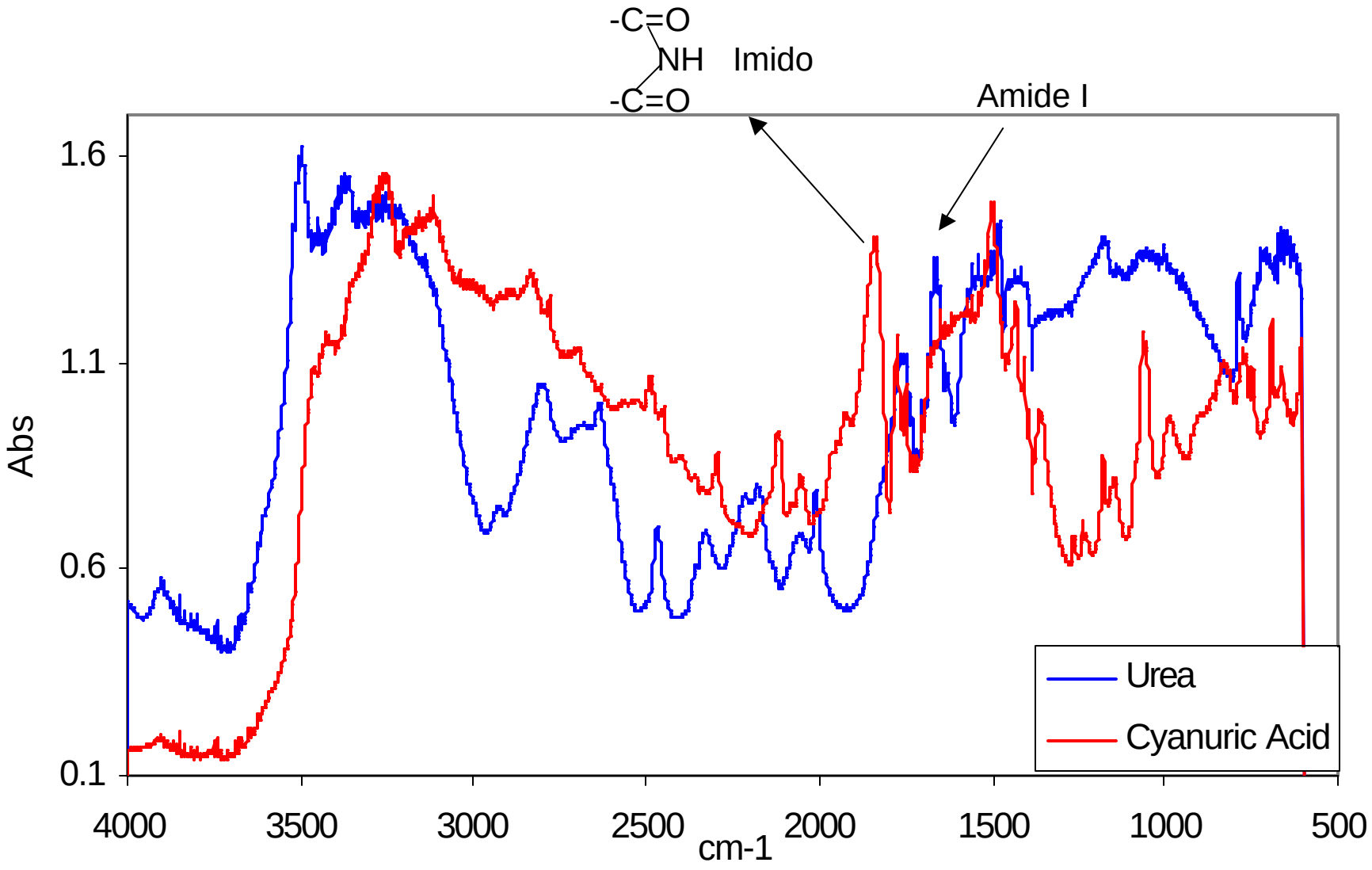
Group D:

Polymeric products from group C and hydrogen bonded aggregates

DRIFTS Spectra of Urea and The Decomposed Deposit at 220°C

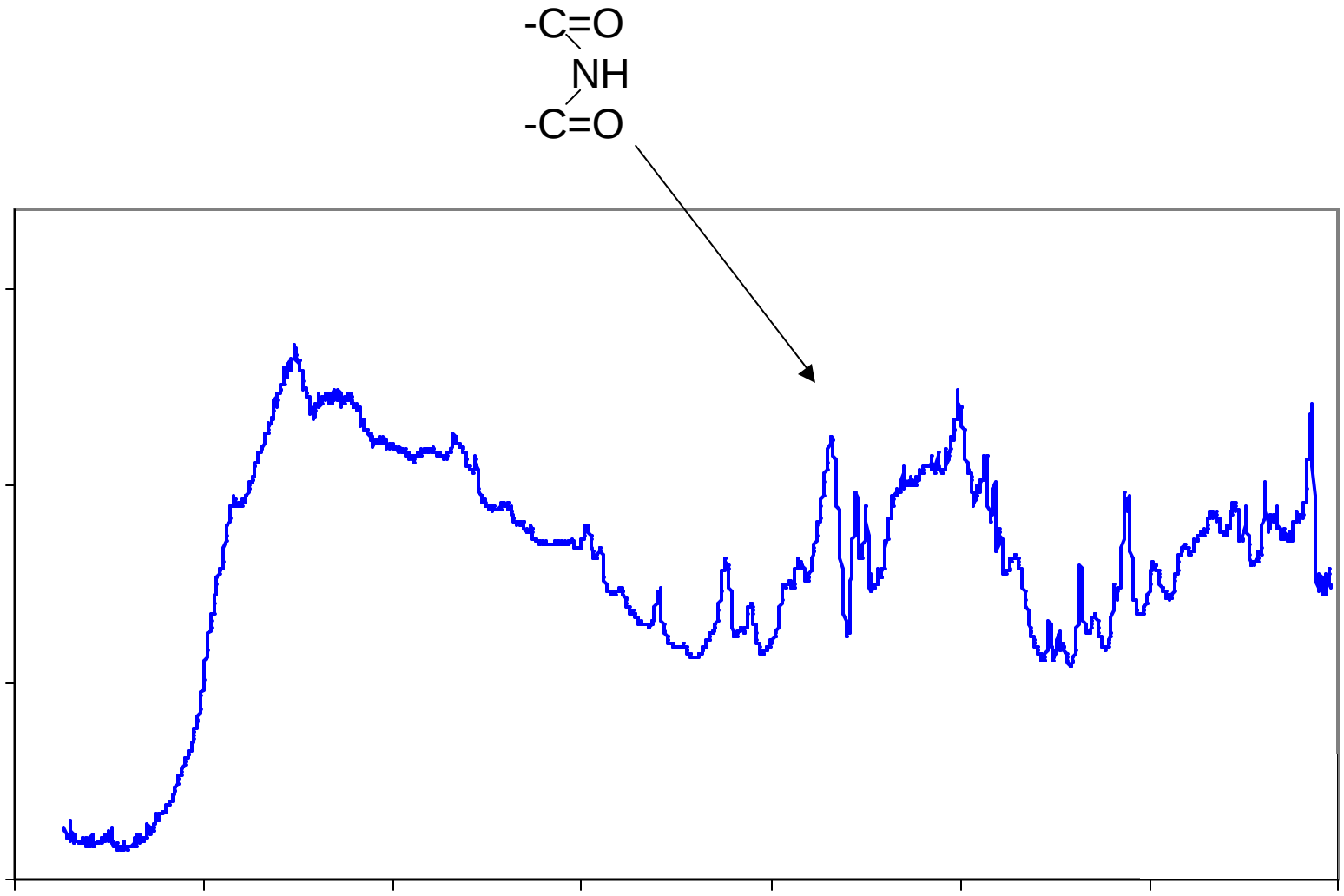
Urea powder was decomposed at 220°C to generate white cyanuric acid powder

-disappearance of primary amide I band at 1668 cm^{-1} and the ν_{NH} at 3500 cm^{-1}



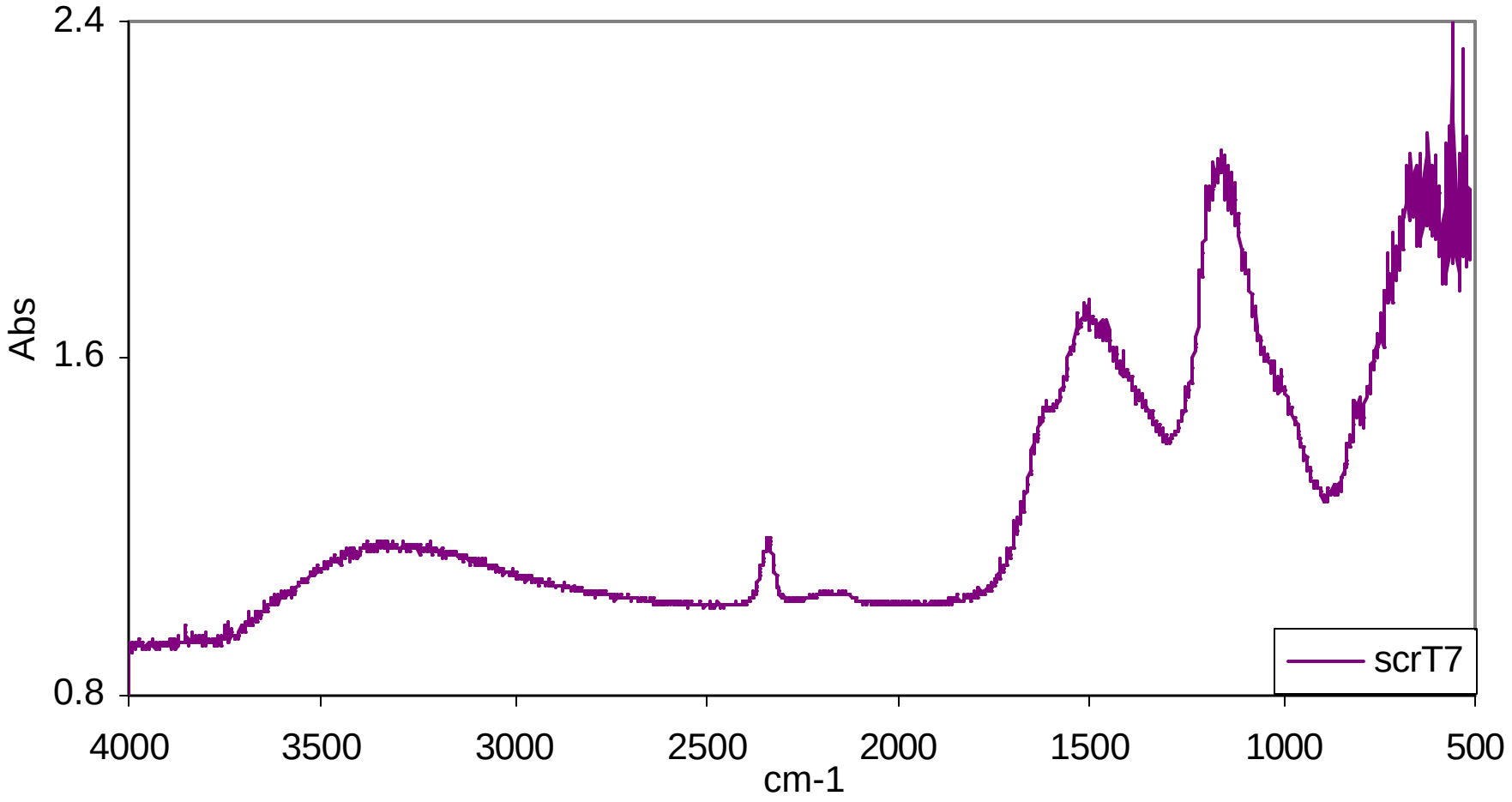
DRIFTS Spectra of Samples in Group B (250 ~ 300°C)

Spectra of samples in Group B match to cyanuric acid with a characteristic 1850 cm^{-1} band representing cyclic imido configuration



DRIFTS Spectrum of Sample in Group D (450°C)

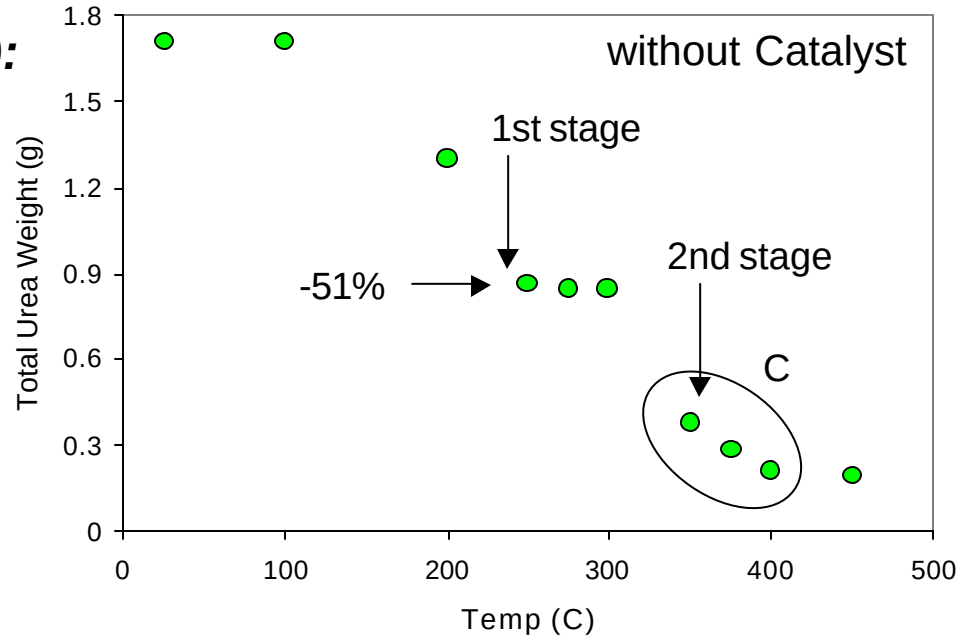
- Typical melamine bands of the final brown product are observed at 1165, 1514 and 1620 cm^{-1}
- Iso-cyanate moiety (-N=C=O) can also be seen at 2200 and 2340 cm^{-1}



Comparison of Urea Decomposition with And without Catalyst

(A) *without catalyst (Siemens V-W-Ti):*

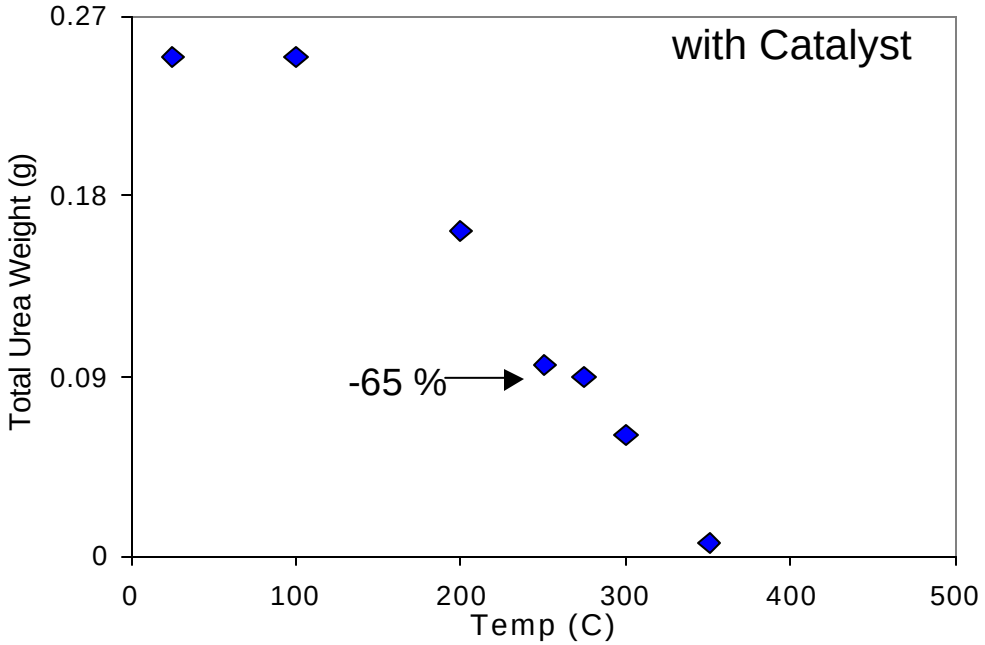
The decomposition of urea follows a normal two-step process; first to cyanuric acid and second to the final polymeric products



(B) *with catalyst (Siemens V-W-Ti):*

The decomposition of the 2nd stage is accelerated

- Final products similar to samples in Group C
- High temperature component (final products in (A)) eliminated

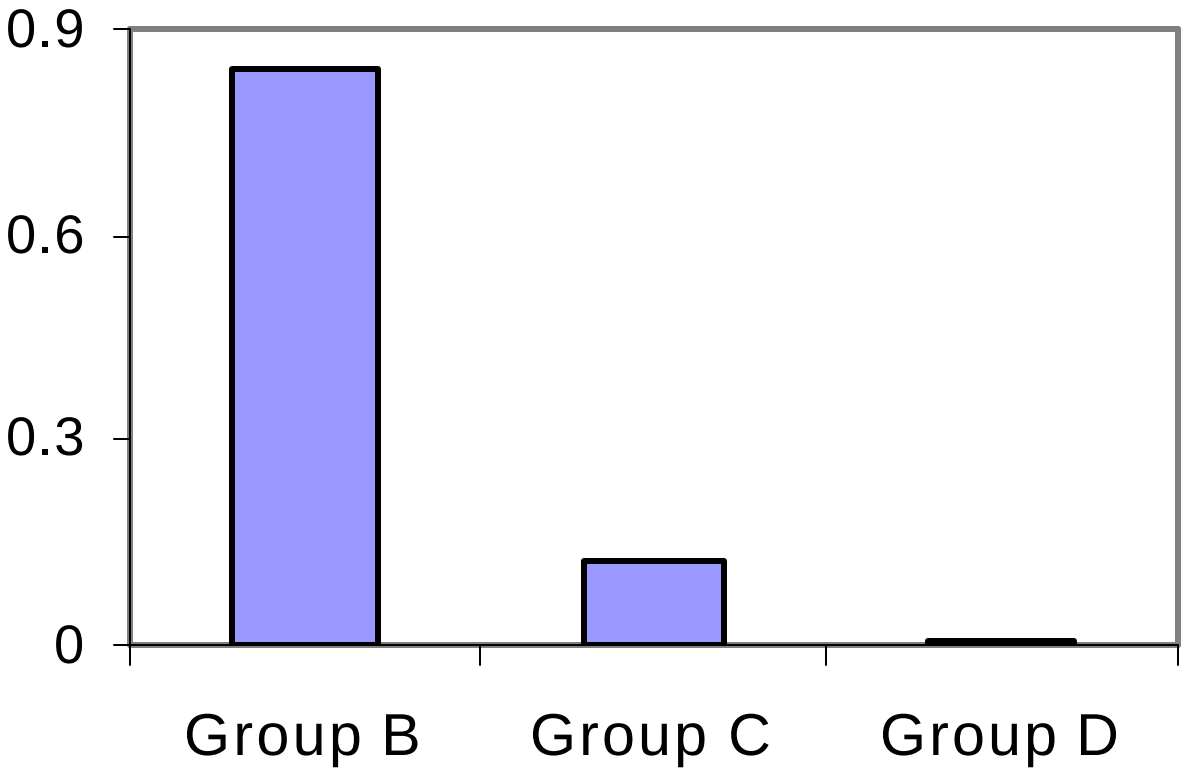


Products of final decomposition stage are resistant to SCR catalytic reactions

(A) Siemens catalyst is mixed with group B samples (Cyanuric acids) in 2:1 ratio:
84 % loss at 320°C

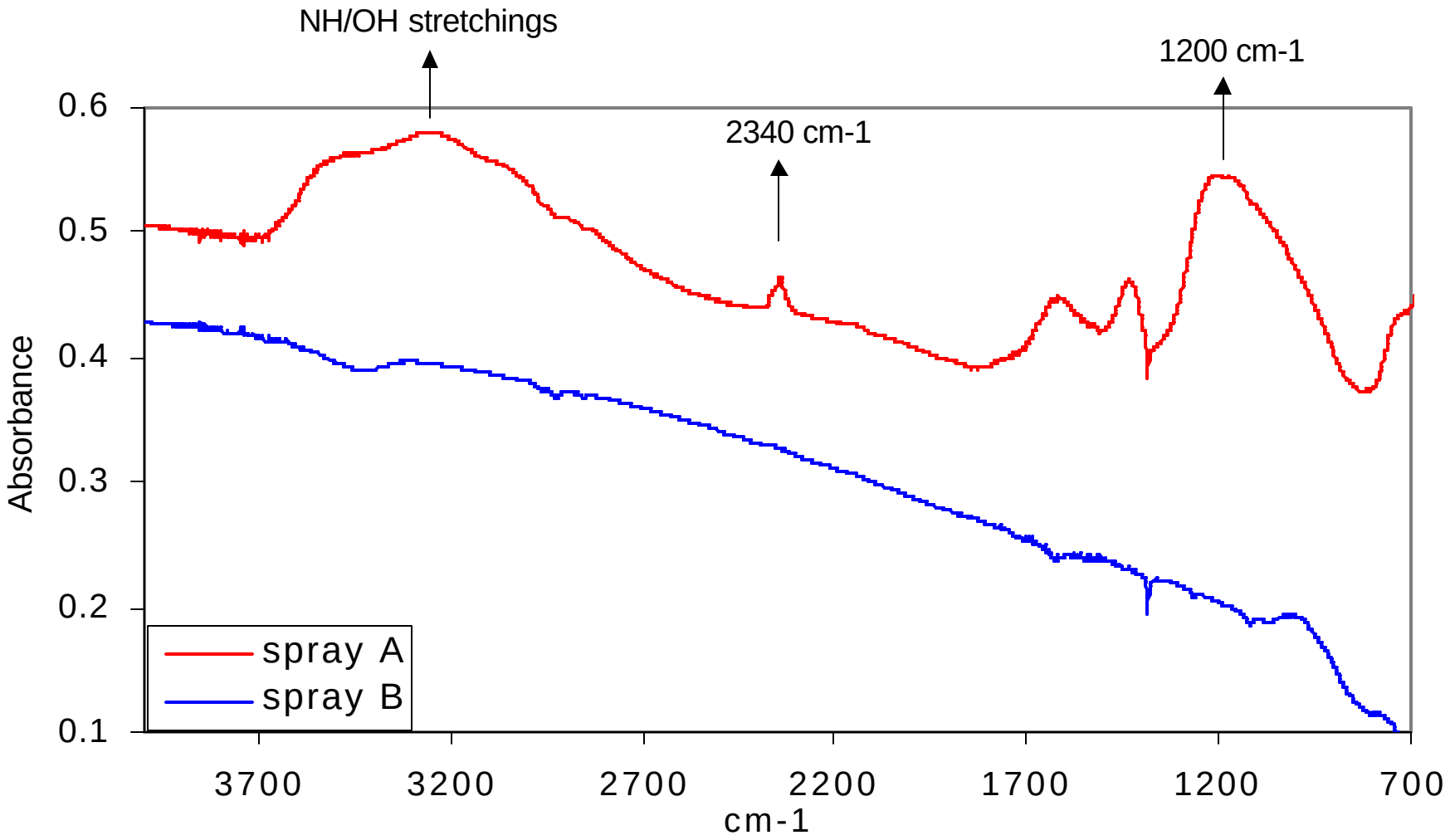
(B) Siemens catalyst is mixed with the brown pipe deposit (Group C samples) in 2:1 ratio:
only 12 % loss at 320°C

(C) Siemens catalyst is mixed with the group D samples (melamines) in 2:1 ratio:
almost no loss observed at 320°C



A good urea spray minimizes the deposit formation

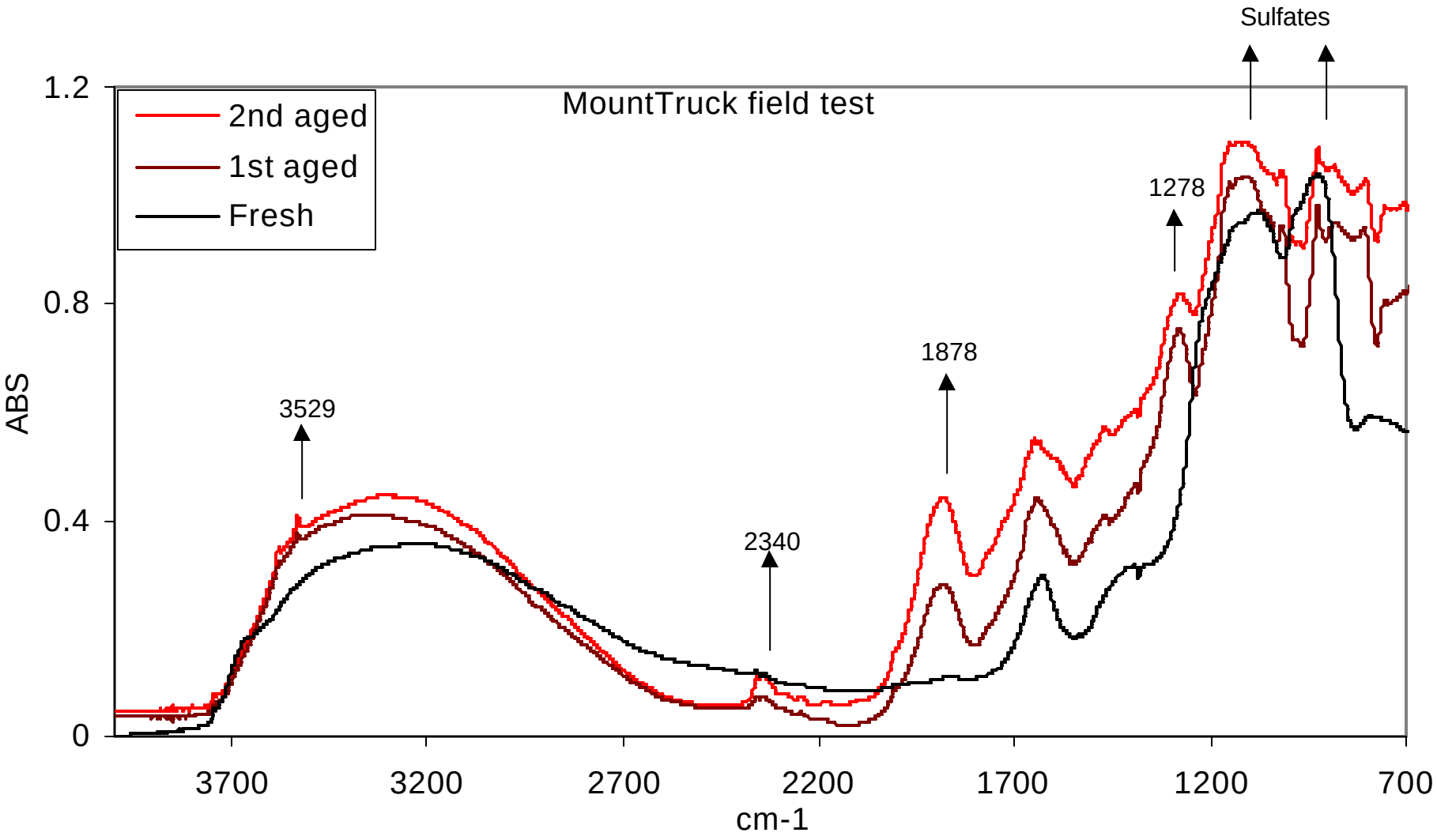
- The DRIFTS spectrum of the wall deposit sample using spray A shows rich hydrocarbon signatures which can be attributed to melamine complexes, (HNCO)x
- The baseline increase towards high frequency is caused by soot scattering

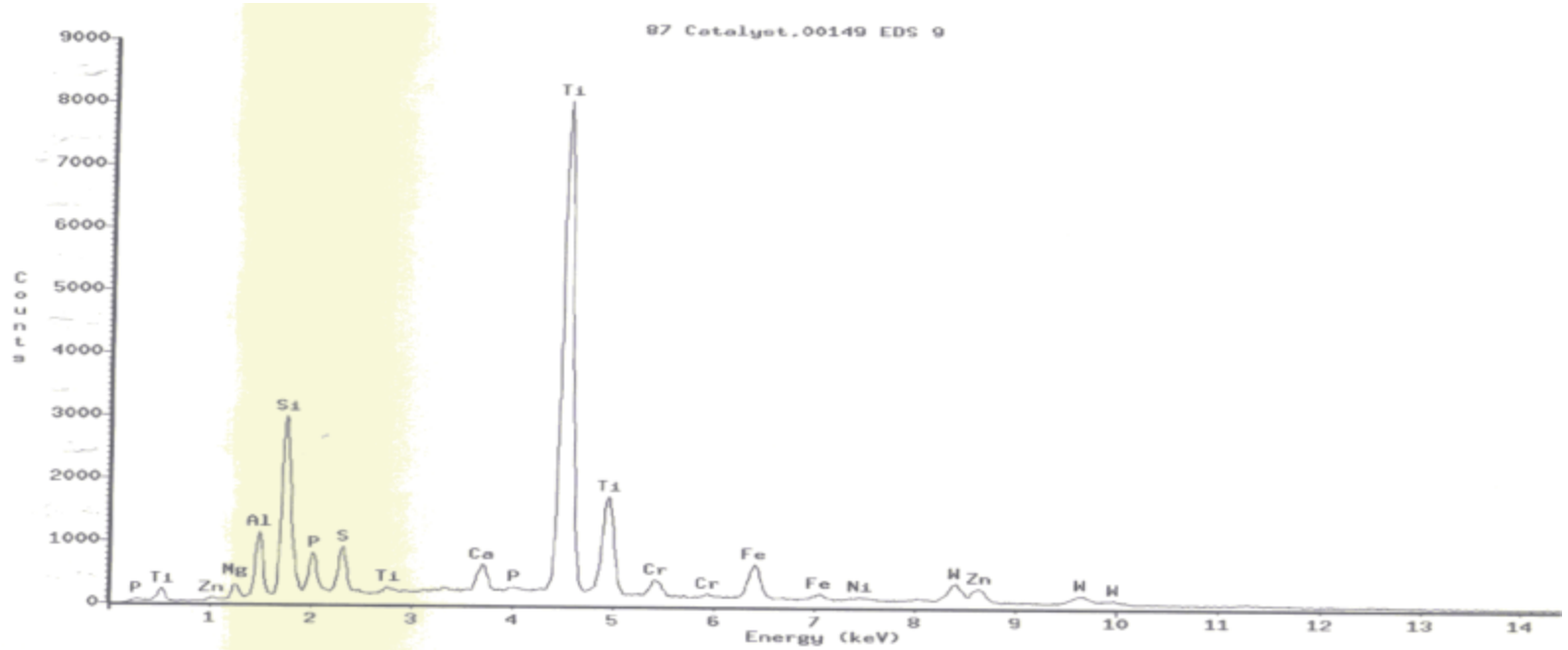


Urea-SCR Catalyst Aging by Mount Truck Field Test

Mileage history: 1st aged sample (after 60 kmiles), 2nd aged sample (after 65 kmiles)

Spectrla changes: 3529 (OH's), 2340 (isocyanates), 1878 (imido functionality of decomposed urea), 1515/1620 (melamine of decomposed urea), 1278 (P-related species ?) and 1105/925 cm^{-1} (sulfates)

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Energy (keV)
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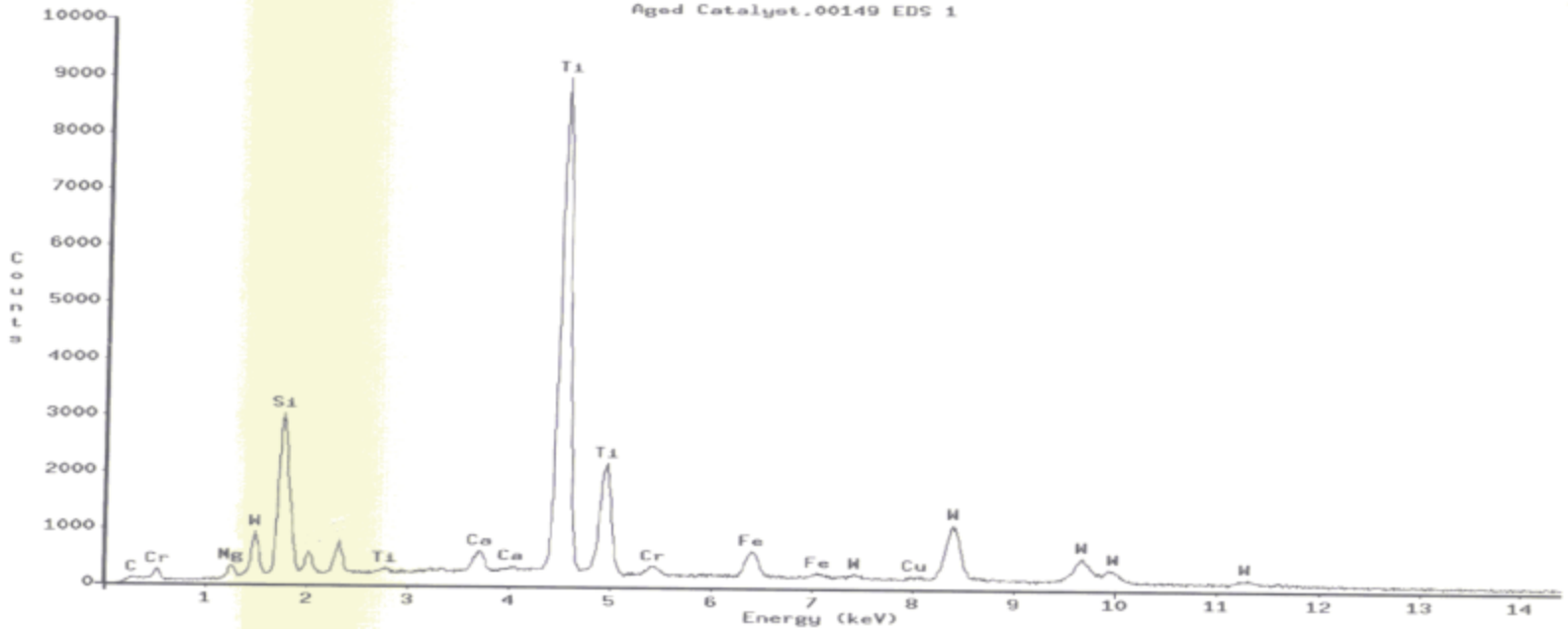
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Counts
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Urea-SCR Mechanism for Vanadium-based Catalysts

Activation of NH_3 leads to a reduction of vanadia surface

$$V^{+5}{=}O \; + \; NH_3 \; \rightarrow \; HO\text{-}V^{+4}\cdots N{\bullet}H_2$$

$$HO\text{-}V^{+4}\cdots N{\bullet}H_2 \; + \; {\bullet}NO \; \rightarrow \; HO\text{-}V^{+4}\cdots(NH_2)\text{-}NO$$

$$HO\text{-}V^{+4}\cdots(NH_2)\text{-}NO \; \rightarrow \; HO\text{-}V^{+4} \; + N_2 \; + H_2O$$

NO_2 radicals re-oxidize the surface

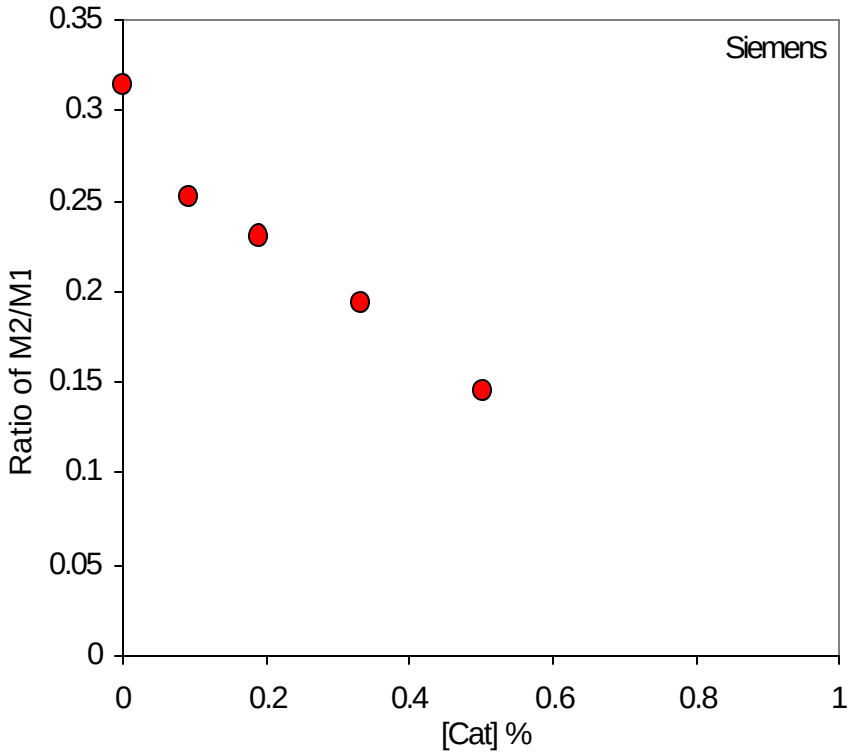
$$HO\text{-}V^{+4} \; + \; {\bullet}NO_2 \; \rightarrow \; V^{+5}{=}O \; + HNO_2$$

HNO_2 begins to neutralize adsorbed NH_3

$$HNO_2 + NH_3 \rightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O$$

- **Surface redox of V=O sites determines the efficacy of SCR catalyst**
  - DRIFTS data are consistent with this mechanism

Concept of Additive Technology for Urea-SCR



- The decomposed products after the 2nd stage of urea decomposition should be avoided due to their resistance to catalytic reactivity
- Elimination of the 2nd stage becomes an indicator in determining catalytic efficacy

Comparison of DM_2/DM_1 for modified catalysts

Sample	DM_1	DM_2	DM_2/DM_1
Urea/Cat in 3:1	**9.0**	**1.75**	**0.194**
Urea/CatA in 3:1	**9.7**	**1.30**	**0.134**
Urea/CatB in 3:1	**7.6**	**1.47**	**0.193**

CatA: an oxidizer

CatB: a reducer

- **Oxidizers can be either doped in the urea solution or mixed in the V-W-Ti catalysts**

CONCLUSIONS

- **Thermal decomposition of urea involves two stages**
  - The 1st stage (NH_3 generation stage) involves formation of biuret/cyanuric acid and the 2nd stage (NH_3 consumption stage) involves formation of polymeric melamine complexes
  - The decomposition of the 2nd stage can be accelerated by $V_2O_5/TiO_2/WO_3$ catalyst
  - Polymeric products are resistant to catalytic reaction and are responsible for non-stoichiometric urea consumption
  - The ratio of $\Delta M_2/\Delta M_1$ can be developed as an indicator to differentiate urea-SCR catalysts
- **Effective urea decomposition requires a close contact with catalyst**
  - The injector distance and spraying quality prior to catalyst surface are critical
- **Redox reaction of V^{+5}=O site is the critical step in urea-SCR mechanism**
  - NO_2 (or other oxidizers, SO_2) assists SCR reduction
  - Additive technology of using oxidizers in urea solution to rejuvenate catalyst surface

Urea-SCR Mechanism

$(NH_2)_2C=O \rightarrow 2\ NH_2\bullet + CO$ [$NH_2\bullet + RH$ or $HOH \rightarrow NH_3 + R\bullet$ or $OH\bullet$]

$(NH_2)_2C=O + H_2O$ ® $2\ NH_3 + CO_2$ [$(NH_2)_2C=O \rightarrow NH_3 + HN=C=O$ &

$HN=C=O + H_2O \rightarrow NH_3 + CO_2$]

Desirable Reduction

$NH_2\bullet + NO \rightarrow N_2 + H_2O$

$4NH_3 + 4NO + O_2$ ® $4N_2 + 6H_2O$ *(standard SCR)* *(1)*

$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$

$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

$4NH_3 + 2NO_2 + 2NO$ ® $4N_2 + 6H_2O$ *(fast SCR)* *(2)*

$4HN=C=O + 6NO \rightarrow 5N_2 + 2H_2O + 4CO_2$

Direct Urea Reduction

$2(NH_2)_2C=O + 6NO$ ® $5N_2 + 2CO_2 + 4H_2O$

This one seems to match the stoichiometric ratio

Undesirable Reaction/Oxidation

$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$

$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$

$$4NH_3 + \begin{matrix} 5\ O_2 \\ 4\ 2N_2O \\ 3\ 2N_2 \end{matrix} \rightarrow \begin{matrix} 4NO \\ \\ \end{matrix} + 6H_2O$$

Undesirable Degradation

$NH_3 + SO_2 + 1/2O_2 + H_2O \rightarrow NH_4(HSO_4)$

$2NH_3 + SO_2 + 1/2O_2 + H_2O \rightarrow (NH_4)_2SO_4$

$(NH_2)_2C=O$ ® polymeric products

At T<200°C, solid formation

$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O$

$HNCO + 3\ NH_3 \rightarrow$ melamine $(C_3N_6H_6)x$

Why is there a stoichiometric imbalance in urea hydrolysis?

- **Theoretical limit:**

$(NH_2)_2C=O \rightarrow HNCO + NH_3\uparrow$ (1) $\Delta H = 186$ kJ

$HNCO\ (g) + H_2O\ (g) \rightarrow NH_3\uparrow + CO_2$ (2) $\Delta H = -96$ kJ

Under theoretical limit, one mole of urea generates two moles of NH_3, and can reduce 2.5 moles of NO, at most. (This implies that 0.9 g of urea is required to reduce 1 g of NO)

- **Experimental Results**

-Process (2) is not kinetically favored and requires catalyst

-Process (1) involves non-hydrolyzable products

$$_{[x+1]}(NH_2)_2C=O \rightarrow HNCO + (HNCO)_x + {}_{[x+1]}NH_3$$

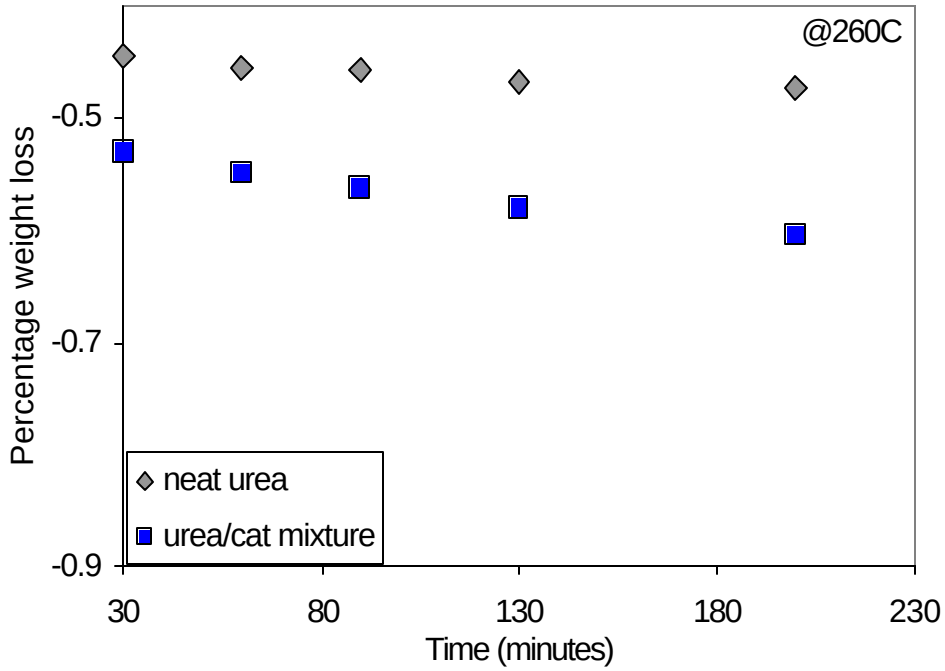
x=2,3 ..

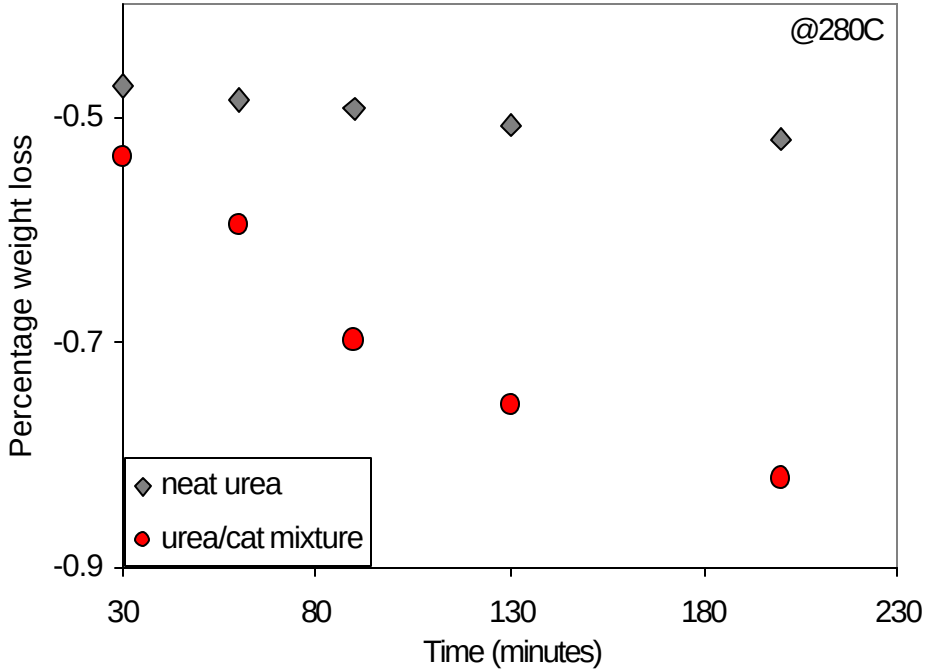
which may form deposits on the pipe wall

-Monitoring CO_2 yield should reflect the reaction percentage of HNCO generation

-Appropriate catalysts and additives in urea solution can speed up the 2nd stage decomposition

Decomposition Kinetics of Urea with and without V-W-Ti Catalyst





urea $\xrightarrow[k_1]{\Delta}$ **products** (bi- & tri-urets) $\xrightarrow[k_2]{Cat}$ **evaporable products** (HNCO, NH_3, etc.)

Percentage weight loss = $(w_f - w_i)/w_i = \exp(-kt) - 1$

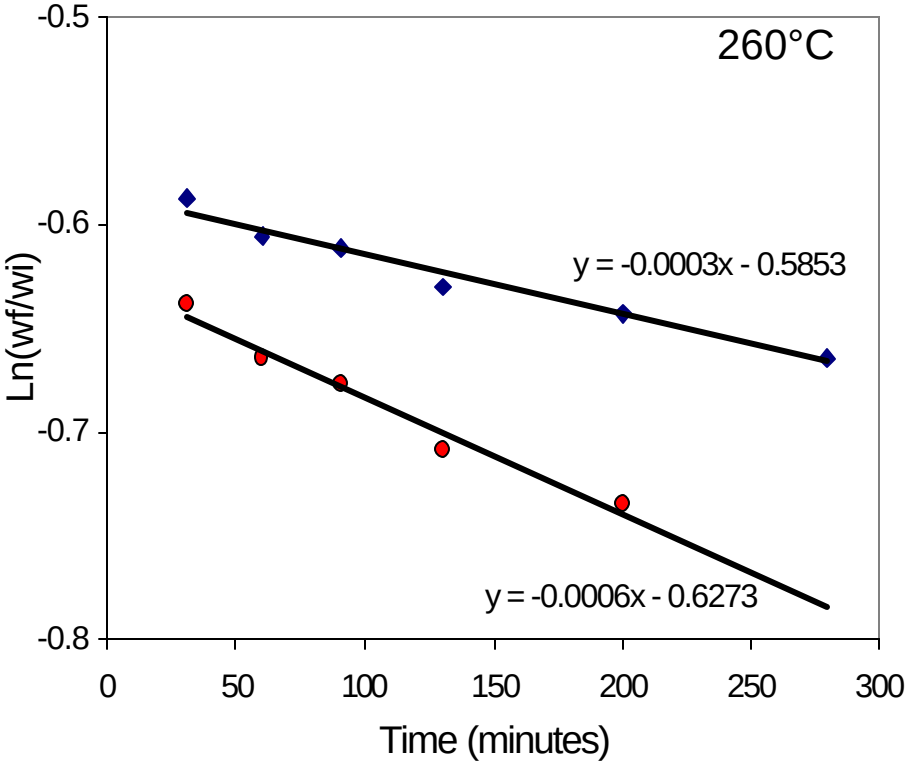
Temperature	k_1 (urea thermal decomposition)	k_2 (catalyzed decomposition)
260°C	0.0003	0.0010
280°C	0.0006	0.0057

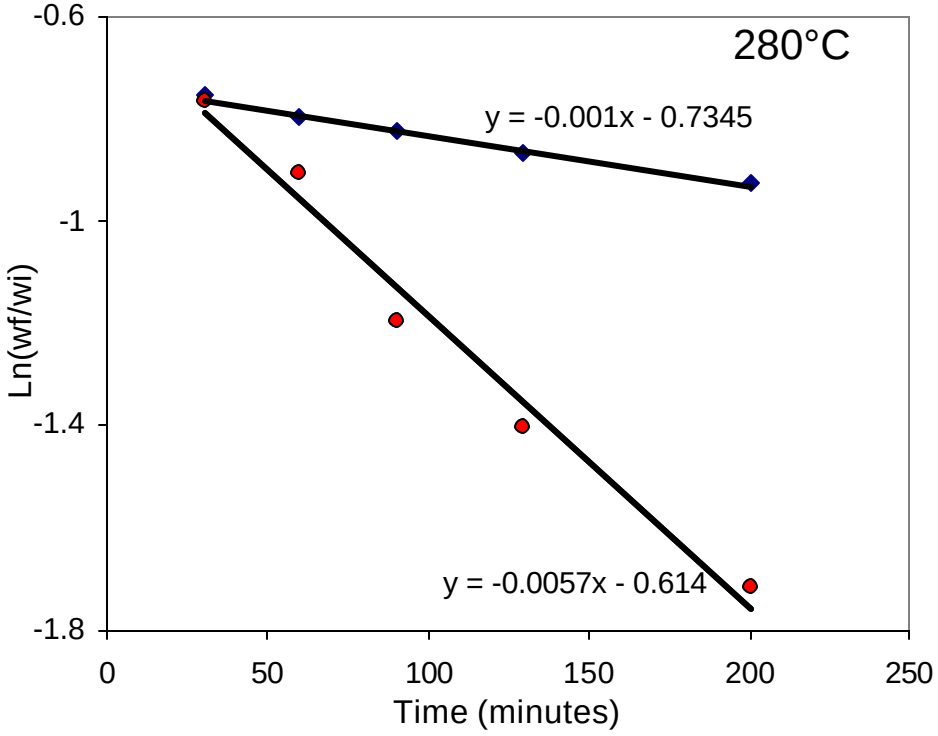
Kinetics parameters can be derived from weight loss data

The percentage weight loss = $(w_f - w_i)/w_i$ = $\exp(-kt) - 1$,

$w_f/w_i = \exp(-kt)$ and

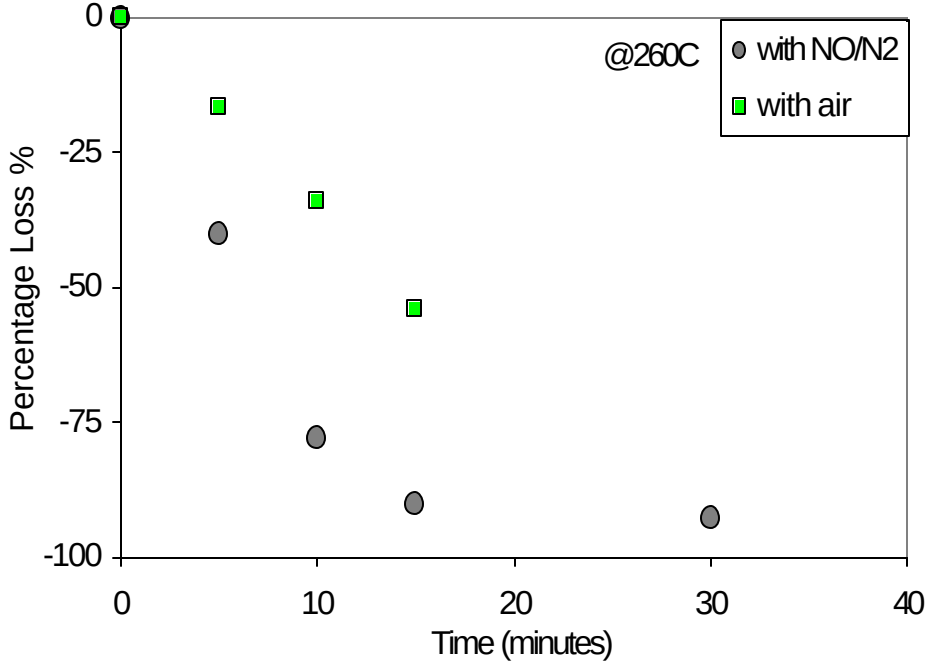
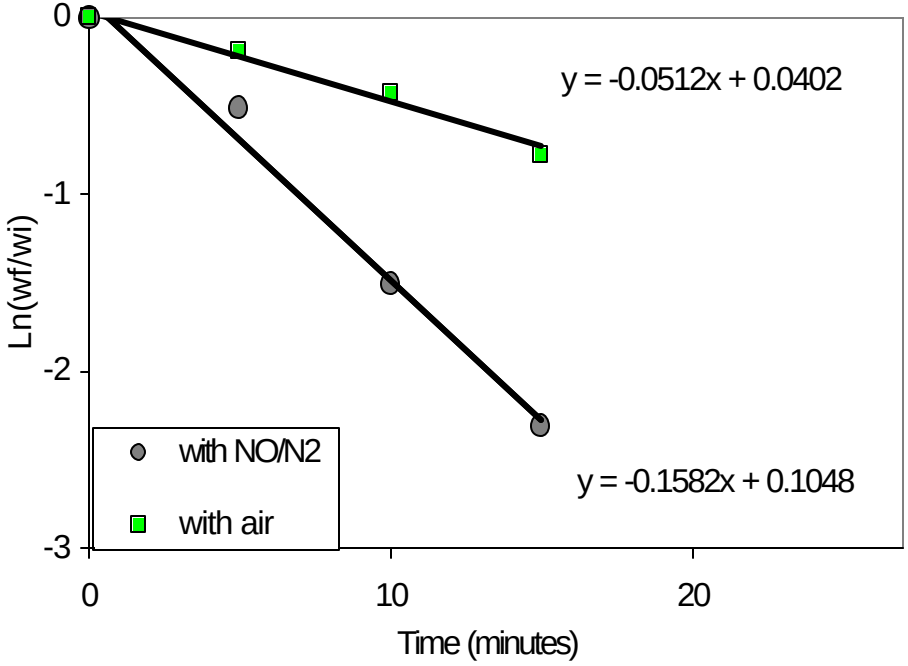
$\ln(w_f/w_i) = -kt$





- At 280°C (the end point of the 1st stage of urea decomposition), the rate of catalyzed decomposition is nearly 6x faster than the rate of thermal decomposition
- The catalyst function is to eliminate and promote the decomposition of the 2nd stage

Reaction rate of $2(NH_2)_2C=O + 6NO \rightarrow 5N_2 + 2CO_2 + 4H_2O$

- Urea samples, mixed with Siemens catalyst in 1:1 weight ratio, are exposed to either NO (1000 ppm/N_2) or air with a fixed flow rate
- NO assists urea decomposition
  - -With a purging of NO/N_2, the urea decomposition rate is much faster than the one under air
  - -The percentage weight loss = $(w_f - w_i)/w_i = \exp(-kt) - 1$ and $\ln(w_f/w_i) = -kt$,

    k (under NO/N_2) ~ 3x k (under air)