Transformation of vanadyl porphyrins in heavy residue during non-catalytic thermal upgrading process under hydrogen

By: Zongxian Wang
Department of Chemical Engineering
China University of Petroleum (East China), China
2015.11.30, Atlanta

Outline

- Introduction
- Experimental section
- Results and discussion
- Conclusions
- Future work
- Acknowledgement

Introduction

Issues

- Various kinds of heavy metals are contained in heavy oils
- Vanadium and nickel are the most abundant and troublesome
- Catalytic process: catalysts deactivation
- Non-catalytic thermal process: coke formation

Transformation of metals

- Reveal the essential fate and behavior of metals
- Benefit the catalysts design

Research Status

- Transformation of model metal porphyrins
  - mechanism, kinetics, morphology of final deposits, etc.
- Transformation of petroporphyrins in real oil system
  - X-ray Absorption Fine Structure (XAFS) [1]
  - UV-vis Spectroscopy [2]
  - Electron Paramagnetic resonance (EPR) [3]
  - Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [4]

[1] Miller, J. T.; Fisher, R. B.; van der Eerden, A. M. J.; Koningsberger, D. C. *Energy Fuels* 1999, *13*, 719-727.
[2] Kekäläinen, T.; Pakarinen, J. M. H.; Wickström, K.; Lobodin, V. V.; McKenna, A. M.; Jänis, J. *Energy Fuels* 2013, *27*, 2002-2009.
[3] Ben Tayeb K.; Delpoux O.; Barbier J.; Marques J.; Verstraete J.; Vezin H. *Energy Fuels* 2015, *29*, 4608-4615.
[4] Liu, T.; Lu, J.; Zhao, X.; Zhou, Y.; Wei, Q.; Xu, C.; Zhang, Y.; Ding, S.; Zhang, T.; Tao, X. *Energy Fuels* **2015**, *29*, 2089-2096.

Introduction

Challenges and Opportunities

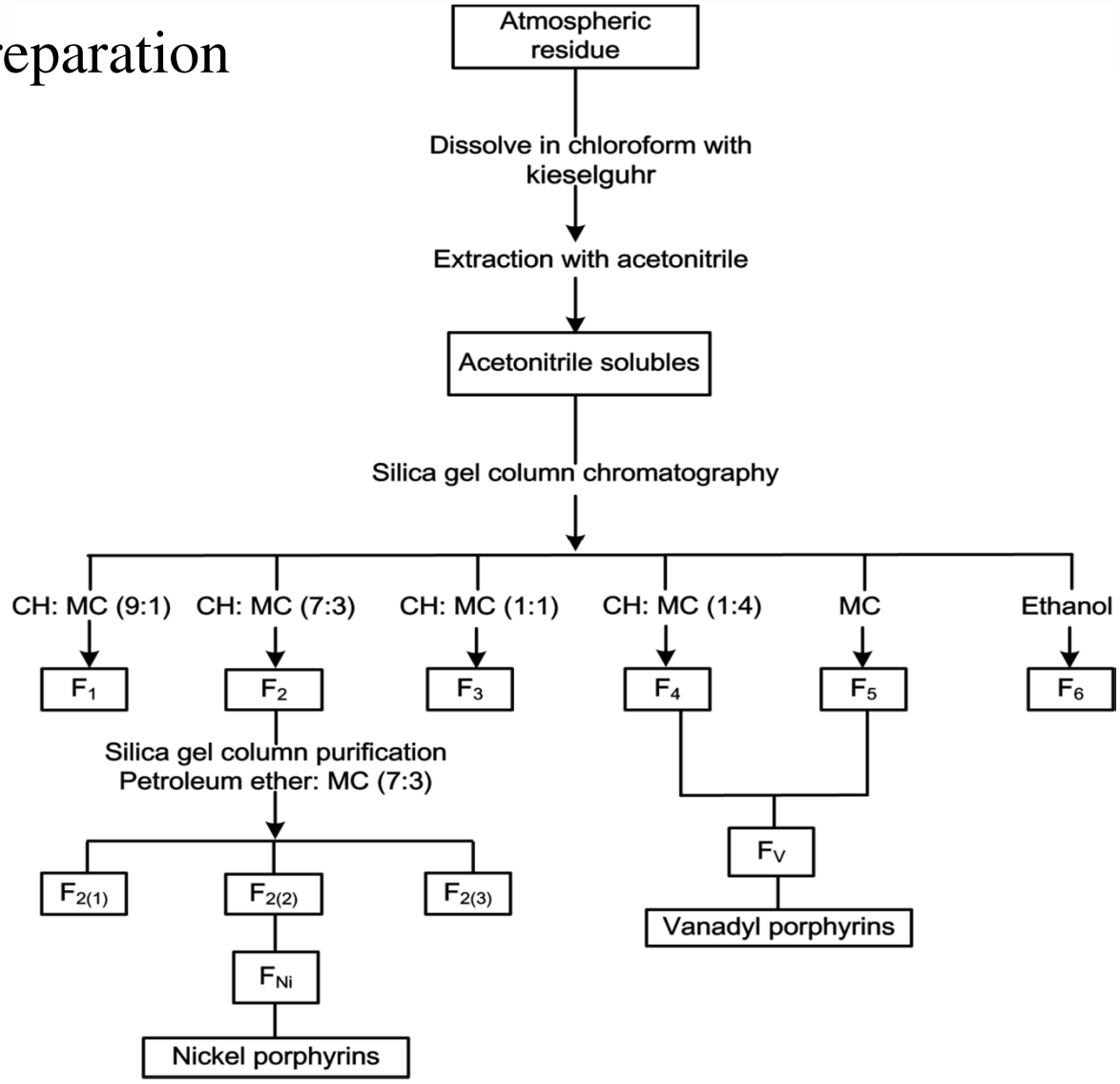
- Low concentration of metals
- High reactivity of metal compounds during hydroprocessing
- Limited characterization methods of petroporphyrins

Our attempts

- Isolation and purification of petroporphyrins
- Non-catalytic thermal process under hydrogen
- Fournier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

Experimental section

Sample preparation



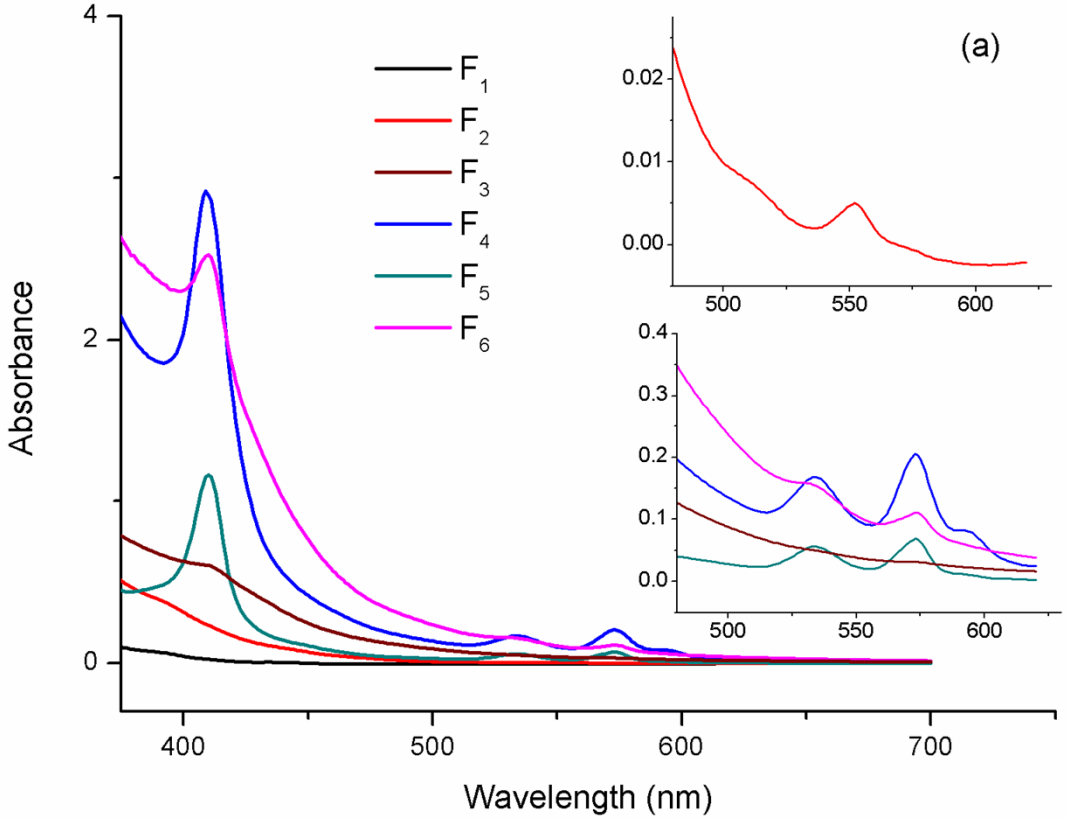
Separation scheme of petroporphyrins (CH: cyclohexane; MC: methylene chloride)

Metal balance in subfractions

Subfractions	Yield (wt%)	Ni content (ppm)	V content (ppm)	Ni yield (%)	V yield (%)	Ni/V
OSAR	100	80.00	190.02	-	-	0.42
Acetonitrile extract	51.40	29.65	103.17	19.05	27.91	0.29
F_1	36.50	**12.68**	0.15	5.79	0.03	**84.53**
F_2	7.34	**85.50**	0.52	7.84	0.02	**219.23**
F_3	1.87	**84.24**	48.51	1.97	0.48	**1.74**
F_4	2.20	35.78	**1502.16**	0.98	17.39	**0.02**
F_5	1.30	30.02	**1072.34**	0.49	7.34	**0.03**
F_6	0.42	31.17	**192.79**	0.18	0.83	**0.16**

- Nickel tends to concentrate into F_2
- Vanadium tends to concentrate into F_4 and F_5

UV-vis spectra of subfractions from OSAR



- F_2 presents characteristic absorptions of nickel porphyrins
- F_3 shows no obvious absorptions
- F_4, F_5 and F_6 show characteristic absorptions of vanadyl porphyrins
- Absorptions in F_6 are relatively weaker than those in F_4 and F_5.

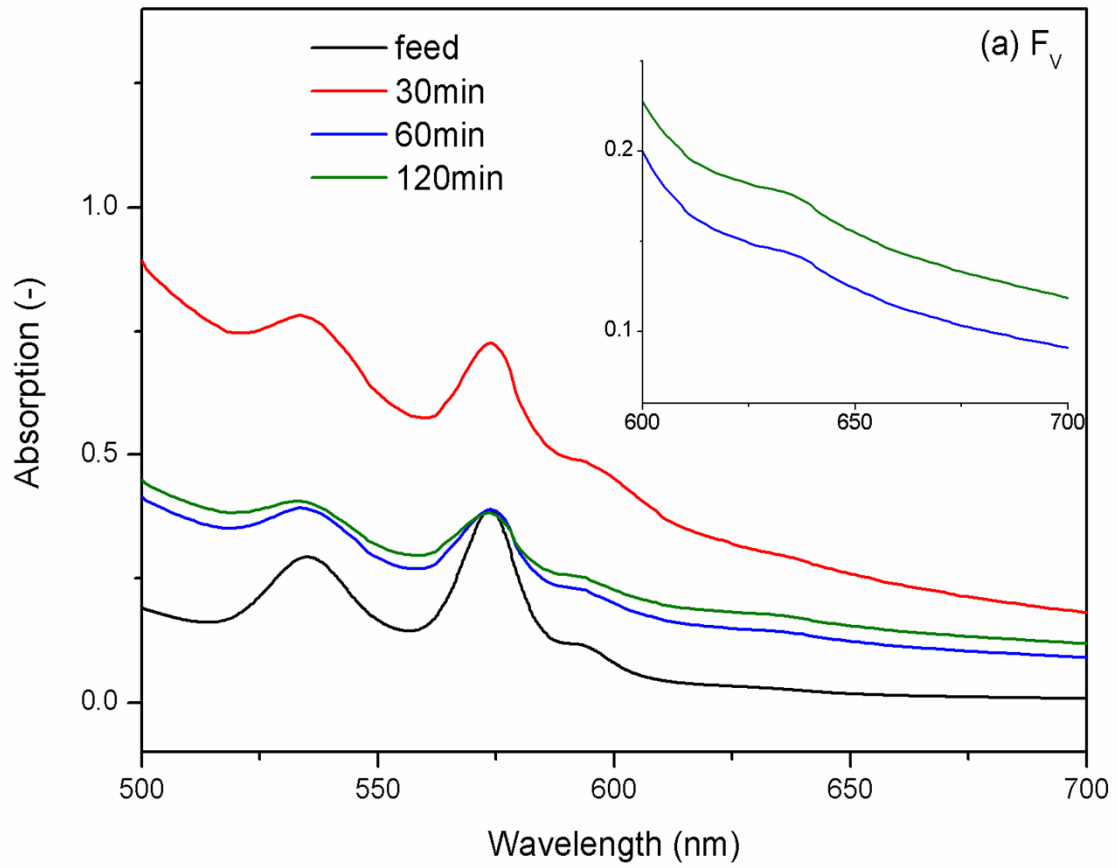
Thermal experiment and FT-ICR MS analysis

- Thermal condition: 380 ^{o}C, 5 MPa
- FT-ICR MS analysis [5-7]
  - Sample: 10 mg, diluted with 1 mL of toluene/methanol (1:1, v/v), 5 μL formic acid
  - Injection rate: 3 μL/min using a syringe pump
  - Operating conditions for positive-ion formation:
    - -4.0 kV emitter voltage
    - -4.5 kV capillary column introduce voltage
    - 320 V capillary column end voltage
  - Ions accumulation: 0.1 s in a hexapole with 2.4 V direct current voltage and 500 V_{p-p} radio-frequency (RF) amplitude

[5] Zhao, X.; Liu, Y.; Xu, C.; Yan, Y.; Zhang, Y.; Zhang, Q.; Zhao, S.; Chung, K.; Gray, M. R.; Shi, Q. *Energy Fuels* **2013**, *27*, 2874-2882.
[6] Zhao, X.; Shi, Q.; Gray, M. R.; Xu, C. *Nat. Sci. Rep.* **2014**, *4*.
[7] Liu, H.; Mu, J.; Wang Z.; Ji S.; Shi Q.; Guo A.; Chen K.; Lu J. *Energy Fuels*. **2015**, *29*, 4803-4813.

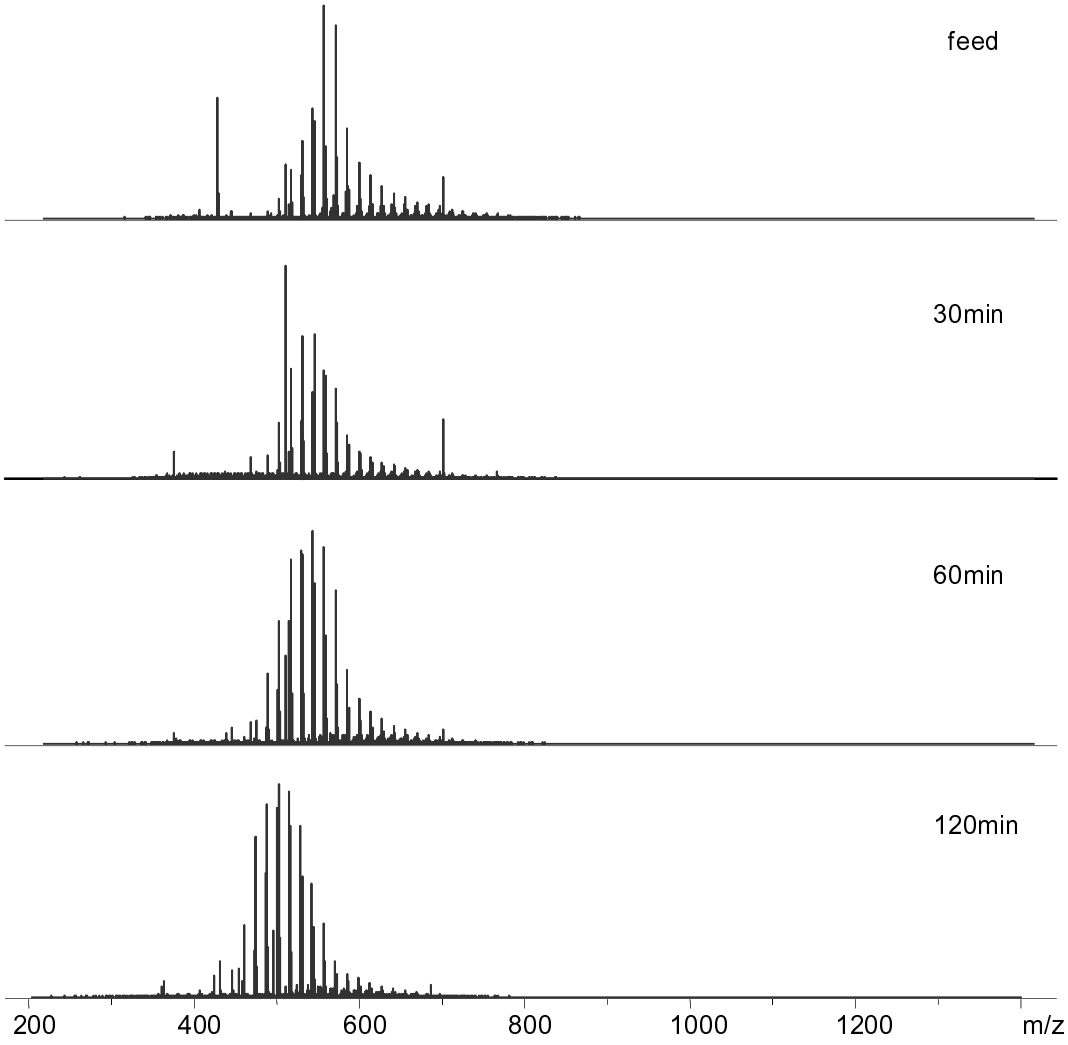
Results and discussion

UV-vis spectroscopy analysis

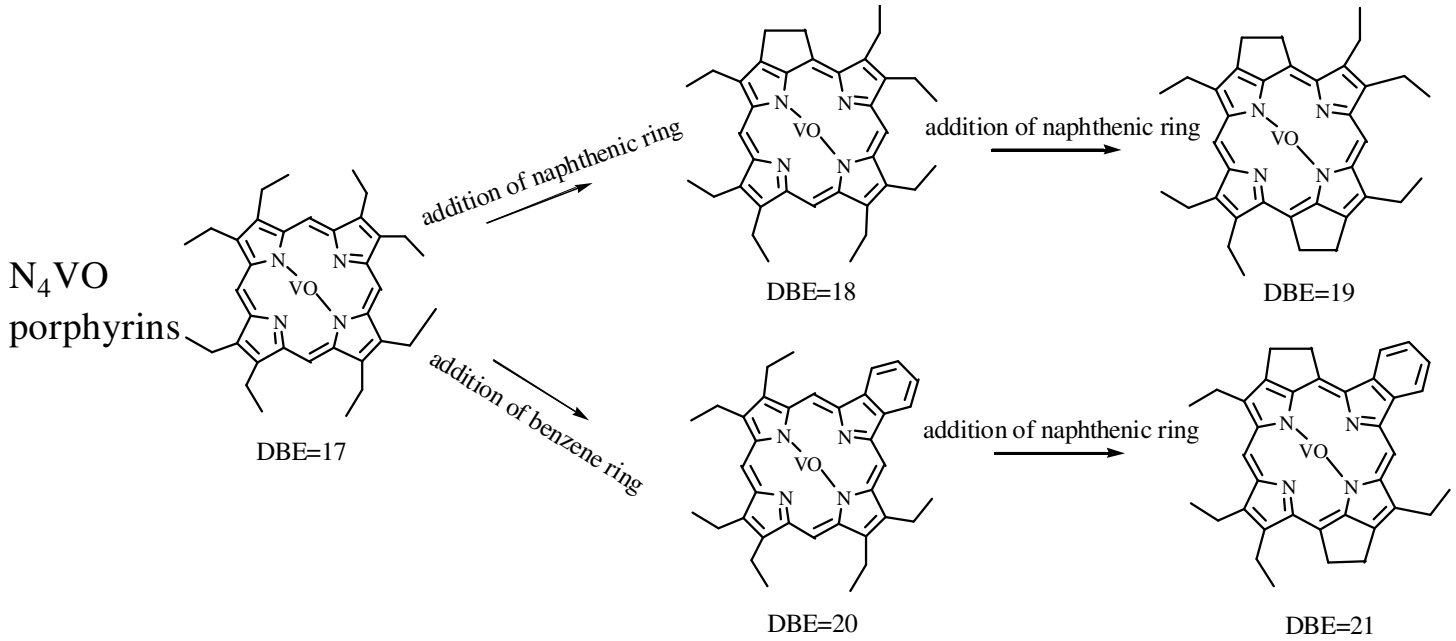


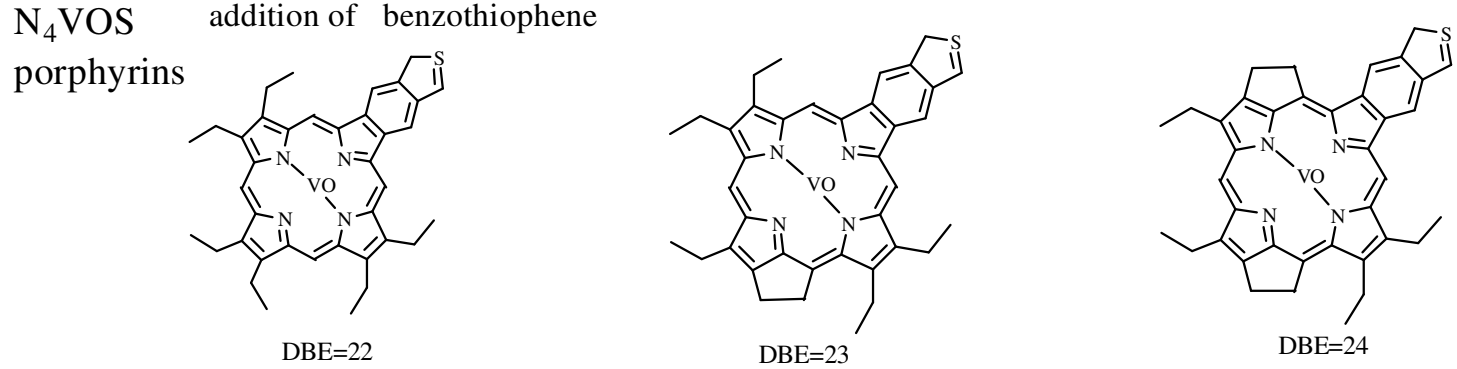
- Decrease of the characteristic absorptions could not all account for hydrogenation of petroporphyrins

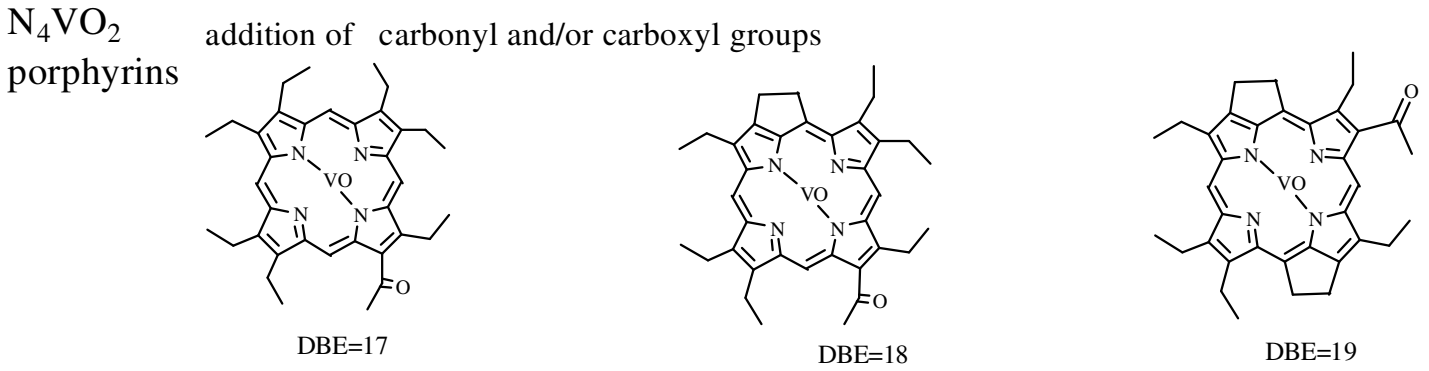
ESI FT-ICR MS analysis



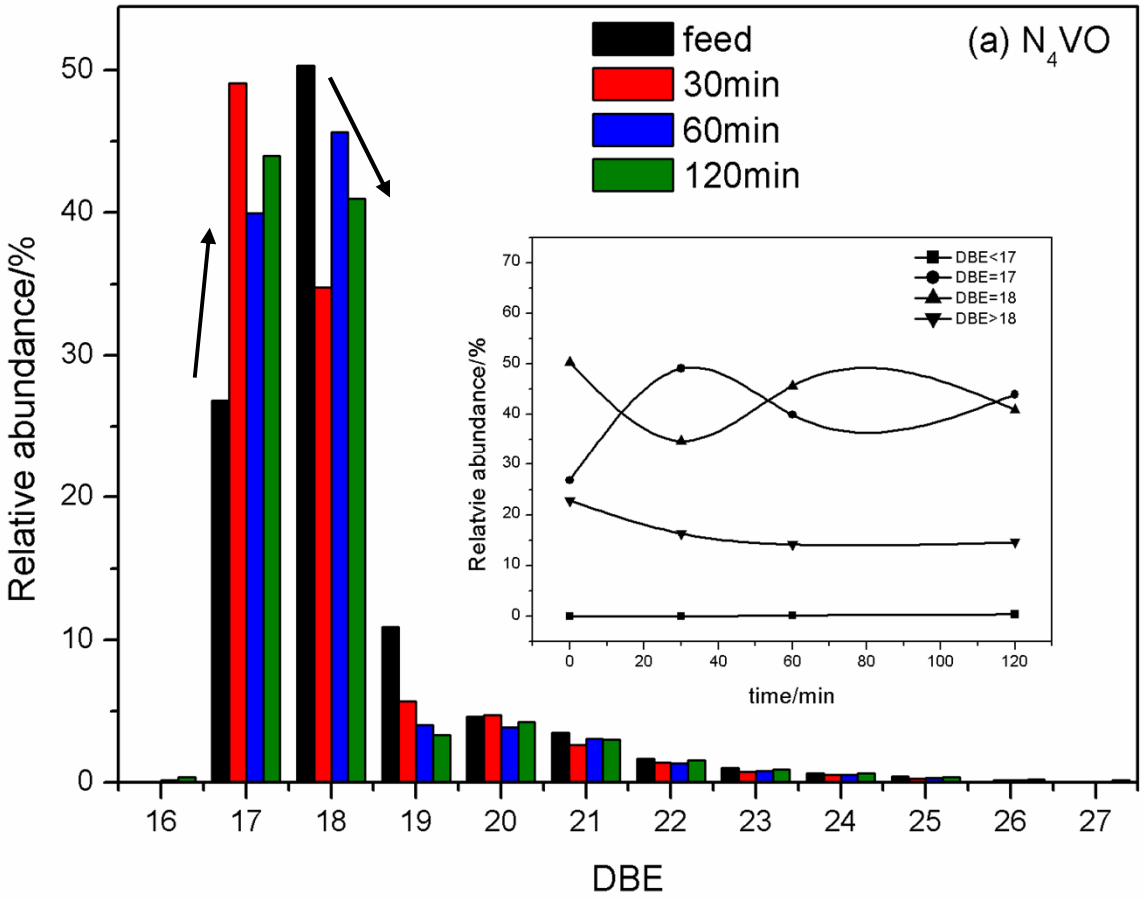
Broadband and expanded positive-ion ESI FT-ICR MS spectra of the feed FV and products under different reaction times (380 °C, 5 MPa).


N4VO
porphyrins
addition of naphthenic ring
addition of benzene ring
addition of naphthenic ring
addition of naphthenic ring
DBE=17
DBE=18
DBE=19
DBE=20
DBE=21


N4VOS
porphyrins
addition of benzothiophene
DBE=22
DBE=23
DBE=24

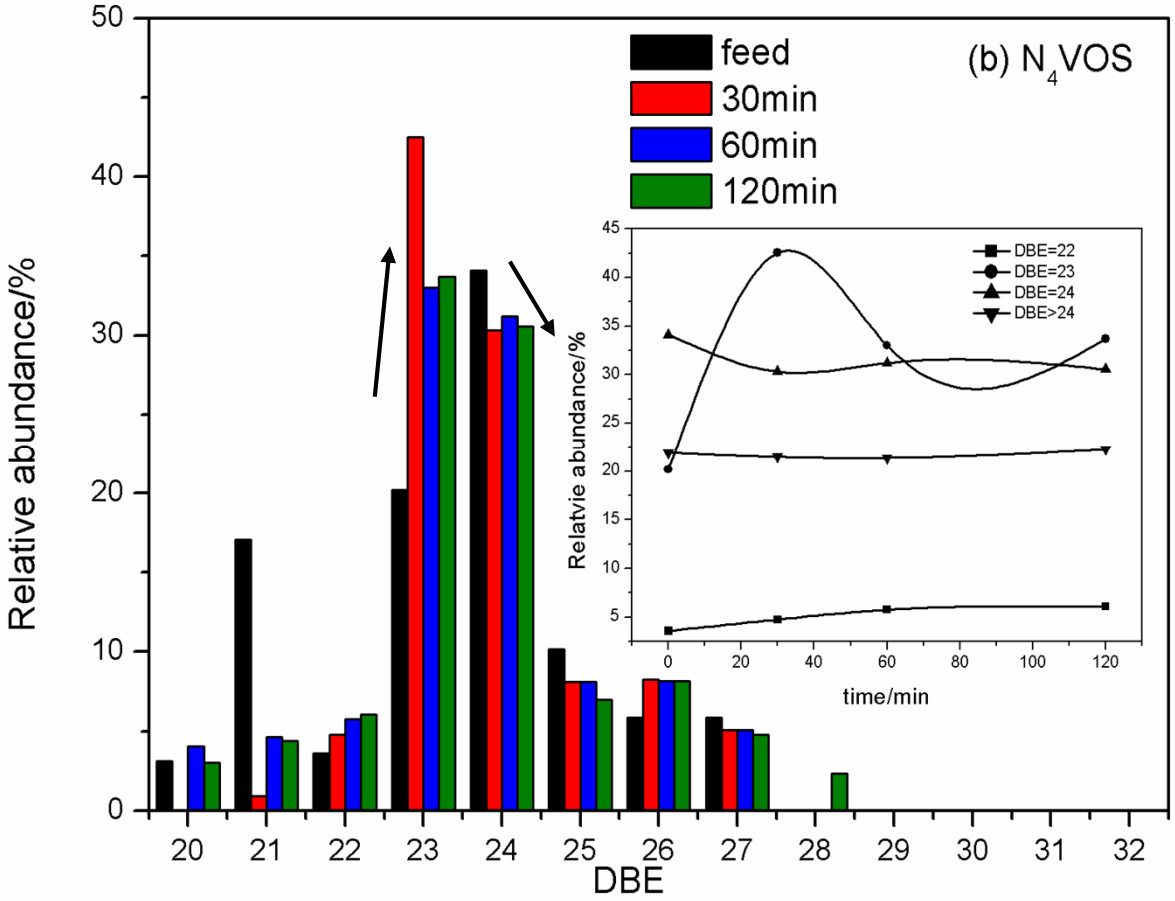

N4VO2
porphyrins
addition of carbonyl and/or carboxyl groups
DBE=17
DBE=18
DBE=19

Variation of DBE distribution of N_4VO porphyrins



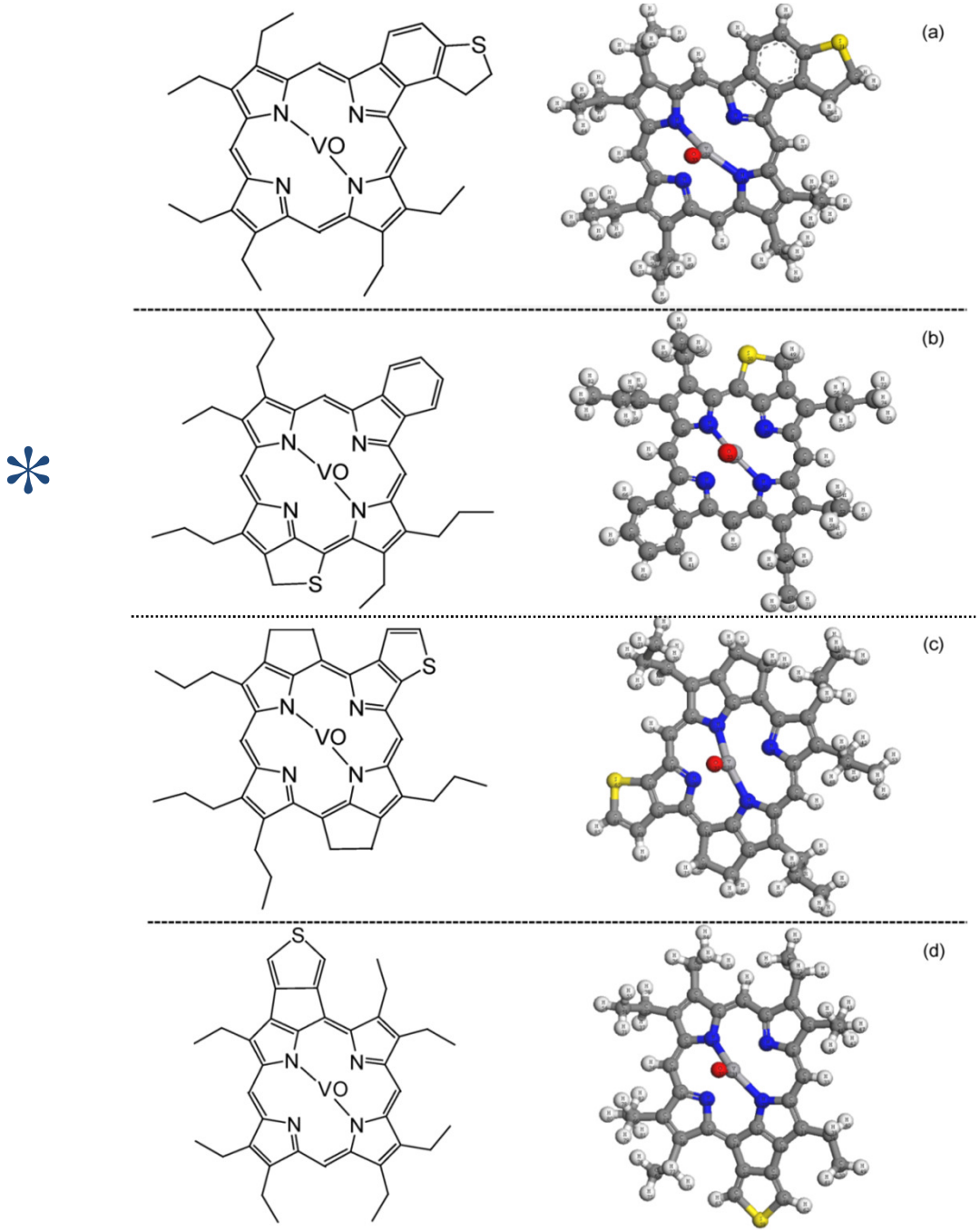
- Abundance of species (DBE<17) increases slightly
- Abundance of species (DBE=17) increases initially and then decreases
- Abundance of species (DBE=18) decreases initially and then increases
- Abundance of species (DBE>18) decreases slightly

Variation of DBE distribution of N_4VOS porphyrins

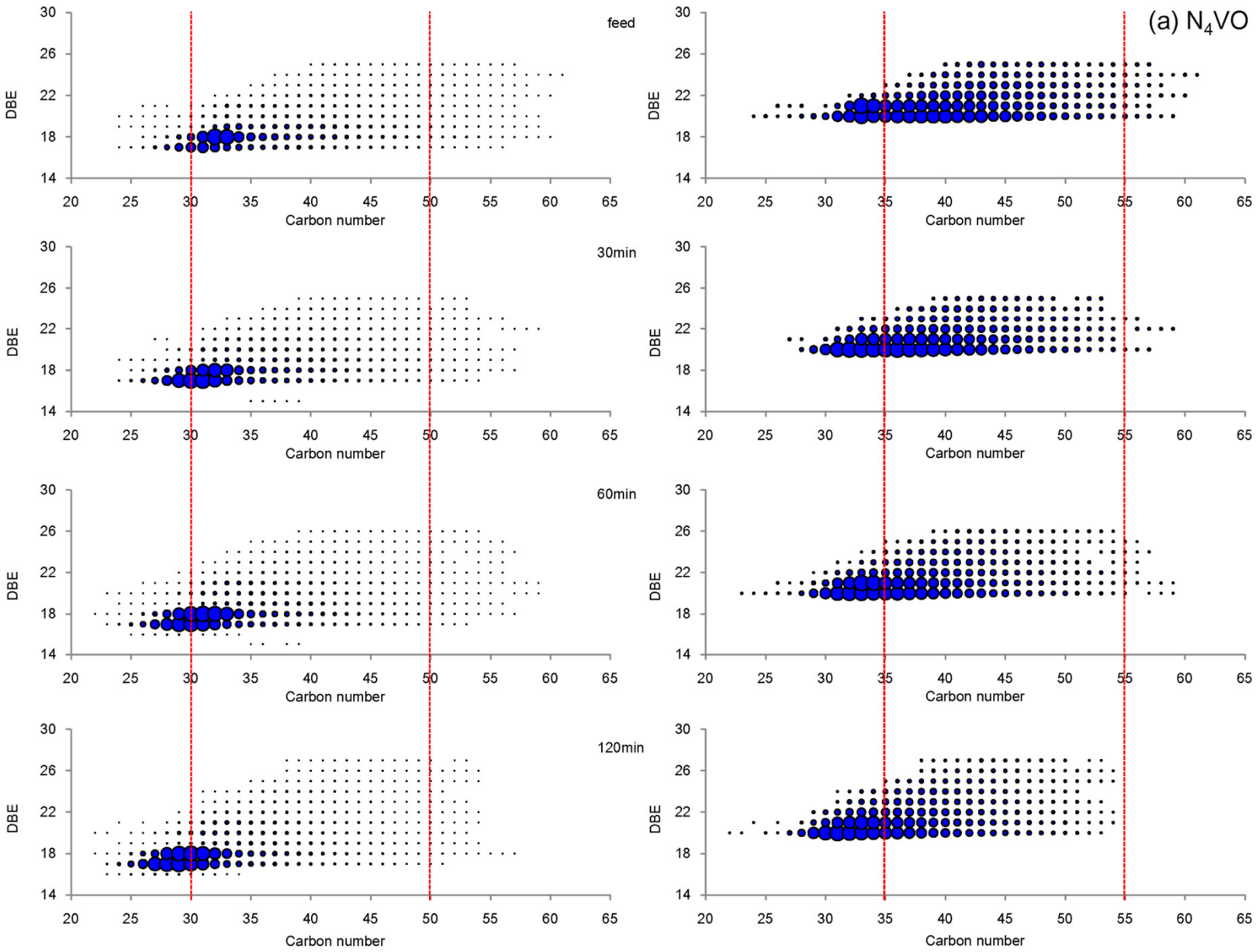


- N_4VOS porphyrins (DBE<21) could present a different structure and variation
- Consistent with that of N_4VO porphyrins
- N_4VOS porphyrins (DBE>21) may occur from N_4VO porphyrins by addition of benzothiophene

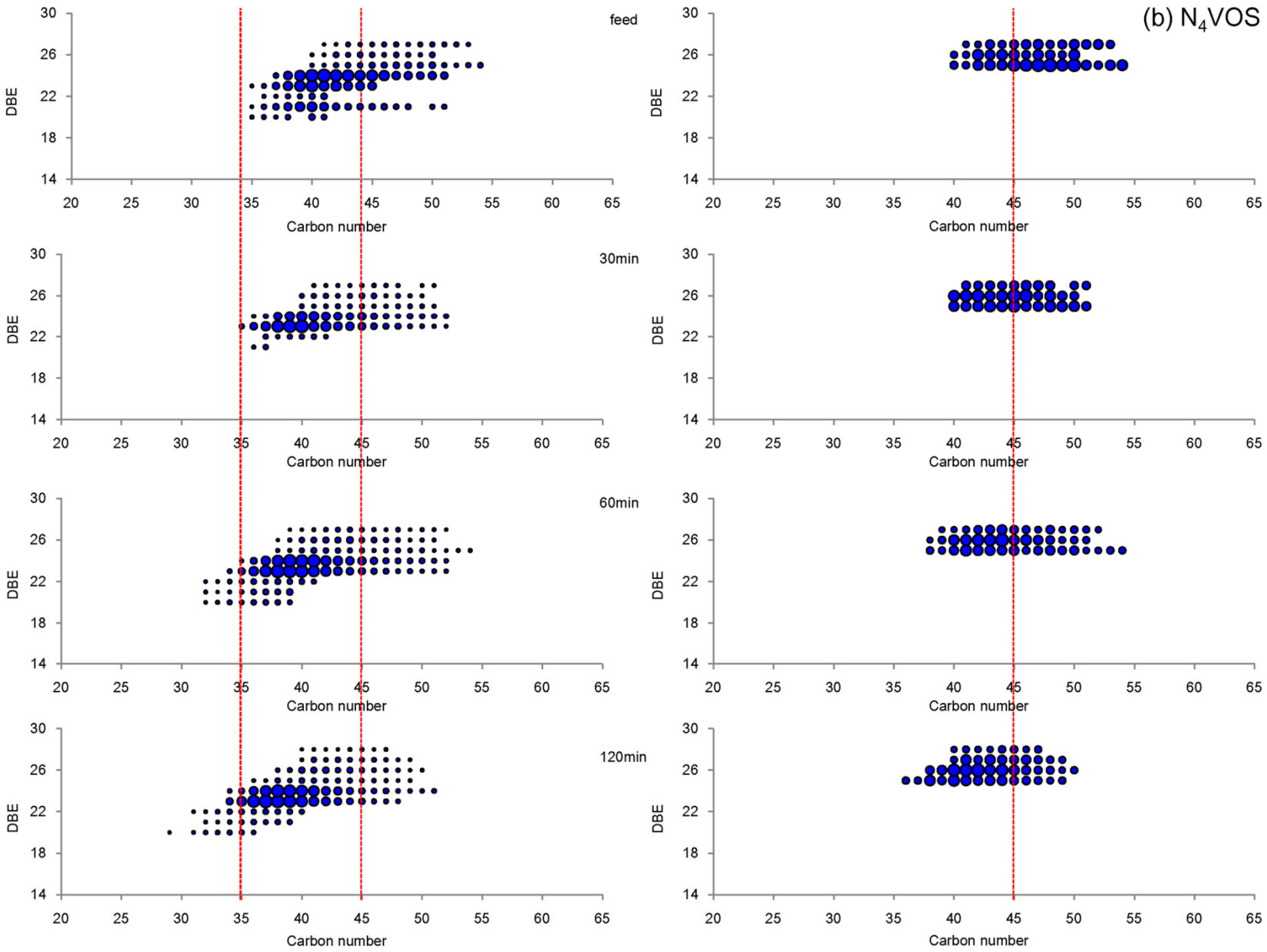
The possible structures of N_4VOS porphyrins with DBE of 21



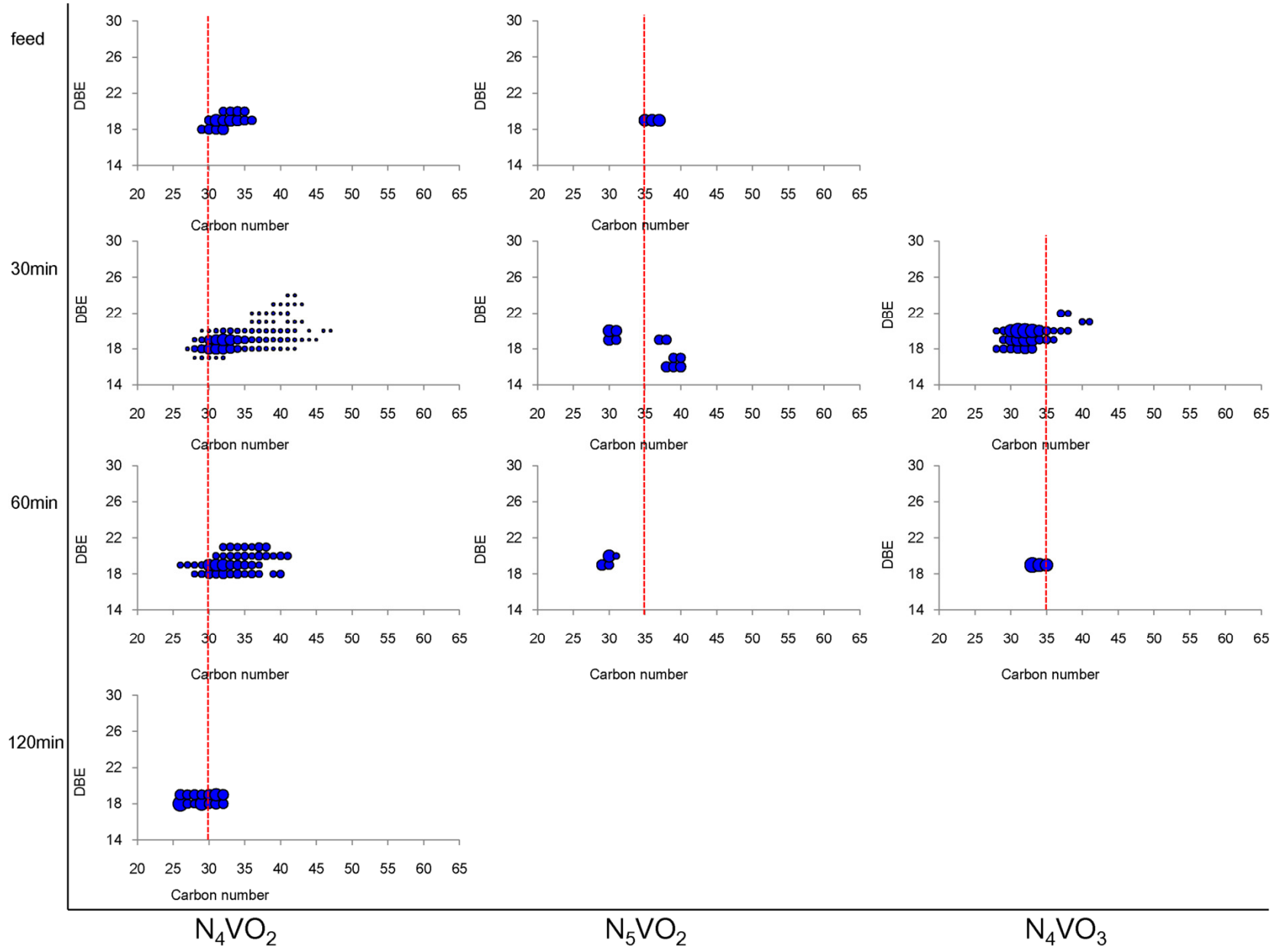
Variation of carbon number distribution of N_4VO porphyrins



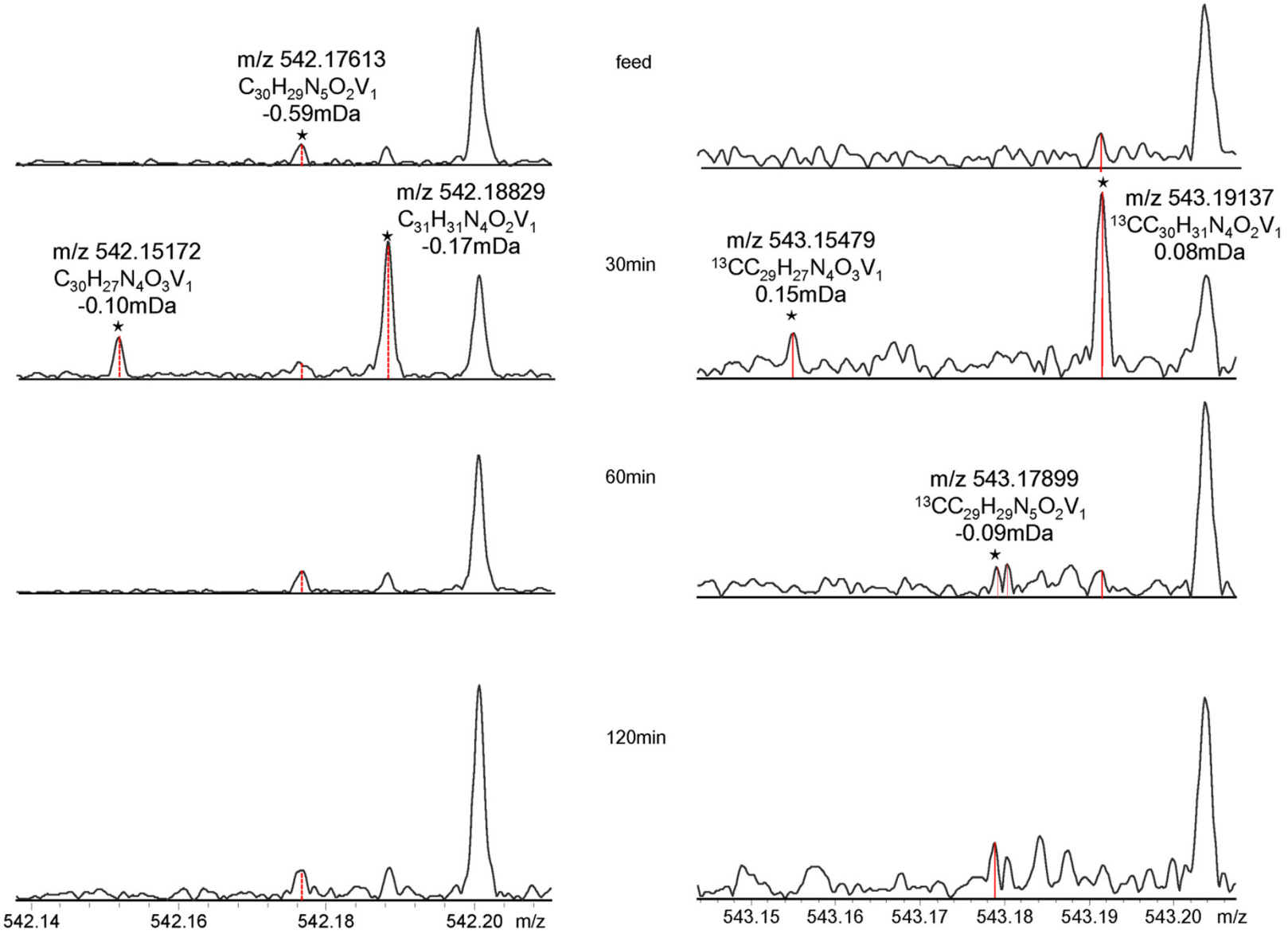
Variation of carbon number distribution of N_4VOS porphyrins



Variation of carbon number distribution of oxygen and/or nitrogen-containing porphyrins



Expanded mass spectra at m/z 542 and 543



Conclusions

- Variation of DBE and carbon number distribution could indicate the hydrogenation and thermal cracking reactions of petroporphyrins, respectively.

- N_4VOS porphyrins show very similar structural transformation with N_4VO.

- A considerable proportion of new types of N_4VO_2, N_4VO_3 and N_5VO_2 are identified after thermal treatment for 30 min.

- Catalysts: active hydrogenolysis property and macropore size distribution

Future work

- Effect of thermal conditions on transformation of petroporphyrins

- Transformation of nickel porphyrins during thermal upgrading process under hydrogen

- Transformation of petroporphyrins in asphaltenes under mild thermal pretreatment

Acknowledgement

State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China)

Professor Quan Shi at China University of Petroleum (Beijing)

Acknowledgement

Our Research Group

- Research group of heavy oil chemistry and thermal processing
- Website : http://ccce.upc.edu.cn/hg/index.asp

Thank you very much for your listening