Decoupling of redox/basic catalytic mechanisms during n-Butanol production

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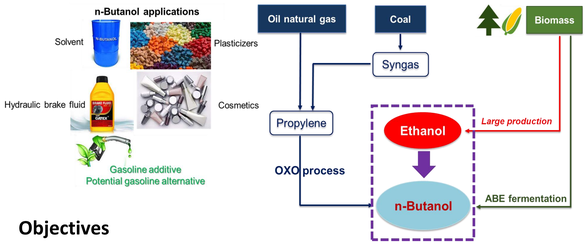
Motivation and background

- n-butanol is widely used as an important industrial intermediate. Based on the combustion performance it is a superior alternative biofuel compared to bioethanol [1].
- The large supply of bioethanol on the market, justifies seeking a green and efficient route for the direct catalytic conversion of ethanol (EtOH) to n-butanol (BuOH).
- Current technology for this route is still limited to bench scale due to the lack of suitable catalysts and optimized reaction systems[2].

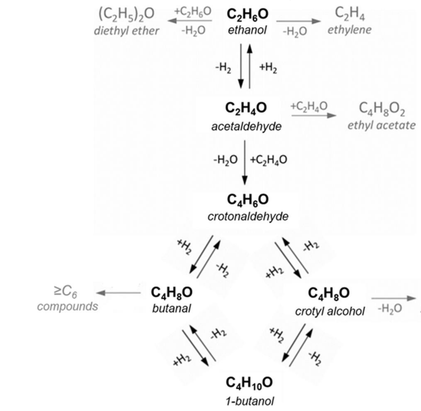


Objectives

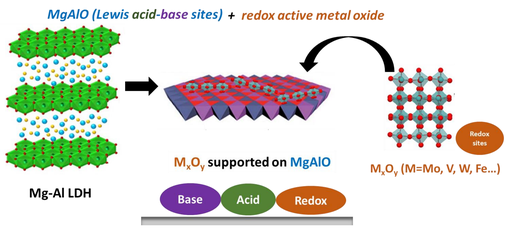
- Regulating the catalytic activity of MgAlO-based catalysts to optimize n-butanol production.
- Develop methodology to identify and qualitatively and quantitatively correlate the relationships between active sites and catalytic performance .

Research Methodology and equipment

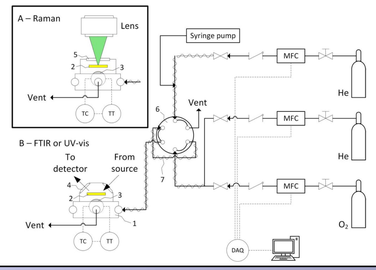
- Reaction network of the EtOH to BuOH process



- Design of MgAlO-based functional catalysts

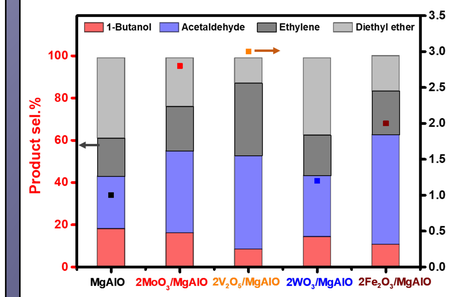


- Operando spectroscopy characterizations system



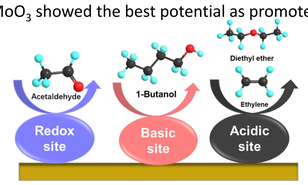
Key results—catalytic performance

- Effects brought by the introduction of redox sites
- Relationship between active sites and product selectivity

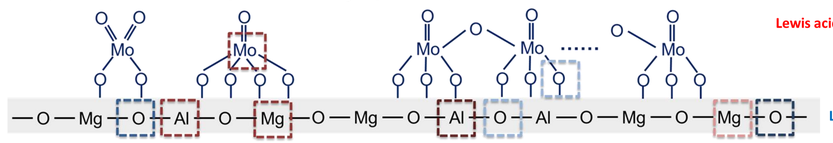


Observations:

- Redox sites greatly increased reaction rate and suppressed acid-catalyzed products.
- Redox sites negatively affect t BuOH selectivity.
- MoO_3 showed the best potential as promoter.



- Proposed active site(s) configuration in MoO_3/MgAlO catalyst



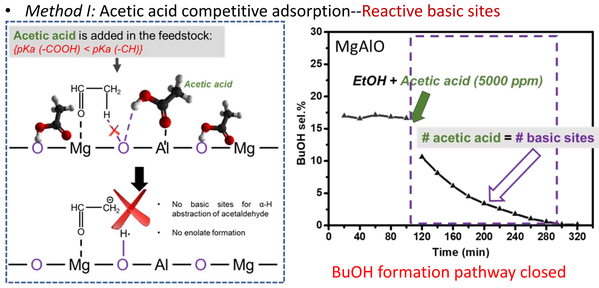
Lewis acidic sites
- Al^{3+} in Al_2O_3 phase: strong
- Mo^{6+} in MoO_3 phase: medium
- Cations of Mg^{2+} and Al^{3+} in MgAlO phase: medium
- Mg^{2+} in MgO phase: weak

Lewis basic sites
- Isolated O^{2-} in MgO phase: strong
- O^{2-} in MgAlO phase: medium
- O^{2-} in MoO_3 and Al_2O_3 phase: weak

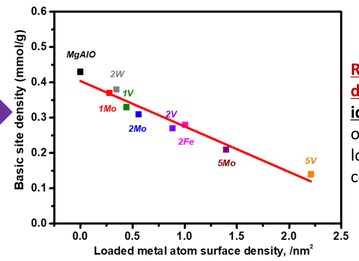
Key results--Qualification and quantification of catalytic relevant basic sites

Basic sites: necessary for enolate formation from acetaldehyde intermediates (generated from EtOH) to realize C-C coupling (key step for BuOH formation).

- *Method I:* Acetic acid competitive adsorption--Reactive basic sites

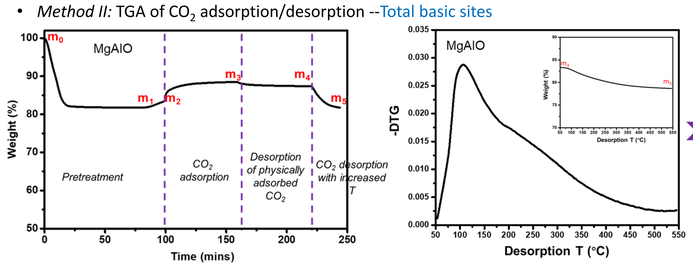


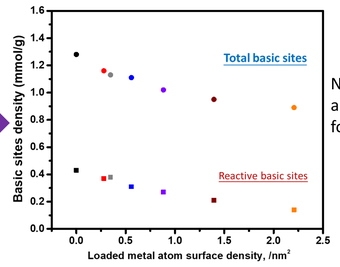
BuOH formation pathway closed



Reactive basic sites density is independent on identity of redox metal, only depends on absolute loading of redox metal covered on surface.

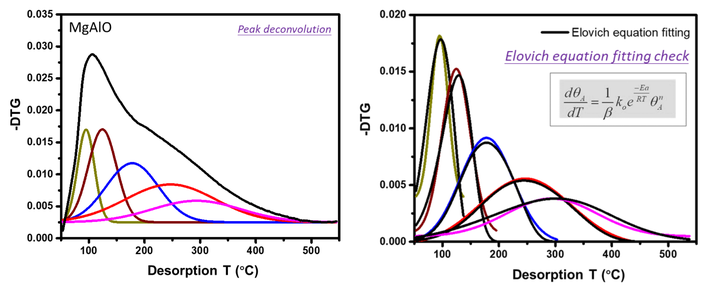
- *Method II:* TGA of CO_2 adsorption/desorption --Total basic sites

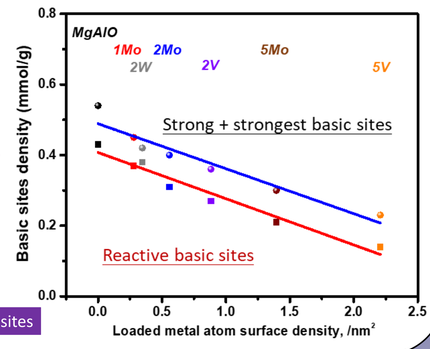




Not all basic sites are active for BuOH formation

- *Method III:* Deconvolution of CO_2-TGA result--Types and amount of different basic sites





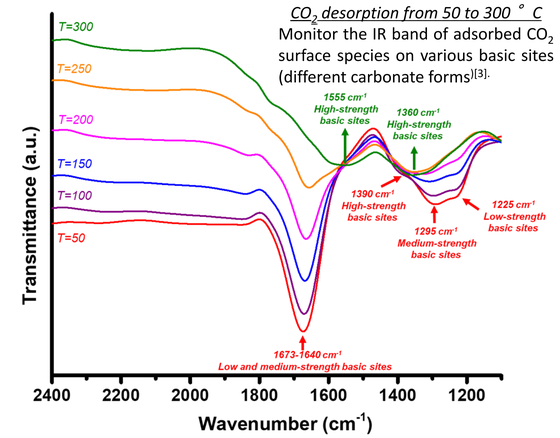
Four types of basic sites with different strength, catalytically relevant functionalities are the strong basic sites

Key results—in situ IR spectra

- Identifying basic sites with different strengths

CO_2 desorption from 50 to 300 ° C

Monitor the IR band of adsorbed CO_2 surface species on various basic sites (different carbonate forms)[3].



- Identifying the basic sites for C-C coupling step

Key conclusions

- Introduced redox functionalities can increase reaction rates by activating the hydrogen-transfer steps.
- n-Butanol formation is limited by the C-C coupling step.
- Strong basic sites are the active center to realize the C-C coupling.

Reference

[1] Sun, J.; Wang, Y., ACS Catalysis 2014, 4 (4), 1078-1090.

[2] Galadima, A.; Muraza, O., Industrial & Engineering Chemistry Research 2015, 54 (29), 7181-7194

[3] Di Cosimo, J. I., Díez, V. K., Xu, M., Iglesia, E., & Apesteguıa, C. R., Journal of Catalysis 1998, 178(2), 499-510.

Acknowledgements

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