Drop-in substitutes: a rare potential on metals, but why?

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Agenda

- Case 1: Substitution of a desiccant in linseed oil paint
- Case 2: Nickel catalysts and their alternatives
- Conclusions

Case 1.

Substitution of desiccant in linseed oil paint

Danish partnership project aiming at reducing the use of harmful chemicals in products.

- ***Kemi i Kredsløb (KIK)*** is a partnership that helps Danish enterprises reduce the use of chemicals of concern in their products
  - The Danish Technological Institute (TI)
  - DHI
  - RPA Ltd
  - SP-Group surface solutions (SE)
  - Department of Public Health, University of Copenhagen
  - Department of Engineering, University of Aarhus

Substitution of Co-contaning desiccant in linseed oil paint from Skovgaard and Frydensberg

- Desiccant reduces the drying time from weeks to hours
- Ensures uniform curing in the paint layer
- Makes drying possible under different temperature, humidity and light conditions

Substitution of Co- contaning desiccant in linseed oil paint from Skovgaard and Frydensberg, paint manufacturer

Parameter	Requirement/	Alternatives				
		Co	1- Mn	2- Mn	3- Fe	4- Mn
Drying time	Max. 12 hr	12	>24	18	23	12
Colour	Neutral (1 - 5)	4	-	3	2	4
Adherence	Good	+	+	+	+	+
Curing	Uniform	+	nd	med	slow	med
Hardness Glossiness	High	good	nd	Good	High	Good
Safety & health	No CMR class.	Repr 2	ok	ok	ok	ok
Classification	Should not trigger further classification		ok	ok	ok	ok
Price	Minimal	-		+2%		+8%

Substitution of Co- contaning desiccant in linseed oil paint from Skovgaard and Frydensberg, paint manufacturer

Conclusions:

- Substitution is possible although longer curing time is expected
- Overall the Alternative 2 and 4 performed technically best
- Further development plans goes in the direction of combining alternative 2 and 4
- Storage and UV stability need be further evaluated

Case 2.

Nickel catalysts and alternatives

Background

- Nickel Institute initiated in 2012 a study on possible alternatives to nickel in catalysts:
  - By independent experts: Dr. Martin Lok, proff. Roel Prins
  - With Involvement of ECMA (Catalysts Europe)

Market/Functionality Matrix
Ni Catalysts, info from ECMA members

Market	Refinery	Hydrogen	Fertilisers	Petro-chemicals	Fine chemicals	Oleoche-micals
Steam reforming/ Methanation	■	■	■	■		
Hydrotreating (HDS, HDN, HDO)	■	■	■	■		
Hydrocracking	■					
Hydrogenation	■			■	■	■
Amination				■	■	
Sulfur trapping	■	■	■	■		

■ = nickel is being used

Steam reforming

- Large scale production of hydrogen used in refineries, chemicals production, fertilizers, etc.
- Currently only Ni is used.
- Ru is an alternative (Rh, Ir, Pd, Pt, Co, identified but not proven)

	Ni	Ru	Pgm	Co
Activity	1	>5	>1	<0.3
Selectivity	1	1	1	1
Stability	1	1-10	>1	lower
Life time	1	>1	>1	unknown
Metal Costs	1	200	>2000	1.7
Commercially used	Yes	Yes	No	No

Steam reforming

- Implications:
  - Ru catalyst are too expensive and has limited availability
  - Decreased hydrogen availability in refineries will limiting sulphur removal thus compromising downstream processes.
  - Increased costs of fuels, fertilizers and petro-and oleochemicals.

- Conclusions:
  - There are currently no realistic alternatives to nickel
  - Ru possible for a few niche applications (biofeed), but has very limited availability (world production 32 tpa (2012)).

Hydrotreating (HDS, HDN, HDO, HDM, HYD)

- Remove sulfur, nitrogen, oxygen and metal atoms from oil fractions.
- Potential alternatives to nickel: CoMo, Mo only, Ru, pgm

	Ni-metal	CoMo	Mo	Ru	pgm
Activity	1	0.1-0.5	0.05-0.1	1	?
Selectivity	1	<1	<1	>1	-
Life time	1	~1	0.1-0.5	?	?
Cost	1	~1	~1	High	high

Hydrotreating (HDS, HDN, HDO, HDM, HYD)

- **CoMo**: lower activity requires higher catalyst loads, or increased reactor capacity. Lower selectivity gives lower S and N removal.
- **Mo**: lower activity requires higher catalyst loads. Revamp will be necessary to maintain capacity. Risk of sulfur poisoning of downstream catalysts.
- **Ru:** increased costs petrochemicals and refinery products. World Ru production capacity is insufficient.

Sulfur trapping (by NiO/ ZnO adsorbent)

- Used for S-removal from natural gas; polishing of naphtha a.o.
- Removal of organic sulphur compounds (fine chem. Industry).
- Available alternative: Cu/ZnO

	NiO/ZnO	CuO/ZnO
Activity	High	Low
Leaching / sulfur slip	No leaching	Leaching risk
Life time	Good	Short
Cost	-	High, due to low activity and short life-time

Sulfur trapping (by NiO/ ZnO adsorbent)

- Replacement of nickel-based by copper-based reactive sulphur adsorbents is possible but
  - Copper is less active and has shorter life time: increased costs for bigger reactors and frequent replacement
  - Risk of sulphur slipping through will impact down-stream catalysts.

Conclusions

Case 1: Alternative to Co-desiccant

- Mn-based alternative with longer curing time (lower activity)
- The alternative has a slightly higher cost

Conclusions

Case 2: Alternatives to nickel in catalysts

- Steam reforming
  - Ru (and maybe pgm) are technically suitable but expensive
  - Ru availability (32 tpa) is a limited ressource
- Hydrotreating
  - Co-Mo catalysts are 2 - 10 times less active
  - Gives higher sulphur and nitrogen content
- Sulphur trapping
  - CuO/ZnO has a lower activity and shorter life time
  - Increased risk of sulphur slipping through

Conclusions, overall

The catalytic activity of metals is based on the inherent properties of the metals elements.

Different metals may catalyse same reactions but with different activity and selectivity

Replacement of Ni in large scale operations means (dramatically) increased costs

No viable alternatives to Ni catalysts are available the most important uses: steam reforming, hydrotreating, hydrogenation and sulphur trapping.

Thank you!

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