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MODIFICATION OF SAPONITE-BASED 3D-METAL CATALYSTS FOR THE CONVERSION OF ETHANOL TO 1,3-BUTADIENE

Marc Greuel[1], S. R. Joshi[2], K. Schindler[3], C. Watermann[3], H. Lohmann[3], S. Kaluza[4], U.-P. Apfel[1], B. Zeidler-Fandrich[3*];

[1] Fraunhofer UMSICHT & Ruhr University Bochum, Oberhausen/Bochum/DE; [2] Fraunhofer UMSICHT & TU Hamburg-Harburg, Oberhausen/Hamburg/DE

[3] Fraunhofer UMSICHT, Oberhausen/DE; [4] Hochschule Düsseldorf, Düsseldorf/DE

Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Osterfelder Strasse 3, 46047 Oberhausen, Germany

Phone* +49 208 8598-1143, E-mail* barbara.zeidler-fandrich@umsicht.fraunhofer.de, www.umsicht.fraunhofer.de

Motivation

1,3-butadiene (BD) is a platform chemical for polymers[1] and produced from naphtha. Shell gas replaces naphtha leading to less BD production. Ethanol to BD reaction (ETB) (**Figure 1**) is an alternative production route.[3,4] This reaction requires a selective and balanced catalyst → Saponites (**Figure 2**).[5,6]

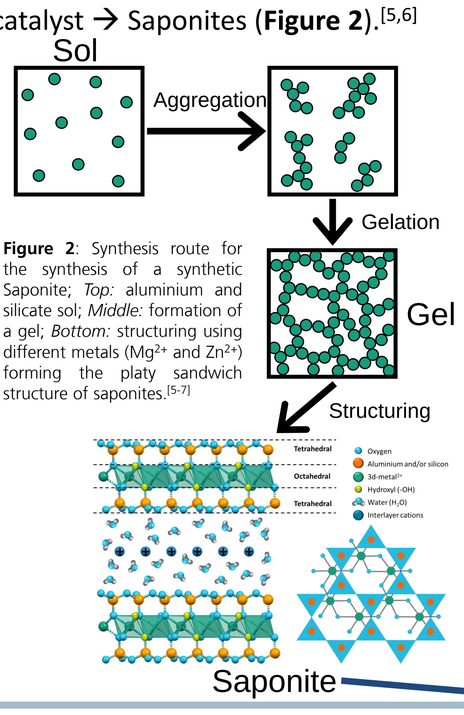

Figure 2: Synthesis route for the synthesis of a synthetic Saponite; *Top:* aluminium and silicate sol; *Middle:* formation of a gel; *Bottom:* structuring using different metals (Mg^{2+} and Zn^{2+}) forming the platy sandwich structure of saponites.[5-7]

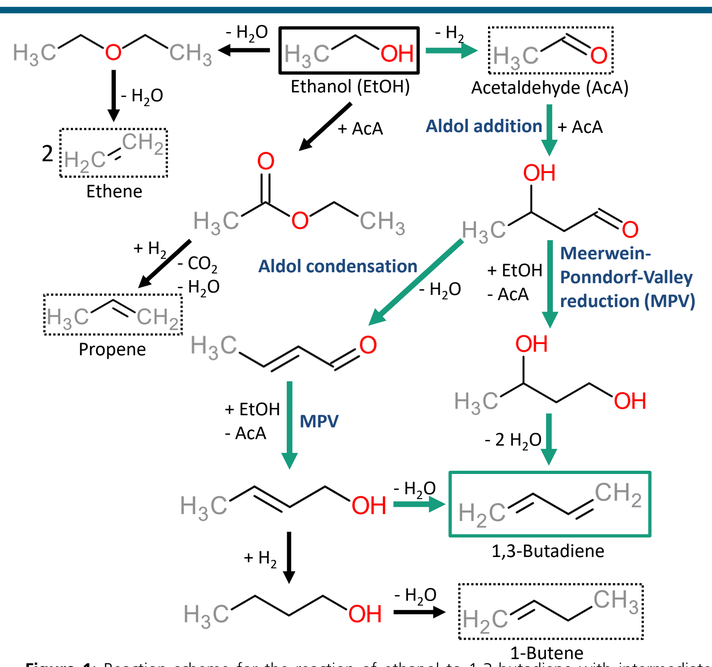

Figure 1: Reaction scheme for the reaction of ethanol to 1,3-butadiene with intermediate products and the main by-products.[3,4]

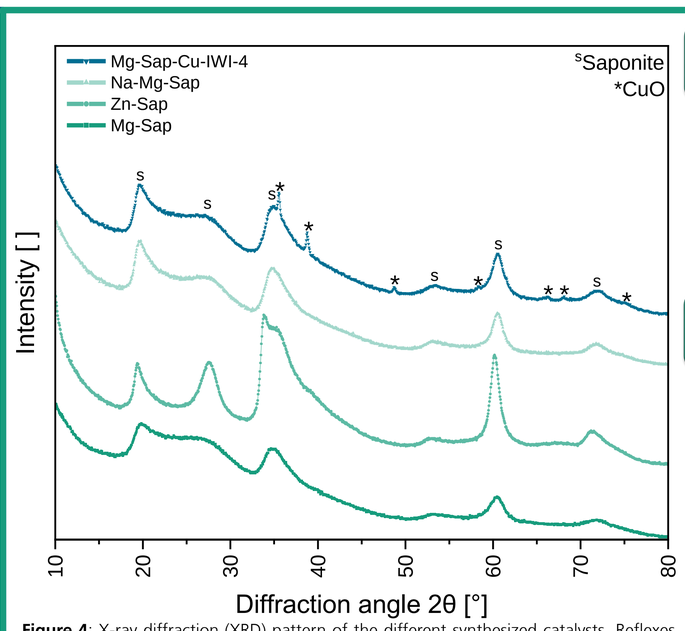

Figure 4: X-ray diffraction (XRD) pattern of the different synthesized catalysts. Reflexes marked with s corresponds to the saponite structure[5], * marked reflexes to CuO[8].

Catalyst structure

- Saponite **structure** for all synthesized materials obtained
- Higher **crystallinity** for Zn-Saponite compared to Mg-Saponite

Catalyst composition

- **Na^+:H^+ ratio** adjustable using cation exchange
- lower Mg content as expected
- **XPS** and **XRD** confirm CuO[8,9] on the surface of the Mg-Saponite impregnated with Cu

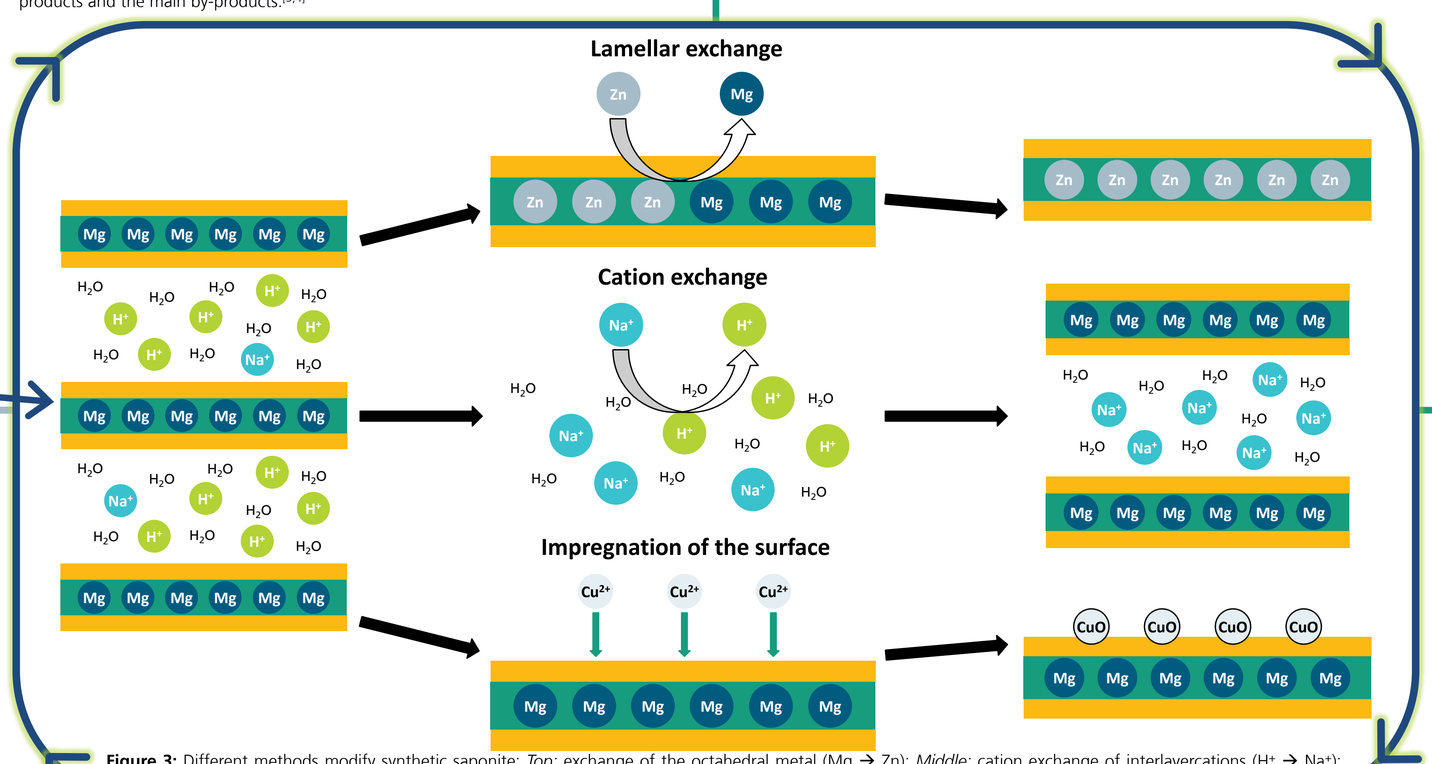

Figure 3: Different methods modify synthetic saponite; *Top:* exchange of the octahedral metal (Mg → Zn); *Middle:* cation exchange of interlayercations (H^+ → Na^+); *Bottom:* loading of a synthetic Mg-Saponite surface with CuO (Surface—CuO).

Table 1: Chemical composition of the different synthesized catalysts (from top to bottom: ideal saponite composition with M and Me being mainly metals), Mg-, Zn-, Na-Mg-, and Mg-Saponite impregnatd with Cu,) determined via ICP-OES, oxygen amount was assumed from the ideal saponite composition.

$M_{x/z}^{z+}[Mg_6][Si_{8-x}Al_x]O_{20}(OH)_4 \cdot nH_2O$ with x = 1.2
$Na^+_{0.3}H^+_{0.9}[Mg_{4.5}][Si_{6.8}Al_{1.2}]O_{20}(OH)_4 \cdot nH_2O$
$Na^+_{0.3}H^+_{0.9}[Zn_{6.6}][Si_{6.8}Al_{1.3}]O_{20}(OH)_4 \cdot nH_2O$
$Na^+_1H^+_{0.2}[Mg_{4.2}][Si_{6.8}Al_{1.3}]O_{20}(OH)_4 \cdot nH_2O$
$Na^+_{0.2}H^+_1[Mg_{4.3}][Si_{6.8}Al_{1.2}]O_{20}(OH)_4 \cdot nH_2O$—$Cu_{0.3}O_{0.3}$

Catalytic activity

- **Unmodified Mg-Saponite**:
  → high conversion
  → low BD production
  → main product: **ethene**
- **Zn-Saponite:**
  → conversion minus ~25 %
  → higher BD production
  → main product: **acetaldehyde**
- **Na-Mg-Saponite:**
  → conversion minus ~50 %
  → good BD productivity (450 °C)
  → **more evenly distributed product mixture**
- **Mg-Sap impregnated with Cu:**
  → high conversion
  → good BD productivity (350 °C)
  → main product: **ethene** (+acetaldehyde)

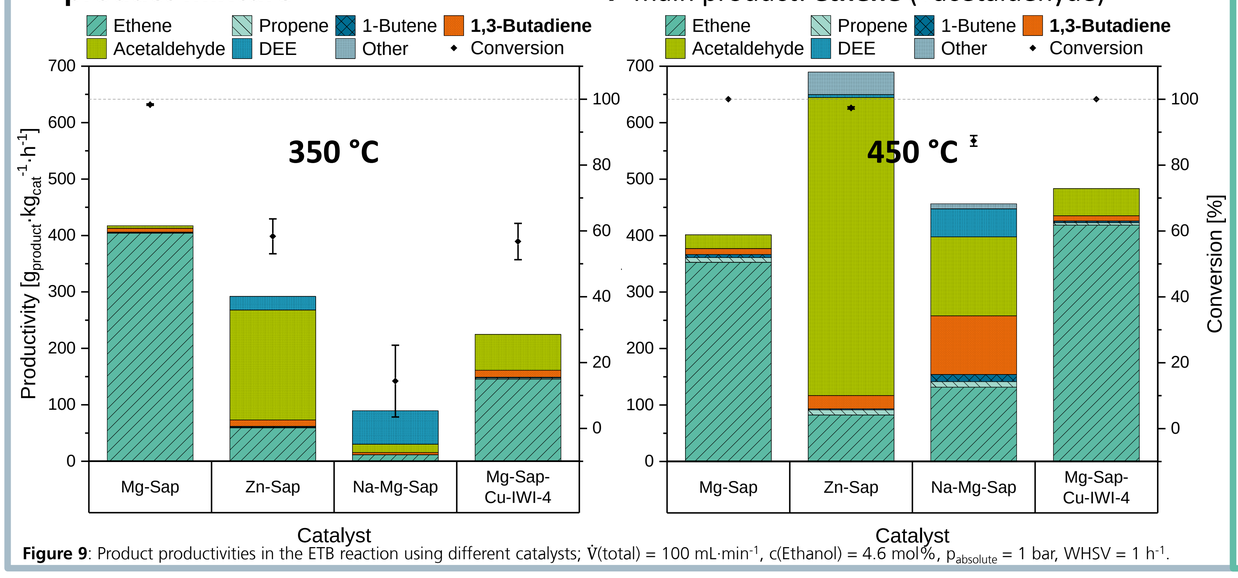

Figure 9: Product productivities in the ETB reaction using different catalysts; $\dot{V}$(total) = 100 mL·min^{-1}, c(Ethanol) = 4.6 mol%, $p_{absolute}$ = 1 bar, WHSV = 1 h^{-1}.

Catalyst	Mg-Saponite	Zn-Saponite	Na-Mg-Saponite	Mg-Saponite-Cu (4wt%)
BET-Surface	555.5 m²·g^{-1}	85.8 m²·g^{-1}	534.3 m²·g^{-1}	470.5 m²·g^{-1}

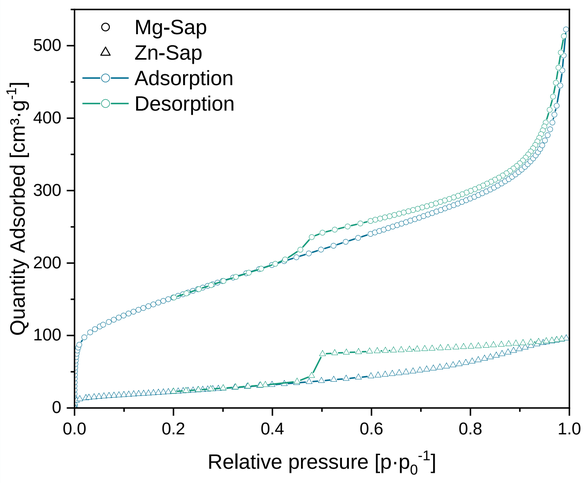

Figure 6: *Top:* Table with BET-surface areas of the catalysts; *Bottom:* N_2 adsorption-desorption curves of Mg- and Zn-Saponite.

Catalyst surface

- **Surface area** of Zn-Saponite smaller and more flat compared to Mg-Saponite
- Mg-Saponite
  → flaky primary clay particles[10]
- Zn-Saponite
  → uneven pore system and interconnected pores with different sizes and shapes[10]
- **EDX** confirms CuO crystals on Cu impregnated Mg-Saponite surface

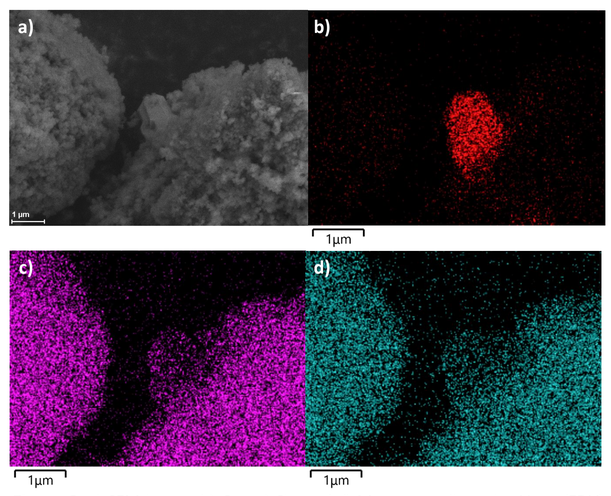

Figure 8: a) SEM image, b) Cu-, c) Si-, and d) Mg-energy dispersive X-ray (EDX) mapping of Mg-Saponite impregnated with Cu; EHT = 5-20 kV, WD = 10.0 mm, magnification 20,000.

SUMMARY AND OUTLOOK

- Testing different modification results in the formation of the expected products confirmed via XRD, ICP-OES, XPS and SEM/EDX
- Comparing the conversions of Mg-, Zn- and Na-Mg-Saponites leads to the assumption, that composition of saponites play a more important role as the size of the surface area
- Zn-Saponite directs the ETB reaction towards acetaldehyde due to an overall lower acidity of the sample, the high acidity due to high H^+ concentration of the non cation exchanged saponites (determined via NH_3 and CO_2-TPD) leads to the formation of ethene → lower ethene selectivity of Na-Mg-Saponite
- **Outlook:** Optimization of the saponite composition (iterative) and reaction parameters to obtain higher BD productivities (highest at the moment:103.9 $g_{BD} \cdot kg_{Cat}^{-1} \cdot h^{-1}$)

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