The challenge for a more sustainable society: catalysis for chemicals and fuels from renewables

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> Divisione di Chimica Industriale della SCI Gruppo Interdivisionale di Catalisi







SESSION: ELEMENTS OF THE PERIODIC TABLE IN ENERGY SAVING AND RECYCLING

Saving and recycling, with a focus on catalysis to convert CO_2 into fuels, CH_4 to CH_3OH and **biomasses to added-value products**.

Novel approaches based on non-noble metals such as **Fe**, **Mn and Cu** will be proposed and discussed to fulfill this goal.

When can a catalyst for the production of fuels and chemicals be considered sustainable ?

III LIIC SYTTETESIS OF CALAIYSES



1														18			
1 H hydrogen						UPAC	Period	dic Tal	ole of	the Ele	ement	5					2 He helium
[1.0078, 1.0082]	2		Key:									13	14	15	16	17	4.0026
3 Li lithium (5.938, 6.997)	4 Be beryllium 9.0122		atomic num Symbo name standard stomic v	ber Ol weight								5 B boron 10.81 [10.805, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 124.304.24.307	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.982	14 Si silicon 20.005 128.084, 28.0861	15 P phosphorus 30.974	16 S sulfur 3206 B2 059, 32 0761	17 Cl chiorine 35.45 135.446, 35.4571	18 Ar argon 39.95 [39.762, 39.963
19 K potassium	20 Ca calcium	21 Sc scandium	22 Ti Stanium	23 V vanadium	24 Cr chromium	25 Mn manganese	26 Fe iron	Co cobalt	28 Ni nickel	Cu copper	30 Zn zinc	31 Ga gallium	32 Ge germanium	33 As arsenic	34 Se selenium	35 Br bromine 73904	36 Kr krypton
39.098 37 Rb rubidium	40.078(4) 38 Sr strontium	39 Y yttrium	47.867 40 Zr zirconium	41 Nb nicbium	42 Mo molybdenum	43 TC technetium	44 Ru ruthenium	45 Rh rhodium	46 Pd paladium	63.546(3) 47 Ag silver	48 Cd cadmium	49 10 indium	50 50 50 50 50 50	51 Sb antimony	78.971(8) 52 Te tellurium	[79.901, 79.907] 53 iodine	83.798(2) 54 Xe xenon
55 Cs caesium	87.62 56 Ba barium	88.906 57-71 Ianthanoids	91.224(2) 72 Hf hafnium	92.905 73 Ta tantalum	9595 74 W tungsten	75 Re thenium	101.07(2) 76 OS osmium	102.91 77 Ir itidium	106.42 78 Pt platinum	107.87 79 Au gold	80 Hg mercury	114.82 81 TI thailium 294.30	82 Pb lead	121.76 83 Bi bismuth	127.60(3) 84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	178.49(2) 104 Rf rutherfordium	180.95 105 Db dubnium	106 Sg seaborgium	186.21 107 Bh bohrium	108 HS hassium	109 Mt meitherium	110 DS darmstadium	196.97 111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 FI flerovium	115 Mc moscovium	116 Lv Ilvermorium	117 Ts termessine	118 Og oganesson



INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

57 La Ianthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 15196	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu Iutetium 17497
89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr Iawrencium

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X critical (for EU) raw materials





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X critical (for EU) raw materials X high-concern elements



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Lr.

lawrencium

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X critical (for EU) raw materials X high-concern elements X conflict elements

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X critical (for EU) raw materials X high-concern elements X conflict elements X more toxic

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X critical (for EU) raw materials X high-concern elements X conflict elements X more toxic A potentially toxic

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Spinel-type Ferrites

Reaction

Oxidative cleavage of styrene to benzaldehyde with H₂O₂ Oxidation of cyclohexane to cyclohexanol/cyclohexanone with O₂ or H₂O₂ Hydroxylation of benzene/phenol to phenol/diphenols with H₂O₂ Oxidation of vanyllol to vanillin with air Oxidation of benzyl alcohol to benzaldehyde with H2O2 Oxidation of monoterpenic alkenes with O2 Oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid (hmf to fdca) with H₂O₂ or O₂ Oxidation of aniline to azoxybenzene with H₂O₂ Oxidation of toluene to benzaldehyde with H2O2 Oxidation of ethanol to acetaldehyde with O₂ Oxidation of veratryl alcohol to veratryl aldehyde with O2 Ketonisation of butanol to heptanone Total oxidation of voc with air Friedel-crafts acylation Knoevenagel condensation Reduction of ketones Reduction of nitroarenes Methylation (alkylation) of phenolics, aniline, pyridine Methanol, ethanol reforming (by means of chemical-loop)

Preparation Method

Coprecipitation Sol-gel Hydrothermal Solvothermal Microemulsion/Reverse micelles Template Mechanical milling Plasma Flux growth Solid phase Combustion Microwave combustion Microwave hydrothermal Pechini method Electrochemical Electrospinning Thermal treatment Ultrasonic wave-assisted ball milling Spray pyrolysis Aerosol Forced hydrolysis Glycol-thermal Refluxing

Spinel-type mixed <u>ferrites</u> as e^{-}/O^{2-} carriers for H₂ production from H₂O

THERMOCHEMICAL CYCLES

Thermal splitting of H₂O

 $H_2O \rightarrow H_2 + \frac{1}{2}O_{2} \Delta 3300K$

Thermochemical splitting of H₂O

 $A-O \rightarrow A + \frac{1}{2}O_2$ $A + H_2O \rightarrow H_2 + A-O$

The two-step process eliminates the need for H_2/O_2 separation

Thermal cycle	Steps	Maximum temperature (°C)	Efficiency (%)
<u>Sulfur cycles</u> Hybrid Sulfur (Westinghouse, ISPA Mark 11)	2	900 (1150 without catalyst)	43
Sulfur-iodine (General Atomics, ISPRA Mark 16)	3	900 (1150 without catalyst)	38
<u>Volatile metal oxide cycles</u> Zinc/zinc oxide Hybrid cadmium	2	1800 1600	45 42
Non-volatile metal oxide cycles			
Iron oxide	2	2200	42
Cerium oxide	2	2000	68
Ferrites	2	1100-1800	43
Low temperature cycles			
Hybrid copper-chloride	4	530	39

The steam-iron process

Reynolds Man Angel No.2 (out of frame) To fill the envelope required five tons of sulphuric acid and four tons of iron filings, costing in all 175 dollars. A Charles A Ital IN Chutes Parks was the home of the Los Angeles Angels baseball club situated at the corner of Washington Boulevard and Grand Avenue and a popular site of many airship exhibitions. A contest between the Man ngel Nº2 and Bullet - judged upon speed, altitude attained and general manoeuvring - resulted in a tie. A dirigible oted by Wordin Trombly wi out tremendous success, 75 in length, 18 feet in diame ter, with a hydro 22,000 cubic gen capacity feet, producing 350 lbs of lift force. To fill the envelope required five tons of sulphuric acid and four tons of iron filings, costing in all 175 dollars.

L. Calvillo, et al, J. Mater. Chem. A, 2018, 6, 7034–7041 F. Carraro, et al, J. Mater. Chem. A, 2017, 5, 20808–20817 O. Vozniuk, et al, ChemCatChem 2017, 9, 2219-2230 C. Trevisanut, et al, Topics Catal. 59 (2016) 1600–1613 O. Vozniuk, et al, Green Chem., 2016, 18, 1038–1050 C. Trevisanut, et al, Intern. J. Hydr. Energy, 40 (2015) 5264-5271 C. Trevisanutet al, Catal. Sci. Technol., 5, (2015) 1280–1289 S. Cocchi, et al, Appl. Catal. B 152–153 (2014) 250–261 J. Velasquez Ochoa, et al, J. Phys. Chem. C 117 (2013) 23908–23918 V. Crocellà, et al, J. Phys. Chem. C 116 (2012) 14998–15009

Ferrites for Chemical-loop reforming

Stefano Cocchi Cristian Trevisanut Olena Vozniuk

The first part of the loop: oxidised spinel + ethanol

The second part of the loop: reduced spinel + water

2nd step: oxidation with water

1st step: reduction with ethanol

5-min cycles (20 cycles)

No coke or **iron carbide** after reduction !

Mössbauer spectroscopy

SAMPLE	species	%
Fe ₃ O ₄ after 5	Fe ³⁺	35
minutes	Fe ^{2,5+}	63
reduction	Fe ⁰	2
Fe ₃ O ₄ after 1	Fe ³⁺	35
complete cycle (5/5minutes)	Fe ^{2,5+}	65
Fe ₃ O ₄ after 19	Fe ³⁺	33
cycles + 5 min	Fe ^{2,5+}	63
reduction	Fe ⁰	4
Fe ₃ O ₄ after 20	Fe ³⁺	37
cycles	Fe ^{2,5+}	63

With only traces of CO_2 and no CO during the second step of the cycle

20 min cycles (450°C)

Evaluation of COKE:

CHNS analysis

Sample	C _{w%} (after 20 min reduction)
CuFe ₂ O ₄	6.9
CoFe ₂ O ₄	11.6
Cu _{0.5} Co _{0.5} Fe ₂ O ₄	16.3
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄	6.1
Co _{0.5} Mn _{0.5} Fe ₂ O ₄	1.5
MnFe ₂ O ₄	1.7

Selectivity to H_2

Sample	H ₂ /CO _x
CuFe ₂ O ₄	3
CoFe ₂ O ₄	6
Cu _{0.5} Co _{0.5} Fe ₂ O ₄	3
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄	6
Co _{0.5} Mn _{0.5} Fe ₂ O ₄	15
MnFe ₂ O ₄	15

Degree of reduction after 20 min

CuFe₂O₄ a~ 82% CoFe₂O₄ a~ 82% Cu_{0.5}Co_{0.5}Fe₂O₄ a~ 100% Cu_{0.5}Mn_{0.5}Fe₂O₄ a~ 73% Co_{0.5}Mn_{0.5}Fe₂O₄ a~ 10% MnFe₂O₄ a~ 8% Redox properties, and more generally their catalytic activity, are strongly influenced by the nature of M and by the Mⁿ⁺ distribution among the 16 octahedral and 8 tetrahedral sites in the crystal lattice.

investigated materials. The spectra were collected in transmission mode.

The cation distribution was determined by **EXAFS**. The **crystallographic site occupancy is defined by the inversion parameter** γ **.**

Sample	Y (EXAFS)	Y (Mössbauer 80K)	SSA, m²/g (BET)	Crystallite size, nm (XRD)	Particle size, nm (BET)
CoFe ₂ O ₄	0,7	0,74	69	12	16,2
FeCo ₂ O ₄	0,6	0,56	4	32	275

 $CoFe_{2}O_{4} : [Co(II)_{0.3}Fe(III)_{0.7}]^{Tet}[Co(II)_{0.7}Fe(III)_{1.3}]^{Oct}O_{4}$ FeCo₂O₄ : [Co(II)_{0.6}Fe(III)_{0.4}]^{Tet}[Co(II)_{0.4}Fe(III)_{0.6}Co(III)_{1}]^{Oct}O_{4}

Investigation of the 1st step (reduction with ethanol)

Time resolved experiments were carried out using the *QuickEXAFS procedure*, monitoring the reduction of the materials collecting a spectra every 5 seconds.

The **cobaltite** is completely reduced at a temperature lower than **ferrite**.

CoFe₂O₄

FeCo₂U

Cations in tetrahedral sites are more prone to reduction with the respect to those in **octahedral sites**. Fe in cobaltite and Co in ferrite (cations A in AB_2O_4) are firstly totally reduced to metal phases. Before reaching the metal phases, **CoO** is formed in **cobaltite** and **FeO** is formed in **ferrite**.

Despite the **good reducibility of FeCo₂O₄** imparted by the high amount of cobalt, its performance in the production of hydrogen is quite poor due to an inefficient oxidation by **water steam**, which is able to oxidize only the outer shell of the nanoparticles. In contrast, a higher iron fraction makes the system more reversible, because in this case an intermediate iron wustite phase, which is a better oxygen buffer, can be stably formed.

Products formed at the beginning of the first step

Fe₃O₄: acetone (20%) NiFe₂O₄ : acetone (4%) CoFe₂O₄: acetaldehyde and dimethylether (11%) **CuFe₂O₄**: acetone (30%) MnFe₂O₄: acetone (27%) Cu_{0.5}Mn_{0.5}Fe₂O₄: acetone (40%) Cu_{0.5}Co_{0.5}Fe₂O₄: acetone (30%)

$\overline{\nabla}$

Chemical-loop ethanol reforming with **short-time cycles** in order to:

- Minimise coke formation during the first step
- Produce cleaner H₂ during the second step
- Obtain higher yield to products (other than CO, CO₂, H₂ and H₂O: fuel gas)
- Also: modify catalyst composition in order to address the formation of more valuable compounds (C4)

OPEX

energy (and

chemical)

industry

- In the **bio-refinery**, the production of both **bio-fuels** and **bio-chemicals** should be integrated
- By-products and co-products should also be valorised (close the cycle in the exploitation of raw materials, in the recovery and reuse of by-products and wastes: **Circular Economy**)
- Technologies should be designed in such a way to follow the Green Chemistry and Green Engineering rules CAPEX
- A **multifunctional approach**, in order to lower the number of steps in complex transformations
- In order to lower investment costs, adopt the **co-location principle**

Circulating molecules

ca 5 M tons/year

Other technologies by Metabolix, Novomer, Genomatica...

One-pot process (with a single catalyst)

HEXAGONAL TUNGSTEN BRONZES: W/V/O

Chieregato et al, **Appl. Catal. B**Chieregato et al, **ChemSusChem**Cespi et al, **Green Chemistry**Chieregato et al, **Coord Chem Rev**Soriano et al, **Topics Catal**Chieregato et al, **ChemSusChem**

Claudia Bandinelli Alessandro Chieregato

W1V0.2, T 318°C, feed 2% glycerol 4% oxygen, 54% steam

<u>Conditions</u>: 290 °C, Tau 0.4 s, feed: Gly-Ox-H₂O = 2-4-40 %mol

W-V-Nb-O Hexagonal Tungsten bronze (monophasic)

Catalyst	Acrolein Yield (%)	Acrylic Acid Yield (%)	Temperature (°C)	Residence Time (s)	Productivity (A+AA) $\frac{Kg}{L_{CT}*day}$	
W-V	10	26	300	0.38	4	Su
W-V-Nb	18	33	290	0.15	16	Su

Tests with oxygen

Surface area of W-V HTB: **20** m²/g Surface area of W-V-Nb HTB: **57** m²/g

- ✓ Sustainable feedstock;
- ✓ Solventless;
- ✓ H_2 efficiency = 100%;

Catalyst 3: 0.2%mol, NaOEt 20%mol, Additive: 1.5%mol.

Mazzoni et al, ACS Sustainable Chem. Eng. 2019

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In collaboration with the team of Valerio Zanotti Rita Mazzoni and coworkers

Giulia Pavarelli Aurora Caldarelli Francesco Puzzo

Pavarelli et al, ChemSusChem 2015, 8, 2250

(VO)₂P₂O₇ catalyst

V redox properties Surface acidity

Non è il possesso naturale delle materie prime che basta a dare la ricchezza, come non è il difetto delle stesse materie prime che produce la povertà: le uniche vere fonti capaci di dare ricchezze durature e di distribuirle nel mondo, annullandone le povertà, sono i commerci e gli scambi onesti di materie prime e di prodotti finiti, le industrie che consumano e che trasformano, i cervelli e le braccia che operano, gli uomini che fraternizzano e che collaborano.

MARIO GIACOMO LEVI, *L'industria chimica italiana e le possibilità del suo avvenire,* in "La chimica e l'industria", Milano, novembre-dicembre 1945, anno XXVII, nn. 11-12, pp. 189-195

It is not the possession of natural raw materials that is sufficient to give the richness, as is not the defect of the same raw materials that produces poverty: the only true sources capable of giving lasting riches and distributing them in the world, eliminating poverty, are the trade and honest exchanges of raw materials and finished products, the industries that consume and transform, the brains and the arms that work, the men who fraternize and work together Non è il possesso naturale delle materie prime che basta a dare la ricchezza, come non è il difetto delle stesse materie prime che produce la povertà: le uniche vere fonti capaci di dare ricchezze durature e di distribuirle nel mondo, annullandone le povertà, sono i commerci e gli scambi onesti di materie prime e di prodotti finiti, le industrie che consumano e che trasformano, i cervelli e le braccia che operano, gli uomini che fraternizzano e che collaborano.

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pp. 189-195 R. SCUOLA SUPERIORE DI CHIMICA INDUSTRIALE annessa alla R. Università ed alla R. Scuola d'Applicazione per gli ingegneri DI BOLOGNA

> ANNO I 1921-1922

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