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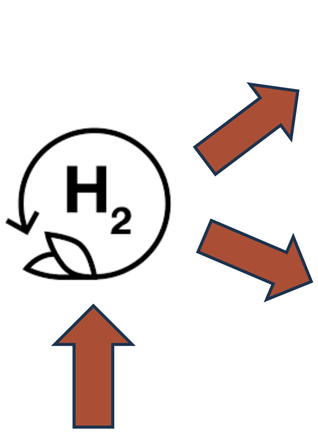
MDPI

Bimetallic and trimetallic catalysts for methanol steam reforming

Concetta Ruocco and Vincenzo Palma

Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy

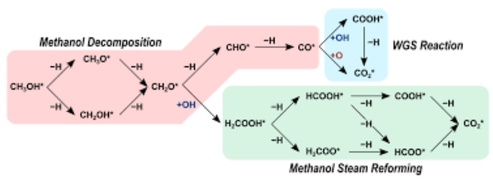
INTRODUCTION & AIM



CHEMICAL INDUSTRY

TRANSPORTS

STEAM REFORMING ROUTE $CH_3OH+H_2O \leftrightarrow CO_2+3H_2$



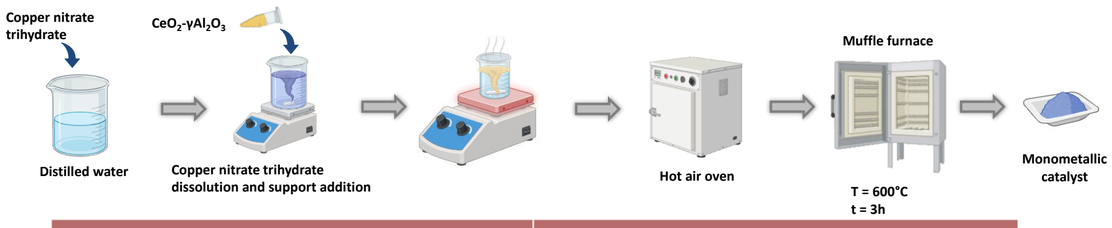
COMPLEX REACTION MECHANISM
Unwanted products[1] (COKE)

AIM: DEVELOPEMENT OF ACTIVE AND STABLE CATALYSTS

- PREPARATION & CHARACTERIZATION OF SEVERAL MONO-, BI- AND TRIMETALLIC CATALYSTS
- ACTIVITY EVALUATION FOR METHANOL STEAM REFORMING UNDER A S/C=1.5, P=1 bar AND T=200-600°C
- INVESTIGATION OF THE DURABILITY OF THE MOST ACTIVE FORMULATION

METHOD

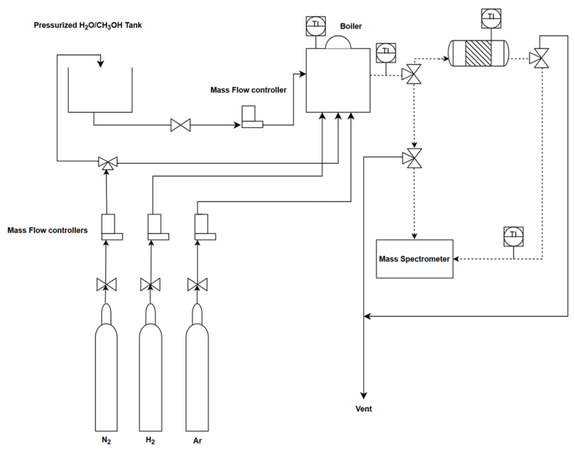
CATALYSTS PREPARATION: Cu/CeO_2-Al_2O_3



Non noble metal-based catalysts	Noble metal-based catalyst
$10Ni/CeO_2$-Al_2O_3	$2Pt$-$10Zn/CeO_2$-Al_2O_3
$20Cu/CeO_2$-Al_2O_3	$2Pt$-$10Ni/CeO_2$-Al_2O_3
$20Cu$-$10Ni/CeO_2$-Al_2O_3	$2Pd$-$10Zn/CeO_2$-Al_2O_3
$10Ni$-$20Cu/CeO_2$-Al_2O_3	$2Pd$-$10Ni/CeO_2$-Al_2O_3
$2Zn$-$10Ni$-$20Cu/CeO_2$-Al_2O_3	$2Pd$-$20Cu/CeO_2$-Al_2O_3

CATALYSTS CHARACTERIZATION: SURFACE AREA MEASUREMENTS (BET METHOD) & TEMPERATURE PROGRAMMED REDUCTION (TPR)

LABORATORY APPRATUS & PROCEDURES



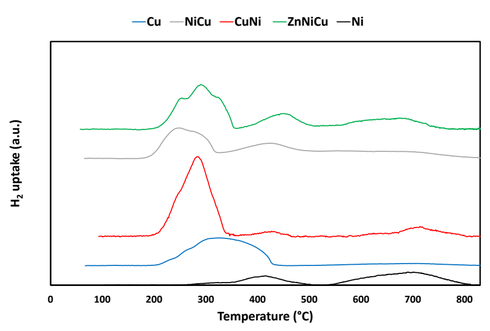
FIXED BED TUBULAR REACTOR

- Catalysts activation under a 5%H_2/Ar stream at 800°C for 1 h (TPR)
- Activity tests between 200 and 600°C under a S/C=1.5 and WHSV=2 h^{-1}
- Durability tests at 300°C for 20 h and carbon formation rate evaluation

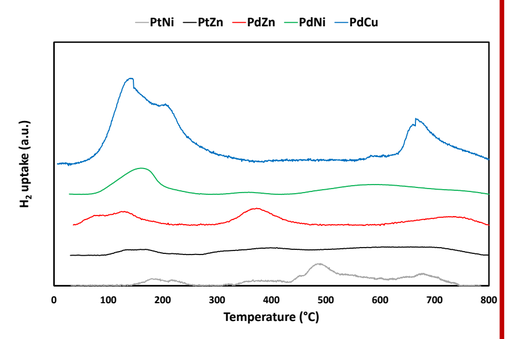
$$X = \frac{mol_{CH3OH,converted}}{mol_{CH3OH,fed}} \qquad Y = \frac{mol_{H2,produced}}{3 \cdot mol_{CH3OH,fed}}$$

RESULTS & DISCUSSION

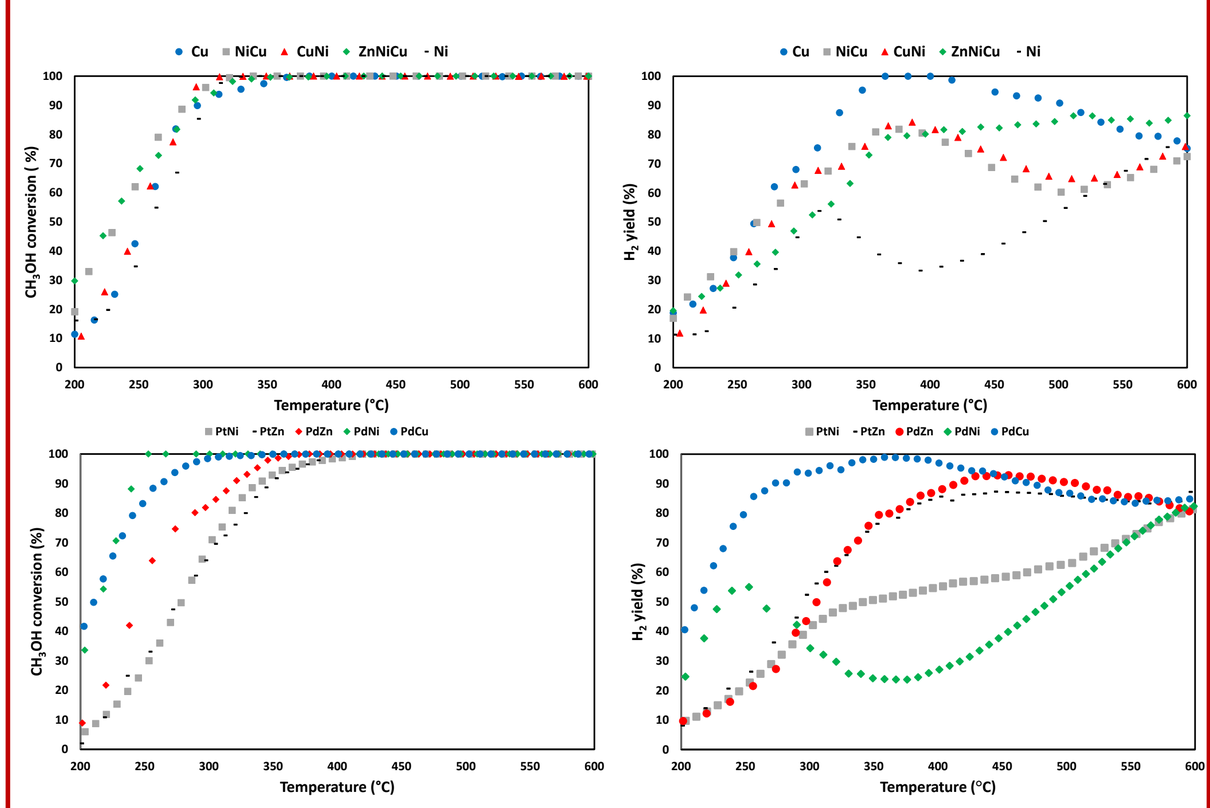
Sample	Symbol	Loading (wt %)	BET area ($m^2 \cdot g^{-1}$)	TH H_2 uptake ($\mu mol \cdot g_{cat}^{-1}$)	EXP H_2 uptake ($\mu mol \cdot g_{cat}^{-1}$)
Calcined Al_2O_3	-	-	136		
CeO_2-Al_2O_3	-	-	111		
Ni/CeO_2-Al_2O_3	Ni	Ni: 10	90	1702	1952
Cu/CeO_2-Al_2O_3	Cu	Cu: 20	78	3150	3645
Cu-Ni/CeO_2-Al_2O_3	CuNi	Ni:10 Cu:20	62	4853	5670
Ni-Cu/CeO_2-Al_2O_3	NiCu	Ni:10 Cu:20	64	4853	5594
Zn-Ni-Cu/CeO_2-Al_2O_3	ZnNiCu	Zn:2 Ni:10 Cu:20	57	5159	5719



Sample	Symbol	Loading (wt %)	BET area ($m^2 \cdot g^{-1}$)	TH H_2 uptake ($\mu mol \cdot g_{cat}^{-1}$)	EXP H_2 uptake ($\mu mol \cdot g_{cat}^{-1}$)
Pt-Zn/CeO_2-Al_2O_3	PtZn	Pt:2 Zn:10	79	1734	2004
Pt-Ni/CeO_2-Al_2O_3	PtNi	Pt:2 Ni:10	84	1909	2362
Pd-Zn/CeO_2-Al_2O_3	PdZn	Pd:2 Zn:10	79	1717	2189
Pd-Ni/CeO_2-Al_2O_3	PdNi	Pd:2 Ni:10	85	1891	2649
Pd-Cu/CeO_2-Al_2O_3	PdCu	Pd:2 Ni:Cu	75	3338	4339



Slight area reduction upon active species deposition; two reduction zones in TPR profiles and experimental (EXP) uptake higher than Theoretical (TH) one due to Ceria spillover[2,3]



Cu/CeO_2-Al_2O_3: best catalyst in the non-noble metals series
Pd-Cu/CeO_2-Al_2O_3: highest methanol conversion and hydrogen yield; rarely investigated in the recent literature[4]
STABILTY: only 5% reduction in methanol conversion and H_2 yield during 20 hours of time-on-stream, with final values of X=95% and Y=88%; coke content of 1.5%, very low compared to the values reported for other Cu/Al_2O_3 catalysts[5,6]

CONCLUSION

- Among the tested active species (Ni, Cu, Pt, Pd, Zn), highest performances recorded over the 2wt%Pd-10wt%Cu/CeO_2-Al_2O_3 catalysts, rarely investigated in the recent literature
- Almost complete conversion up to 300°C andH_2 yield higher than 90%
- Promising durability performances at 300°C, with only 5% activity loss and coke yield of 1.5%

REFERENCES

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[2] I. Luisetto et al., Appl. Cat. A. Gen., 2015, 50, 12-22.
[3] K. Van der Borght et al., Catalysts, 5, 2015, 1948-1968.
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[5] O. Tajrishi et al. Int. J. Hydrogen Energ., 43, 2018, 14103-14120.
[6] S. Bepari et al., Top. Catal., 66, 2023, 375-392.