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Unexpected Catalytic Performance of Cu-Ni Bimetallic Catalysts in Hydrogen-Free In-Situ Glycerol Hydrogenolysis: A Failed Attempt Toward 1,2-Propenediol Production

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This work reports an unsuccessful attempt to develop Cu–Ni bimetallic catalysts for hydrogen-free in-situ glycerol hydrogenolysis to 1,2-propanediol (1,2-PDO). Based on the known strengths of monometallic Cu (high 1,2-PDO selectivity under external H_2) and monometallic Ni (in-situ hydrogen production via glycerol reforming), a series of Cu–Ni/Al_2O_3 catalysts with varying Cu/Ni mass ratios and Ni-based catalysts modified with different promoters (Y, La, Ce, Cu) were evaluated under identical hydrogen-free conditions.were prepared and evaluated under identical hydrogen-free conditions. Contrary to the expected synergistic effect, the bimetallic catalysts delivered inferior performance compared to monometallic Ni/Al_2O_3: glycerol conversion decreased significantly with increasing Cu content, and 1,2-PDO selectivity was suppressed in all bimetallic formulations. Instead, the reaction shifted toward undesired C–C cleavage and formation of acetol and light oxygenates.

KEYWORDS: Glycerol; 1,2-propanediol; in-situ hydrogenolysis; Cu-Ni bimetallic

1 Introduction

Biodiesel production generates large quantities of crude glycerol as a low-value by-product, creating an urgent need for sustainable valorization routes[1-2]. Catalytic hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) is one of the most promising pathways[3-4], but conventional processes rely on high-pressure external H_2, which increases cost and safety risks. Hydrogen-free in-situ hydrogenolysis, which utilizes hydrogen produced in situ via glycerol reforming, is therefore an attractive alternative[5-7].

Monometallic Cu catalysts are widely known for their high selectivity to 1,2-PDO under external H_2, due to their ability to promote C–O bond cleavage while minimizing C–C bond scission[8-9]. Monometallic Ni catalysts, by contrast, exhibit high activity for glycerol reforming and C–C cleavage, producing H_2 but low 1,2-PDO selectivity[10-11]. It was hypothesized that combining Cu and Ni into a

bimetallic catalyst would allow Ni to provide in-situ H_2 while Cu directs the reaction toward selective hydrogenolysis to 1,2-PDO.

In this work, we prepared two series of catalysts: (1) Cu–Ni/Al_2O_3 with varying Cu/Ni mass ratios (Cu_2Ni_1, Cu_1Ni_1, Cu_1Ni_2, Cu_1Ni_4, monometallic Ni/Al_2O_3); and (2) Ni-based catalysts modified with promoters (Y, La, Ce, Cu) on γ-Al_2O_3. The only data collected were conversion, liquid product selectivity, and gas phase distribution, presented here without additional characterization, to emphasize the unexpected and unambiguous failure of the bimetallic strategy.

2 Materials and Methods

Catalyst Preparation

All catalysts were prepared by incipient wetness impregnation of γ-Al_2O_3 support with aqueous solutions of metal nitrates, with Ni metal loading fixed at 10 wt%. The Cu/Ni mass ratios were adjusted to 2:1, 1:1, 1:2, 1:4, and 0:1 (monometallic Ni). After impregnation, the samples were dried at 100 °C for 12 h, calcined at 450 °C for 3 h, and reduced in H_2 flow at 700 °C for 3 h before reaction.

Catalytic Reaction and Product Analysis

Glycerol in-situ hydrogenolysis was carried out in a batch reactor. 0.2 g of catalyst, 3 g of 20 wt% glycerol aqueous solution were charged into the reactor. The system was purged with N_2 three times to remove air, then heated to 230 °C under autogenous pressure, and held for 10 h with stirring at 500 rpm. Liquid products were analyzed by gas chromatography (GC) with a flame ionization detector (FID), using a capillary column suitable for oxygenate separation. Glycerol conversion and product selectivities were calculated based on carbon balance.

The total glycerol conversion was calculated as follows:

$$Conversion\ (\%) = \frac{moles\ of\ C_3H_8O_3\ consumed}{initial\ moles\ of\ C_3H_8O_3} \times 100 \quad (1)$$

The selectivity of product was calculated as follows:

$$Selectivity\ (\%) = \frac{moles\ of\ specific\ product}{moles\ of\ C_3H_8O_3\ consumed} \times 100 \quad (2)$$

3 Result and Discussion

3.1 Effect of Cu/Ni Mass Ratio on Catalytic Performance

The performance of catalysts of the different loading ratios is summarized in Figure 1 and Table 1. Monometallic Ni/Al_2O_3 achieved the highest conversion (>95%), consistent with its known high activity for glycerol reforming (no shown). As Cu content increased (moving from Ni/Al_2O_3 to Cu_1Ni_4/Al_2O_3, Cu_1Ni_2/Al_2O_3, Cu_1Ni_1/Al_2O_3, and Cu_2Ni_1/Al_2O_3), glycerol conversion decreased

progressively to ~46%. There was no evidence of enhanced activity in any bimetallic formulation; all Cu-containing catalysts showed lower conversion than monometallic Ni/Al_2O_3. As for 1,2-PDO selectivity: Peaked at ~60% for Ni/Al_2O_3, and decreased significantly as Cu content increased. For Cu_2Ni_1/Al_2O_3, 1,2-PDO selectivity was ~42%, representing a substantial drop from the monometallic Ni baseline.

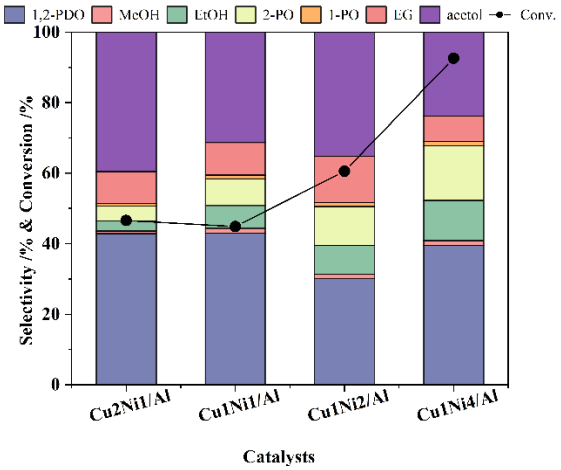

Figure 1. Activity and selectivity of glycerol in-situ hydrogenolysis over the different $Cu-Ni/Al_2O_3$ catalysts

Table 1. Activity and selectivity of glycerol in-situ hydrogenolysis over the different $Cu-Ni/Al_2O_3$ catalysts

Catalysts	Conv. / %	C_{Liquid} / %	Yield /%	Sel. / %						
				1,2-PDO	Acetol	1-PO	2-PO	MeOH	EtOH	EG
Cu2Ni1/Al	65.06	6.24	2.35	37.64	37.80	0.98	6.13	1.01	4.23	12.22
Cu1Ni1/Al	58.65	5.96	2.35	39.42	39.90	0.68	2.35	2.19	6.62	8.84
Cu1Ni2/Al	60.54	7.77	2.33	30.05	35.20	1.11	11.04	1.34	8.13	13.12
Cu1Ni4/Al	92.55	18.53	7.32	39.50	23.78	1.21	15.57	1.36	11.38	7.21

3.2 Effect of Different Promoters on Ni-Based Catalysts

To further investigate the performance gap between monometallic Ni and Cu-containing systems, we evaluated a series of Ni-based catalysts modified with different promoters (Y, La, Ce, and Cu) on γ-Al_2O_3. The full reaction data are presented in Figure 2(a) and 2(b), which allows a direct comparison of how different additives affect both glycerol conversion, liquid product distribution, and gas-phase reforming activity.

Figure 2a and 2b show liquid and gas product distribution of Ni-based catalysts modified with Y, La,

Ce and Cu. Ni-Y, Ni-La and Ni-Ce catalysts kept high glycerol conversion above 95%. Ethanol was the main liquid product and 1,2-PDO selectivity remained at a low level. Acetol was almost negligible on these rare-earth promoted samples.

Ni-Cu catalyst showed lower conversion about 60%. Acetol became the dominant liquid product and 1,2-PDO selectivity was only about 40%. The gas products of Ni-Y and Ni-La were mainly CO_2 and CH_4, which indicated effective glycerol reforming. Ni-Ce and Ni-Cu samples produced more C_2H_6 and higher total gas yield. Hydrogen selectivity was very low in all samples, especially on Ni-Cu catalyst. The lowest hydrogen production corresponded to the highest acetol selectivity.

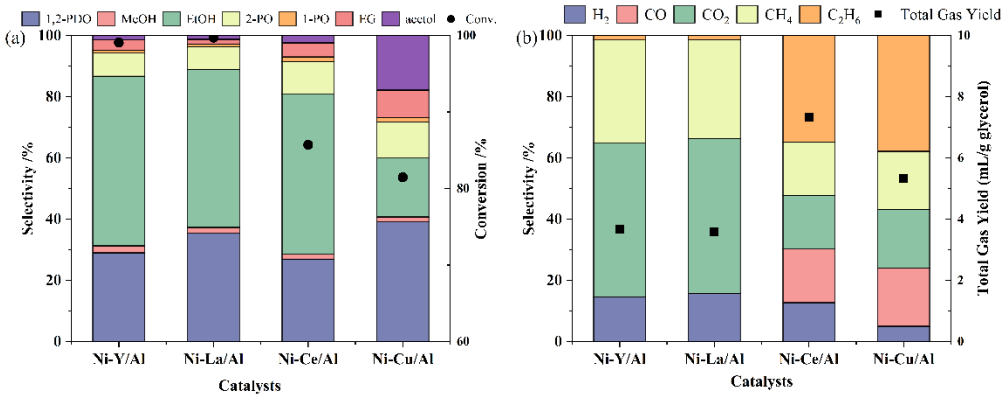

Figure 2. Activity and selectivity of glycerol in-situ hydrogenolysis over the different promoters (Y, La, Ce, and Cu) on Ni/Al_2O_3 catalysts

Table 2. Gas product distribution over the different promoters (Y, La, Ce, and Cu) on Ni/Al_2O_3 catalysts

Catalysts	Total Gas Yield. / ml g^{-1} gly.	Sel. / %				
		H_2	CO	CO_2	CH_4	C_2H_6
Ni-Y/Al	3.66	14.48	0.09	50.21	33.77	1.45
Ni-La/Al	3.58	15.65	0.10	50.58	32.30	1.37
Ni-Ce/Al	7.33	12.73	17.54	17.54	17.43	34.76
Ni-Cu/Al	5.34	4.97	19.10	19.10	18.98	37.85

Discussion

Combined with all activity data, we can explain why the Cu–Ni bimetallic strategy failed completely. Cu significantly suppressed the reforming ability of Ni and reduced in-situ hydrogen production. Without enough hydrogen, Cu sites could not convert acetol into 1,2- PDO, so acetol accumulated in large quantities. The desired synergistic effect did not appear at all.

Rare-earth promoters could maintain high glycerol conversion but shifted the reaction path to C–C bond cleavage and ethanol formation. They could not improve 1,2-PDO selectivity either. The high

selectivity of Cu to 1,2- PDO reported under external hydrogen is not suitable for hydrogen-free in-situ system. The reaction environment and hydrogen supply mode are totally different, leading to completely different catalytic behavior.

We have no further characterization data to support structural analysis. But the catalytic performance itself is enough to prove that our initial design was unreasonable. Simply combining Cu and Ni cannot achieve efficient hydrogen-free glycerol conversion to 1,2- PDO.

4 Conclusion

This work reports the failed attempt of Cu–Ni bimetallic catalysts for hydrogen-free in-situ glycerol conversion. Monometallic Ni catalyst shows better performance than all Cu–Ni bimetallic samples. Adding Cu reduces both glycerol conversion and 1,2-PDO selectivity. Rare-earth promoters cannot balance activity and target product selectivity either. No expected synergistic effect is observed in any bimetallic catalyst.

These results remind researchers not to rely too much on hypothetical synergy without sufficient experimental verification, especially when transferring catalytic systems between different reaction atmospheres. Publishing negative results like this can help other researchers avoid similar mistakes in catalyst design for hydrogen-free glycerol valorization.

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