Interface-Promoted Dehydrogenation and Water-Gas Shift toward High-Efficient H_2 Production from Aqueous Phase Reforming of Cellulose

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Abstract: Hydrogen production from cellulose via aqueous phase reforming (APR) has aroused increasing attention, but its efficiency remains challenging. Here, we report an interface-promoted Ni particle catalyst, in which Ni particles are distributed on the surface of layered double oxide (LDO) in narrow size and form abundant Ni-support interfaces and interfacial interactions. The Ni-LDO interfaces and interfacial interactions are enhanced by preparing the LDO-supported Ni from in situ reduction of Ni-containing Mg/Al layered double hydroxides (LDHs). A H_2 production activity of up to 40.8 mmol•$g_{catal}^{-1}g_{cellulose}^{-1}h^{-1}$ with a H_2 yield of up to 30.9 % was achieved.

Keywords: hydrogen production, supported Ni particles, interfacial promotion.

1. Introduction

Hydrogen is identified as the energy of twenty-first century because it possesses highly calorific value and affords a clean combustion.[1] Almost 96 % of H_2 has been produced from fossil resources and 3.9 % from electrolysis of water till now.[2] H_2 production from renewable cellulose via aqueous phase reforming (APR) has aroused increasing attention due to its mild reaction conditions and low CO concentration in products.[3, 4] Although impressive progress has been achieved in the development of efficient catalyst and/or catalytic system for APR H_2 production, its efficiency remains challenging. Here we report a highly-efficient and stable APR catalyst for H_2 production from cellulose, where Ni nanoparticles uniformly dispersed on layered double oxides (LDO). And the LDO is supposed to serve simultaneously as a solid base to cooperate with supported Ni. The strong interfacial interactions between Ni particles and LDO facilitate both of dehydrogenation and WGS reactions, affording a H_2 production activity and a H_2 yield higher than reported so far. The LDO-supported Ni also demonstrated good stability in the APR.

2. Experimental

The NiMgAl-LDHs and MgAl-LDHs were synthesized by the co-precipitation method. For comparison,[5] Ni^{2+}/MgAl-LDHs with various Mg/Al molar ratio were prepared by incipient wetness impregnation of MgAl-LDHs with Ni^{2+} solution. Then the NiMgAl-LDHs was reduced under H_2 flow. All catalysts investigated in this study were with Ni loading of 20 wt%. The catalytic materials were characterized by XRD, TEM, STEM, CO_2-TPD, and quasi in-situ XPS.

The catalytic testing was performed in a homemade batch reactor with a mechanical stirrer. The products were detected with a Chromategraph (GC) equipped with TCD detector.

3. Results and discussion

The LDO-supported Ni particle catalysts were applied as the catalysts for catalytic H_2 production from cellulose. The H_2 production activity and H_2 yield are clearly observed to increase with increasing amount of medium-strong and strong base sites, indicating a possible promotion of surface basic sites on the H_2 production. Almost no H_2 production activity and H_2 yield were observed over Mg_3Al-LDO containing almost the same base sites as the Ni/Mg_3Al-LDO, indicative of the dominating catalysis of Ni particles in the APR of cellulose. But it is interesting that higher H_2 production activity and H_2 yield achieved over Ni-Mg_3Al-LDO than over all the supported Ni catalysts with Ni-loaded by impregnation, while the amount of medium-strong and strong base sites on Ni-Mg_3Al-LDO is less than that on Ni/Mg_4Al-LDO or Ni/Mg_5Al-

LDO. This interesting result suggests that the basic sites promoted the H_2 production on Ni sites, which is consistent with the observations that the Ni-LDO interfaces are more abundant and the Ni-LDO interfacial interaction is stronger in Ni-Mg3Al-LDO observed in the quasi in-situ XPS analysis.

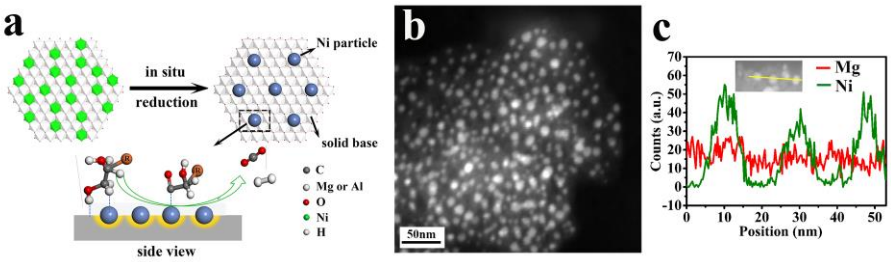

Figure 1. (a) Schematic illustration for the preparation of Ni particles supported on LDO from LDHs precursor and the catalytic mechanism of the APR process of oxygenated hydrocarbons for H_2 producing. (b) HAADF image and (c) line scan profiles of Mg and Ni elemental distribution for Ni-Mg_3Al-LDO.

Table 1. The catalytic evaluations toward H_2 production from APR of cellulose over Ni nanoparticle supported on solid base supports prepared by LDHs precursors or initial wetness impregnation method.[a]

Entry	Catalyst	Solid base sites /(mmol CO_2/g)		Activity of H_2 / mmol /mmol$_{\text{surface Ni}}$	Yield of H_2/ %
		Medium-strong	strong		
1	Ni/Mg_2Al-LDO	0.33	0.42	232.5 (225.2)	19.1 (18.5)
2	Ni/Mg_3Al-LDO	0.63	0.34	310.9 (305.1)	24.9 (24.4)
3	Ni/Mg_4Al-LDO	0.59	0.57	384.5(381.8)	28.9 (28.7)
4	Ni/Mg_5Al-LDO	0.48	0.54	338.7 (341.4)	26.7 (26.9)
5	Mg_3Al-LDO	0.59	0.39	9.5(10.1)	1.8 (1.9)
6	Ni-Mg_3Al-LDO	0.74	0.26	396.7 (399.1)	30.9 (31.1)

[a] Conditions: cellulose 1.0 g, catalysts 140 mg, initial pressure 0.4 MPa N_2 (30 °C), T = 260 °C, 50 mL H_2O.

4. Conclusions

In summary, interface-promoted Ni catalyst has been developed in this work for the H_2 production directly from the real biomass cellulose. This interface-abundant structure was achieved through the in situ topological transformation of Ni containing Mg/Al-LDHs precursor. 40.8 mmol•$g_{\text{catal}}^{-1}g_{\text{cellulose}}^{-1}h^{-1}$ with a H_2 yield of up to 30.9 % was achieved and the yield for H_2 production only decrease by 9 % even in fifth run,, showing superior performance to the catalysts reported so far.

References

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