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Program Title (English) : Research of the strong metal-support interaction involving low melting point metals in reverse water gas shift reaction
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1. Summary

For the loaded NPs, we found that the liquid metals can form metal-oxygen bonds from the support even at room temperature. At high temperatures, the diffusion of liquid metals can cause the formation of Intermetallic compounds, the real active species for CO_2 hydrogenation. The catalysts can achieve over 99% CO conversion and enhanced CO yields under reaction conditions. The transformation process and structural changes of catalysts can be characterized by XAFS.

2. Experimental

Experimental conditions and beamtime:

1. X-ray energy calibration of Ni K-edge using Si 111 monochromator and In K-edge using Si 311 monochromator.
2. Chamber set-up and gas system set-up.
3. Edge jump check and sample preparation.
4. For In and Ni *K*-edge of In/NiO before and after calcination under Ar atmosphere: XAFS measurements at RT and 350 ºC under Ar atmosphere.
5. For In and Ni *K*-edge of samples (including In/NiO, In/NiO-T catalysts) under CO_2/H_2 atmosphere at 400 ºC:

(1) Warming process: 0.5 h
(2) Cooling to 50 ºC: 0.5 h
(3) XAFS measurement at 450 ºC. Conduct six consecutive tests.

3. Results and Discussion

The coordination structures of In species before and after calcination under Ar atmosphere were further compared by XAFS. The In *K*-edge EXAFS spectrum of In/NiO revealed the presence of In-O bonds (Fig. 1a), suggesting that In maybe extracted lattice oxygen from the NiO surface during preparation. Notably, the In-O bond length in the In/NiO catalyst was shorter than that of standard In_2O_3, and no characteristic peaks attributed to the In-O-In bond were observed within the 2-4 Å range, demonstrating that the In atoms were randomly dispersed on the NiO surface and bonded with oxygen atoms. Compared to In/NiO, In/NiO-T exhibited the decreased In-O peak intensity and shortened In-O bond length in the EXAFS spectra, implying a reduced average In-O coordination number and potentially stronger confinement of In atoms within the NiO crystal structure after calcination. Additionally, according to Ni *K*-edge EXAFS spectra of In/NiO and In/NiO-T, the average Ni-O coordination number of In/NiO-T maintained stable after calcination, indicating that metallic In primarily affected the NiO surface structure (Fig. 1b). Thus, metal In can be uniformly dispersed on the NiO surface through melting, migration and bonding, forming abundant In/NiO interfaces.

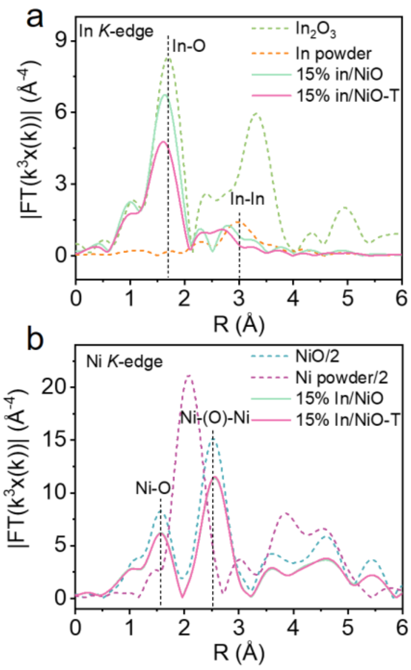

Fig. 1 (a) In K-edge and (b) Ni K-edge EXAFS spectra of 15%In/NiO and 15%In/NiO-T.

To probe the hyperfine structure of In and Ni species in In/NiO-T catalyst during the reaction, in-situ XAFS measurements were performed at 400 °C under CO_2/H_2 atmosphere. According to the In K-edge EXAFS spectra (Fig. 2a), the In-O bond disappeared rapidly, and a new peak appeared at 2.2 Å, which could be attributed to the formation of In-Ni bonds based on our XRD results. Subsequently, Ni K-edge EXAFS spectra of NiO and In/NiO-T catalysts showed a progressive decrease in the Ni-O-Ni peak intensity and a corresponding increase in the Ni-Ni peak intensity, suggesting the reduction of NiO to metallic Ni (Fig. 2b, 2c).

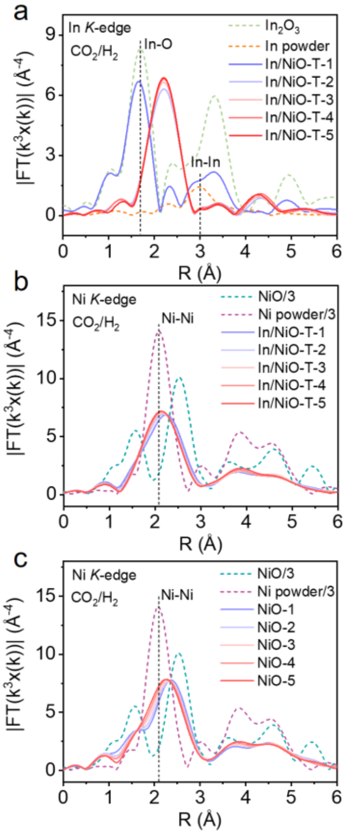

Fig. 2 (a) In situ In K-edge EXAFS spectra of In/NiO-T. In situ Ni K-edge EXAFS spectra of (b) In/NiO-T and (c) NiO. (Reaction conditions: CO_2:H_2=1:3, 80 mL/min, P = 0.1 MPa, 400 °C).

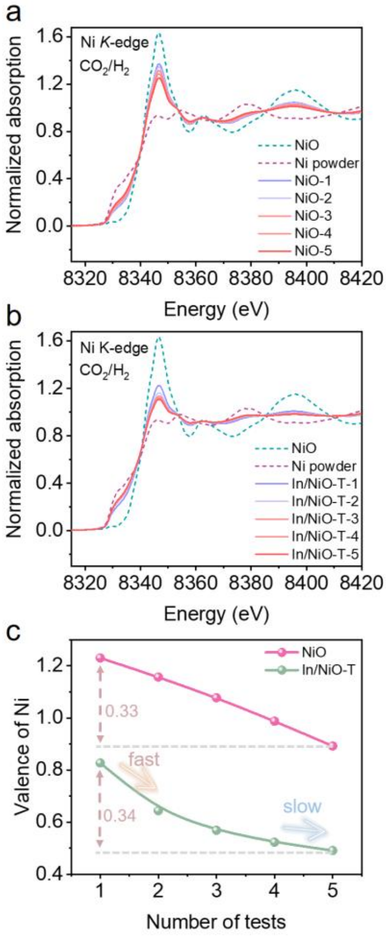

Fig. 3 In situ Ni *K*-edge XANES spectra of (a) NiO and (b) In/NiO-T at 400 °C under CO_2/H_2 atmosphere. (c) The Ni valence change during the reaction determined by XANES linear combination fitting.

By fitting the XANES spectra to track the change in the average valence state of Ni over time, the reduction rate of NiO in the In/NiO-T catalyst was initially rapid but then slowed, whereas the reduction rate of pristine NiO remained stable (Fig. 3). This disparity may be attributed to the inductive effect of In species, which extracted lattice oxygen from the NiO surface, accelerating its reduction process. The generated In-O-Ni bonds exhibited higher lattice oxygen stability than Ni-O-Ni bonds. Consequently, the In-O-Ni bonds may inhibit the full reduction of NiO, affecting the generation of active hydrogen species and mitigating the over-hydrogenation of CO.