Project Number : 2024B-E18

Program Title (English) : Indium-Induced Surface Reconstruction of NiO Significantly Enhances Reverse Water Gas Shift Reaction Performance

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Key words : Liquid metal, Transition metal oxides, Reverse Water Gas Shift Reaction, Strong metal-support interaction

1. Summary

This experiments aims to reveal the Strong metal-support interaction (SMSI) between liquid metal nanoparticles (LM NPs) and transion metal oxides (TMO). Through our lab XRD data insitu DRFTS, we found that In NPs can extract the O from NiO even at room temperature. With increasing temperature, the In will change into In2O3 under Ar atomsphere and InNi3C0.5 under CO2+H2 atomshpere, which change the reaction pathway of NiO. Our catalytic performance shows that NiO produce CH4 only and In NPs doesnot have any activity. While In/NiO showed high activity and selectivity for CO production. Such phenonmenon is across multi LM-TMO systems. In this proposal, we would like to check the In K-edge and Ni/Fe K-edge change under different atomsphere with varied temperatures.

2. Experimental

Prepare pellets: In, NiO, In/NiO, Fe2O3, In/Fe2O3

[1] In, Ni and Fe K-edge under Ar atmosphere in from RT 300 oC, collecting samples every 50oC

[2] In, Ni and Fe K-edge under H2/He atmosphere in from250oC to 500 oC, collecting samples every 50oC

[3] In, Ni and Fe K-edge under CO2/He atmosphere in from250oC to 500 oC, collecting samples every 50oC

3. Results and Discussion

The In *K*-edge EXAFS spectrum of In/NiO showed In-O bonds at 1.63 Å (Fig. 1b), confirming that In extracted lattice oxygen from the NiO surface during preparation, consistent with the XRD results（Fig.1a）. Notably, compared to standard In_2O_3, the In/NiO catalyst had shorter In-O bond length, and lacked characteristic In-O-In bonds in the 2-4 Å range, indicating the absence of long-range order of the surface In-O species. After thermal treatment, In/NiO-T exhibited both decreased In-O peak intensity and shortened In-O bond length. Furthermore, Ni *K*-edge EXAFS spectra showed that the In/NiO-T maintained a stable average Ni-O coordination number after calcination, indicating that metallic In primarily affected the NiO surface structure rather than its bulk properties (Fig. 1c).

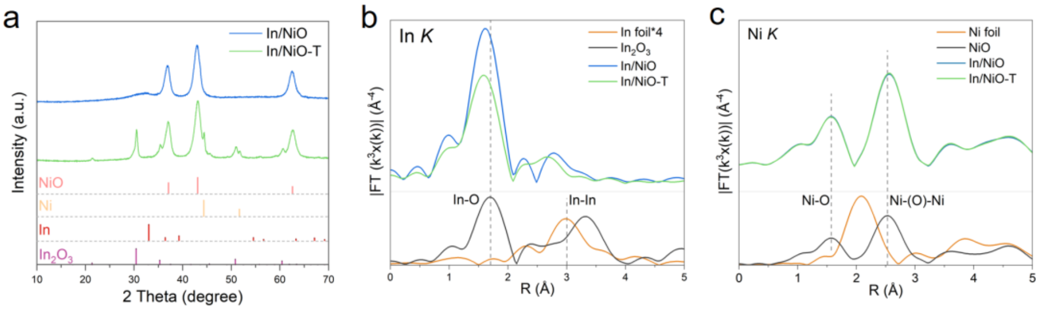

Fig. 1. (A) XRD patterns of 15% In/NiO and 15% In/NiO-T samples. -T indicated that the catalysts were calcined under Ar atmosphere at 350 ℃ for 2 h. **(B)** Fourier-transformed k^3-weighted In *K*-edge and **(C)** Ni *K*-edge EXAFS spectra of In/NiO and In/NiO-T, respectively.

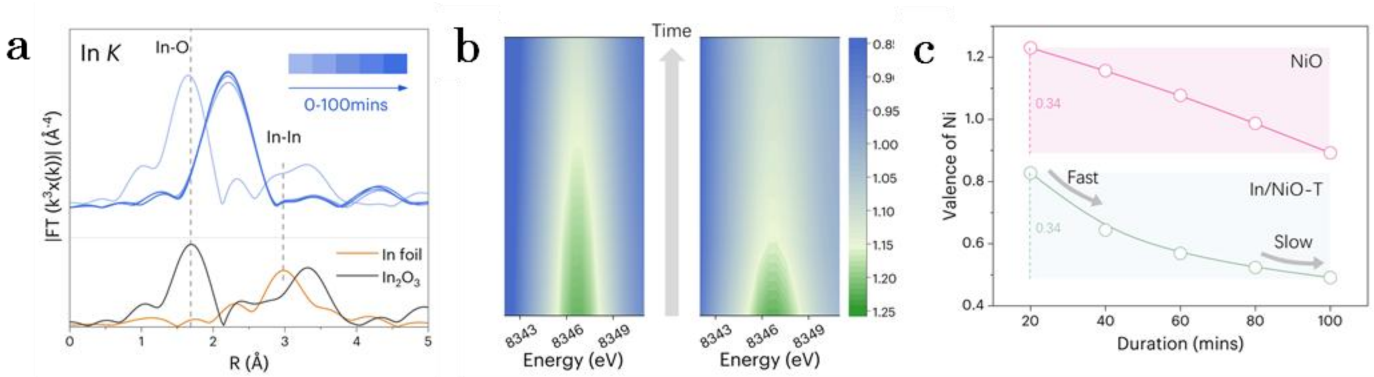

Fig.2. **(a)** *In-situ* In *K*-edge EXAFS spectra of In/NiO-T at 400 ^{o}C under CO_2/H_2 atmosphere. **(b)** Part of *in-situ* Ni *K*-edge XANES spectra over time at 400 ^{o}C under CO_2/H_2 atmosphere. The numbers of the color bar are white line intensity of XANES spectra. **(c)** The Ni valence change during the reaction determined by XANES linear combination fitting.

In *K*-edge EXAFS spectra of In/NiO-T (Fig. 2a) showed rapidly disappearance of the In-O bond and emergence of a new peak at 2.2 Å, attributable to metallic In-Ni bonds based on XRD results. XANES spectra fitting, used to track the average valence state of Ni change over time, revealed distinct reduction patterns: In/NiO-T catalyst showed rapid initial NiO reduction that later slowed, while pristine NiO maintained a steady reduction rate (Fig. 2b, 2c). This disparity likely stemmed from the inductive effect of In species-In atoms extracted lattice oxygen from the NiO surface, accelerating initial reduction process.

4. Others

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