CO temperature-programmed desorption of hexameric copper hydride nanoclusters catalyst supported on functionalized MWCNTs for kinetics study of low-temperature water-gas shift

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Highlights
- CO-TPD provides means to hypothesize catalytic activity.
- Cu nanoclusters/MWCNTs is hypothetically active for LTWGS.
- LTWGS over Cu nanoclusters/MWCNTs could satisfy LH and surface redox mechanisms.

1. Introduction
A novel catalyst made of crystallized hexameric copper hydride nanoclusters (Cu₆) ligated with triphenylphosphine [(PPh₃)CuH]₆ deposited on functionalized multi-walled carbon nanotubes (MWCNTs) support is synthesized for a catalytic activity investigation in low-temperature water-gas shift (LTWGS) reaction. CO temperature-programmed desorption (CO-TPD) technique is employed to analyse the strength of the CO interaction with the catalyst surface, indicated by the CO desorption peak temperatures (lower temperature peak; weaker site and vice versa) and the breadth of the peak shoulders (broader shoulder; stronger site and vice versa). An actual LTWGS reaction run over the synthesized catalysts will be conducted to evaluate their actual performance based on CO conversion for the reaction kinetic study. The rate of reaction based on the catalyst sample that gives the highest CO conversion based on turnover frequency will be developed based on the expression derived from Moe or power-law model. A comparison of the activation energy value from the optimal catalyst developed in this work with the experimentally determined values from literature will be made. The overall finding will conclude if the LTWGS over the optimal Cu/MWCNTs catalyst follows regenerative/surface redox or Langmuir-Hinshelwood (LH) mechanism.

2. Methods
The MWCNTs support (used as purchased) was functionalized by acid reflux treatment using 3:1 volume ratio of H₂SO₄ (98%): HNO₃ (62%) as the oxidizing agent at 80 °C for 0.5 hr [1]. A further purification step was introduced post the acid-reflux treatment by performing an air oxidation at 550 °C for 10 minutes [2], at a ramping rate of 10.6 °C/min from the ambient condition.

The Cu₆ nanoclusters were synthesized by preparing a colloid of copper (I) chloride and PPh₃ in dry tetrahydrofuran ((CH₂)₄O = THF) under argon at ambient temperature [3]. The crystallized Cu₆ nanoclusters were deposited on the functionalized and purified MWCNTs by an overnight wet impregnation at varied copper loading content (between 0.5 and 15 wt.%), and the samples were then vacuum-dried. Techniques such as CO chemisorption, CO-TPD and powder X-ray diffraction (XRD) were employed to measure the copper dispersion and crystallite size, and to characterize the surface chemistry of the synthesized catalysts in order to hypothesize their performance in the LTWGS reaction.

The optimal copper loading was identified to be 1% based on the copper dispersion and particle size. This information was used to fix the Cu₆ nanoclusters content on pristine MWCNTs and alumina in order to study the effect of the copper interaction with the non-functionalized MWCNTs and a different type of support, and the loading content was also fixed on the sample of copper nanoparticles prepared using copper (II) chloride dihydrate salt dissolved in water and methanol on the treated MWCNTs, to examine the effect of different copper nanostructures. The copper nanoparticles catalyst samples underwent a calcination step in nitrogen flow at 400 °C post wet impregnation and drying.
3. Results and discussion

The acid-reflux functionalization effectively modified the degree of the MWCNTs’ surface hydrophobicity in polar solvents based on dispersion and suspension stability test, and increased the negative surface charge of the support in water dispersant from $-12.36$ to $-51.47$ mV based on zeta potential measurement. The purification by air oxidation removed the thermally less stable carbonaceous components through combustion and left behind only the crystallized, well-graphitized, stable functionalized MWCNTs. The purification however removed the carbon components that are of higher negative surface charge, and resulted in the zeta potential to increase to $-24.42$ mV. Single crystal X-ray diffraction (XRD) revealed a crystallized nanoclusters of an overall empirical formula of $[(\text{PPh}_3)\text{CuH}]_6\text{THF}$, which was further confirmed by thermogravimetric analysis that indicated the decomposition of the THF molecule (3.5% weight loss) at a temperature of slightly below 100 °C followed by the removal of the PPh$_3$ ligand in the temperature range of 150 to 260 °C (74.9% weight loss).

The measurements by pulse CO chemisorption at 50 °C in general showed an increasing copper crystallite size and a reducing copper dispersion in the direction of increasing copper loading content, increasing pretreatment temperature, and increasing pretreatment duration. Referring to Figure 1, the CO-TPD spectrum of 1 wt.% Cu$_6$ on functionalized MWCNTs showed a small shoulder, low peak at 120 °C; and a broader, higher peak at 250 °C. The desorption peak at the lower temperature indicates a weak interaction between CO and this active site. Hypothetically, this peak could be assigned to the first step of LH mechanism model where CO is adsorbed on the active site’s surface ($\text{CO} + \text{S} \leftrightarrow \text{CO–S}$) without undergoing dissociation into C and O, or the second step in redox mechanism where CO is surface-oxidized with the adsorbed-oxygen ($\text{CO} + \text{O–S} \leftrightarrow \text{CO}_2 + \text{S}$) produced from water molecule surface-dissociation in the first step ($\text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2 + \text{O–S}$) [4 – 5]. The second peak at the higher temperature could be assigned to a stronger interaction between CO and the active site containing surface oxygen grafted on MWCNTs by acid-functionalization, as this peak was also present in the bare functionalized MWCNTs. At this moment, we are not able to determine if this second peak indicates desorption of CO or CO$_2$. A H$_2$ temperature-programmed reduction on the bare functionalized MWCNTs will be performed to determine if the oxygen-moiety groups created an active site for CO adsorption, or were reactive in the reaction environment.

![Figure 1. CO-TPD of 1%Cu/MWCNTs and bare functionalized MWCNTs.](image)

4. Conclusions

The catalysts prepared in this work are hypothetically active for LTWGS. An actual LTWGS reaction run over the synthesized catalysts will be conducted to evaluate their actual performance based on CO conversion at varied operating conditions for the reaction kinetic study.

References


Keywords

chemisorption; copper nanoclusters; reaction mechanism; water-gas shift.