2D Polymeric Network of Cu/Na, A Route for the Preparation Truncated Octahedral Catalyst Applicable in the WGS Reaction

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Research Article

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Abstract

A 2D heterometallic copper(II)–sodium(I) complex based on pyridine 2,6-dicarboxylato (dipic$^{2-}$) formulated as [Cu(μ-dipic)$_2$(Na$_2$(μ-H$_2$O)$_4$)$_n$. 2nH$_2$O (1) has been synthesized. Thermal stability of complex 1 was studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). Single-crystal X-ray diffraction (SC-XRD) analysis showed that the parallelepiped colorless crystal of complex 1 crystallizes in a monoclinic system with the space group P2/c. A highly dispersed truncated octahedral catalyst formulated as Cu-Na/Al$_2$O$_3$ (CNM) was prepared by thermal decomposition of complex 1. Besides, the reference catalyst of Cu-Na/Al$_2$O$_3$ (CNR) was prepared by impregnation conventional method. The catalysts were examined by FT-IR, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area, and subjected to water-gas shift (WGS) reaction in the temperature range of 150-400 °C. The catalysts showed strong surface structure-activity dependence in WGS reaction. Improved catalytic performance during the water-gas shift reaction was observed for CNM compared to CNR due to its high dispersion, smaller particle size, and higher BET specific surface area.

1. Introduction

The coordination compounds have been extensively studied due to their potential applications such as heterogeneous catalyst for photo-Fenton reaction in degraded dyes, gas storage, host-guest chemistry, anti-convulsant, anti-inflammatory, and anti-cancer agent [1–7]. Numerous researchers became interested in the preparation of transition metal oxide nanoparticles by thermal decomposition of coordination compounds [8–10]. The morphology, purity, distribution, and size of the nanoparticle can be influenced by the method of preparation. A number of nanoparticles have been reported for application in the WGS reaction as heterogeneous catalysts [11–14]. Recent studies show that the nanoparticles such as CuO display higher activity in the WGS than the bulk materials [15]. The water-gas-shift (WGS) reaction (CO + H$_2$O→CO$_2$ + H$_2$, $\Delta H^0_{298 K}$ = -41.1 kJ.mol$^{-1}$) is a moderately exothermic and most important heterogeneous reaction and has attracted considerable interest due to its application in pure hydrogen production. Hydrogen is clean energy that can be used as a fuel in rocket engines, as a fuel in polymer electrolyte membrane fuel cells, and as a coolant in electrical generators [16, 17]. In recent years, many researchers have focused their studies on the use of Cu-based catalyst as a very active heterogeneous catalyst for the WGS reaction [18–21]. The application of Cu/CeO$_2$ catalyst in the WGS reaction was recently published by Liu et al [22]. They reported that Cu/CeO$_2$ catalyst exposes a combination of (100) and (111) faces in a pyramidal structure. According to their report, the nanoparticles are more active than their parent bulk surfaces due to the low-coordinated corner and the edge sites. As mentioned previously, WGS is mildly exothermic; therefore it is thermodynamically favored at lower temperatures. Because of kinetic limitations, the reaction is faster at higher temperatures. In practice, the WGS reaction is typically performed in two stages, the high-temperature reaction (310–450°C) employing iron oxide-based catalysts, and the low-temperature reaction (180–250°C) employing copper-based catalysts [23, 24]. In the present study, we employed a new precursor to prepare a truncated octahedral Cu-Na/Al$_2$O$_3$ catalyst.
with a high surface area by thermal decomposition of a two-dimensional polymeric complex formulated as \([\text{Cu}(\mu\text{-dipic})_2\{\text{Na}_2(\mu\text{-H}_2\text{O})_4\}]_n\). The synthesized catalyst was analyzed by various characterization methods such as FT-IR, XRD, SEM, and BET-specific surface area. It was established that the catalyst prepared by thermal decomposition of the inorganic complex has higher catalytic activity compared to those prepared by the impregnation conventional method.

2. Experimental

2.1. Materials and instruments

All chemicals and reagents were purchased from a commercial source and used without further purification. Parallelepiped colorless crystal of good quality of complex 1 was selected to perform structural analysis by single-crystal X-ray diffraction. Simultaneous thermal analysis TGA and DTA were made on a NETZSCH STA 409 PC/PG device in the air atmosphere with a heating rate of 10 °C.min\(^{-1}\) over a temperature range of 25–700°C in a quartz crucible. The powder X-ray diffraction (XRD) measurements were recorded by a Philips X-Pert MPD diffractometer (Philips electronics Co, The Netherlands) with Cu K\(\alpha\) radiation (\(\lambda = 0.154178\) nm) with an scattering angles of 0°-80° at a rate of 0.02 °s\(^{-1}\). The morphology of the catalysts was examined by scanning electron microscopy (SEM) on a MIRA3TESCAN-XMU electron microscope with accelerating voltage 15 kV. The BET surface area and textural measurements of the catalysts were performed using nitrogen adsorption/desorption isotherms using a PHS-1020 (PHSCHINA) apparatus at liquid nitrogen temperature (77 K).

2.2. Synthesis of complex 1

To an aqueous solution (20 mL) of Cu(NO\(_3\))\(_2\).3H\(_2\)O (0.241g, 1mmol), was added and ethanolic solution (10 mL) of pyridine 2,6- dicarboxylic acid (0.334 g, 2 mmol) and an aqueous solution (10 mL) of sodium hydroxide (0.16g, 4 mmol). The resulting solution was stirred at room temperature for 2 h. The mixture solution was filtered by fine pore What-man filter paper and allowed to stand at room temperature. After two weeks, under slow evaporation, several single crystals of complex 1 suitable for X-ray crystallographic analysis were collected. Yield (78.2%). Elemental analysis (%) calculated for 1: C, 30.67; H, 3.28; N, 5.11. Found: C, 30.65; H, 3.19; N, 5.15%.

2.3. Preparation of the catalysts

Synthesis of the main catalyst of Cu–Na/Al\(_2\)O\(_3\) (hereinafter CNM): In a typical procedure, for the preparation of the catalyst of Cu-Na/Al\(_2\)O\(_3\), 6 g of Al\(_2\)O\(_3\) and an aqueous solution containing 5.8 g of complex 1 were mixed in a conical flask. Then the resulting solution was kept under ultrasonic irradiation for 10 min. In the last step, the mixture was evaporated at 100°C to dryness and followed by calcination at 700°C in the static air in an electric furnace for 4 h. In the end, the corresponding Cu-Na/Al\(_2\)O\(_3\) catalyst was prepared.
Synthesis reference catalyst of Cu–Na/Al₂O₃ (hereinafter CNR): CNR was prepared by a typical impregnation conventional method. To an aqueous solution (10 mL) of NaOH (0.08 g, 2 mmol) was added an aqueous solution of Cu(NO₃)₂·3H₂O (0.241 g, 1 mmol) and allowed to stir at room temperature. With constant stirring, 6 g of Al₂O₃ was added to the above solution. The resulting aqueous suspension was heated at 150 °C for 10 h and followed by calcination at 700°C in an electric furnace for 4 h.

2.4. Catalytic performance for WGS reaction

The WGS tests were conducted in a fixed bed micro reactor using Cu-Na/Al₂O₃ in the presence of CO/H₂O stream under 2.5 bars of pressure. Prior to all activity and stability tests, the catalyst sample (1.0 g) was reduced in situ in 50 mL min⁻¹, the flow of N₂/H₂ = 1 stream at 400°C for 20 h. After roughly 20 h, the N₂/H₂ was replaced by the H₂O/CO (4:1) mixture with a GSHV of 3600 h⁻¹, and the catalyst was cooled or heated to the reaction temperature. The water-gas shift reaction temperature was gradually raised from 150 to 400°C, 8 h for each temperature, while the temperature was controlled using a thermocouple. The inlet and outlet gas were continuously recorded online using a gas chromatograph (Varian, Model 3400 series) equipped with a 10-port sampling valve (Supelco company, USA, Visi Model), a sample loop, and a thermal conductivity detector. The activity of the catalyst was evaluated using the following parameters:

\[
\text{CO conversion} = \frac{1 - F_{\text{CO}_\text{out}}}{F_{\text{CO}_\text{in}}}
\]

Where \(F_{\text{CO}_\text{out}}\) and \(F_{\text{CO}_\text{in}}\) represent the molar flow of CO measured at the exit and inlet of the reactor, respectively.

Selectivity of j product(%) = Mols of j product/(Mols of CO in - Mols of CO out)

3. Results And Discussion

3.1. Characterization of the complex

The structure of the title complex was determined using the single-crystal X-ray diffraction. The molecular structure of complex 1 with a selective atom numbering scheme is shown in Fig. 1[25, 26]. The structure determination reveals that the molecular structure of complex 1 comprises [Cu(dipic)₂]²⁻ units and polymeric \([\text{Na}_2(\text{µ-H}_2\text{O})_4]_2\) chains, which generate the 2D network (Fig. 2). The TGA/DTA analyses gave information concerning the thermal behavior of complex 1. The simultaneous TGA/DTA plots of the complex were investigated under the air atmosphere in the temperature range of 25 to 700°C and are shown in Fig. 3. The TGA curve can be ascribed to three weight losses. The first weight loss observed between 110–250°C is attributed to the dehydration step and the removal of lattice and coordination water molecules. The decomposition and release of all organic moieties of the complex occurred in two steps between 250 °C and 600°C. All decomposition steps eventually lead to the formation of metal oxides as metallic residues. The DTA pattern of the complex is shown in Fig. 3b. DTA results showed two characteristic endothermic and two exothermic peaks. The first endothermic peak between 100 to 140°C
corresponds to the release of the lattice water molecules. The second one between 210°C to 240°C is attributed to the removal of coordination water molecules. Two exothermic peaks from 280°C to 600°C are related to the decomposition of the organic matter.

3.1. Catalysts characterization

3.2.1. FT-IR study

Figure 4 shows the FT-IR spectra of CNM (Fig. 4a) and CNR (Fig. 4b) catalysts. It can be seen from the figures that the FT-IR spectra of both catalysts are perfectly matched. The broad absorption band which appears at 3200–3600 cm⁻¹ is due to the stretching frequencies of adsorbed water molecules. The prominent band observed at 1620 cm⁻¹ is due to the bending frequency of adsorbed water molecules. The characteristic peak at 732 cm⁻¹ is assigned to Al–O stretching vibration bond [27]. Absorption bands at 553 and 467 cm⁻¹ are attributed to the Cu–O and Na–O stretching modes, respectively.

3.2.2. XRD data

The crystal structure and crystal phase of CNM and CNR was characterized by X-ray powder diffraction (XRD) and the result is presented in Fig. 5. The CNM and CNR catalysts show the diffraction peaks that matched well to pure of CuO (JCPDS No. 89-5895), space group C2/c of a monoclinic system with cell constants of a = 4.6820, b = 3.4240, and c = 5.1270 Å. The diffraction lines of CuO was observed at 2θ = 32.61°, 35.63°, 38.81°, 48.90°, 53.56°, 58.33°, 61.65°, 65.81°, 68.13°, 72.45° and 75.1° corresponded to (110), (002), (111), (202), (020), (202), (113), (311), (113), (311) and (004) [28]. The XRD patterns of CNM and CNR show the diffraction lines at 2θ = 25.23°, 34.13°, 43.15°, 52.11°, 57.27° and 66.29°, which can be attributed to α-Al₂O₃ according to the standard JCPDS card (No: 42-1468). Both catalysts show diffraction lines at 28.02, 32.24, 54.91 and 57.29° which indexed for Na₂O. The particle sizes of CuO and Na₂O in CNM catalyst were calculated by the Scherrer equation (Eq. 1) and are found to be 32.4 and 27.9 nm, respectively. The average crystalline sizes of CuO and Na₂O in CNR catalyst were estimated to be about 53.5 and 46.6 nm, respectively.

\[ D = \frac{K\lambda}{\beta\cos\theta} \] (1)

D is the mean crystal size (nm), K is the Scherrer constant (shape factor) (0.89), λ is the X-ray wavelength (0.154056 nm), β is the full width of the peak at half maximum of diffraction peak and θ is the Bragg diffraction angle.

3.1.4. Scanning electron microscopy

Figure 6 (a-c) shows the SEM images of CNM catalyst. It can be seen that the prepared catalyst has truncated octahedral morphology with a smooth surface. Note that the distributions of particle size are not uniform. Figure 6d shows the SEM image of the CNR catalyst. The micrographs reveal that the particles of CNR are irregular and bigger in comparison with CNM catalyst.
3.2.3. Textural properties

Table 1 shows the BET surface area, pore-volume and average pore diameter of CNM and CNR catalysts. The results show that the surface area of CNM is higher compared to CNR. These results are in agreement with the result of SEM and XRD analysis which can be related to the preparation method.

| Catalyst | BET surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Average pore diameter (nm) |
|----------|----------------------------|------------------------|---------------------------|
| CNM      | 145                        | 0.521                  | 11.2                      |
| CNR      | 86                         | 0.231                  | 10                        |

3.2. Catalytic performance

The CNM and CNR catalysts prepared by thermal decomposition of complex 1 and impregnation conventional methods were utilized in the water gas shift reaction (WGS). The catalytic activities represented by carbon monoxide conversions on the CNM and CNR catalysts at the temperature range 150–400°C and 2.5-bar pressure at a gas hourly space velocity (GHSV) of 3600 h$^{-1}$. All tests were performed at a constant ratio of H$_2$O/CO (4:1). Table 2 shows the CO conversion over CNM and CNR catalysts as a function of the reaction temperature that was cycled between 150°C and 400°C. It can be seen, that CNM catalyst has higher CO conversion and activity than CNR at all observed reaction temperatures. For instance, the CO conversions of CNM and CNR catalyst were found to be 61.8 and 54.2, respectively at 150°C. The improved catalytic performance of CNM can be related to the high dispersion of the metal oxide particles and higher surface area of this catalyst compared to CNR, as evidenced by the preparation method, particle size, morphology, and textural properties [29–31].

Following the increase of temperature from 150 to 300°C, a significant increase in the catalytic activity for CNM and CNR was absorbed, reaching a maximum at 300°C. It has been reported that the increasing reaction temperature facilitates CO conversion[32–34]. The chemical kinetics or Arrhenius law is temperature-dependent and with increasing reaction temperature, the CO conversion rises] 35 [. With further increase in temperature (>300°C), the catalytic activity decreases. Water-gas shift reaction is a moderately exothermic reaction, thus CO conversion is favored at low temperatures. From Le chatelier’s principle it is known that the reaction equilibrium tends to shift towards reagent formation at high temperatures] 36]. As a result, the synthesized catalysts exhibit the maximum catalytic performance at 300°C. Recently, Salehi Rad et al. have been studied the effect of the preparation method and temperature on the catalytic activity of the Zn–Ni/SiO$_2$ catalysts in the WGS reaction] 37]. They found that the method of preparation and temperature have an important role in the catalyst properties such as surface area and catalytic activity. Next to the activity of a catalyst, stability is also a valuable and important feature of a catalyst which can reduce the cost of the catalyst and possible disposal expense. In this regard, the stability of the CNM catalyst was examined at temperature with maximum catalytic performance (300 °C) in a stainless-steel and fixed-bed reactor. Figure 7, presents the CO conversion over CNM for 10 cycles. As shown in the
figure, CNM showed excellent catalytic activity and stability. In the 6 cycles, the CO conversion was maintained at around 98%. After the 6th cycle, CO conversion decreased around 10% during the reaction cycle which could be assigned to the deactivation of the CNM by blocking active sites.

| Temperature (°C) | CO conversion (%) |
|------------------|-------------------|
|                  | CNR       | CNM       |
| 150              | 54.2      | 61.8      |
| 200              | 68.2      | 76.6      |
| 250              | 79.1      | 87.7      |
| 300              | 85.3      | 98.7      |
| 350              | 81.5      | 91.8      |
| 400              | 76.3      | 83.7      |

### Table 2

CO Conversion of the water-gas shift reactions

4. Conclusion

Two kinds of Cu-Na/A$_2$O$_3$ catalysts were prepared by thermal decomposition of a hetero-nuclear, air-stable, and water-soluble complex of Cu (II) and Na (I) based on pyridine-2,6-dicarboxylic acid and impregnation conventional method. The chemical structure and morphology of catalysts were studied by FT-IR, SEM, BET, and XRD. The results showed that the catalysts have different particles size, morphology, and BET surface area. The water-gas shift reaction was examined over Cu-Na/A$_2$O$_3$ catalysts. The results showed that the CNM catalyst exhibited substantially better activity than CNR catalyst. The higher activity of CNM was associated with its high active surface and small particles size. The stability test represented that the CNM was quite stable for the WGS reaction.

### Declarations

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Figures

Figure 1

The molecular structure of the title complex 1 with atom labels showing displacement ellipsoids at the 50% probability level.
Figure 2

Fragment of the crystal packing diagram of complex 1 along the b axis (a) and the c axis (b) of 2D metal–organic layer.
Figure 3

TGA (a) and DTA (b) plots of complex 1.

Figure 4
The FT-IR spectra of (a): CNM and (b): CNR.

Figure 5

The XRD patterns of CNM (a) and CNR (b) catalysts. (●: Al2O3, ○: CuO, ◊: Na2O)
Figure 6

SEM micrographs of (a-c): CNM and (b): CNR.
Figure 7

Stability performances of CNM catalyst at 300 °C.