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Preparation of CuO/SBA-15 catalyst by the modified ammonia driven deposition precipitation method with a high thermal stability and an efficient automotive CO and hydrocarbons conversion

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ABSTRACT

Copper oxide (CuO) loaded heterogeneous catalysts are a potential candidate to replace the critical precious metals Pt and Pd for the automotive oxidation reaction. However, a good CuO dispersion on the supports is necessary to compensate for its low intrinsic activity. Moreover, regarding the high operating temperature within the vehicle, a strong metal-support interaction is also required for providing a high thermal resistance to the catalyst. In this work, a series of CuO loaded SBA-15 catalysts has been prepared according to a modified ammonia driven deposition precipitation method (ADP). Herein, the Cu/NH_3 ratio of the synthesis has been varied with the aim to assess its influence on the CuO particles dispersion and CuO-support interaction. The morphology and porosity of the catalysts, the copper oxide dispersion and the chemical state of CuO were characterized and compared by a combination of techniques. In addition to this, the catalysts' thermal stability and their performance towards the automotive emission control have also been addressed. Results demonstrated that the ADP method is an efficient and scalable approach to fabricate a copper oxide based catalyst with a distinct automotive oxidation activity. Furthermore, it has been shown that, when a higher Cu/NH_3 ratio has been applied, a higher copper oxide dispersion degree can be achieved which has a strong metal-support interaction. The latter feature leads to its excellent thermal stability up to 700 °C, accompanied with a prolonged catalytic life-span in comparison with the conventional wet impregnation approach

1. Introduction

During the last decades, a significant increase in the development of copper oxide-based heterogeneous catalyst has been documented. The reason behind is its excellent redox property, low-cost and high recyclability, leading to its application in several industrial processes [1–3]. Furthermore, Kummer et al. even suggested its potential for replacing the precious metals for the automotive oxidation reactions [4]. The current three-way catalyst based on Pt, Pd and Rh effectively converts the hazardous CO, NO and hydrocarbons (HCs) originating from fuel combustion to less harmful CO_2, H_2O and N_2. Despite the high activity and durability, the rising scarcity and cost of the precious group metals (PGM) active elements drive research for a more common and economical beneficial alternative [5]. For this reason, CuO nanoparticles supported on a porous carrier form a promising candidate for automotive oxidation reactions. However, challenges arise for improving its activity and stability as CuO has an activity that is 50 times lower than that of Pd for CO oxidation and even 100 times lower than Pt for HCs conversion [4]. Secondly, due to its low melting point (1083 °C) and Tamann temperature (405 °C), the high reaction temperature within the catalyst (e.g. for automotive applications up to 800 °C) accelerates the particles migration

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and aggregation phenomena, resulting in catalyst deactivation and shortening its life-span [6–9]. In order to overcome these obstacles, literature emphasizes the importance of a well-designed metal deposition method affording highly dispersed active sites and a strong metal-support interaction [10,11]. On the other hand, its industrial applicability and environmental impact also need to be taken into account, regarding the high production volumes and rates of the vehicle exhaust catalyst for the automobile industry [12].

Recently, preparations involving the adsorption of copper tetraamine complex ($Cu(NH_3)_4(H_2O)_2^{2+}$) has been widely applied as a simple and efficient copper oxide deposition strategy [13]. Methods such as selective adsorption (SA), ammonia evaporation (AE) and ammonia driven deposition precipitation (ADP) are all categorized under this approach [14–17]. During the synthesis, a certain amount of ammonia is added into an aqueous solution containing a Cu^{2+} precursor and the support material, followed by a thermal activation treatment (calcination and/or reduction). Catalysts prepared through this procedure demonstrate a high dispersion state of copper oxide particles onto the support. Moreover, Toupance et al. postulates the existence of two types of copper oxide species within the material, namely grafted Cu^{2+} and copper phyllosilicate [18]. The latter material is a type of copper silicate with a lamellar structure, wherein the layers of SiO_4 tetrahedra were sandwiched between discontinuous layers of CuO_6 octahedra [17–19]. A large number of studies reported the superior thermal behavior of copper phyllosilicate due to a strong metal-support interaction. For example, Zhu et al. successfully synthesized a Cu/SiO_2 catalyst with a dominant copper phyllosilicate phase by using a modified ammonia evaporation hydrothermal (AEH) method. This method leads to the formation of a pure-phase copper phyllosilicate which is stable upon heat treatment at 400 °C [20]. Also, Yue et al. prepared a copper phyllosilicate nanotube sheath by using hydrolytic adsorption method with a significant reactivity and stability [21].

Although considerable research has been focused on maximizing the copper phyllosilicate phase in the catalysts, less attention has been paid to the structural and catalytic property of the grafted copper oxide species. In the current study, we investigated the automotive catalytic performance, durability and thermal stability of a CuO/SBA-15 catalyst with a dominant grafted Cu^{2+} phase. This catalyst has been realized by modifying the ADP method developed by Guo et al. [22,23]. During the synthesis, we varied the Cu^{2+}/NH_3 ratio while keeping the solution's pH at a fixed value. In this way, CuO-loaded catalysts with a different CuO dispersion and metal-support interaction have been realized. This leads to their divergent behavior towards the automotive emission control, in particular the catalysts' thermal stability. The emphasis of this work is to assess the influence of the Cu^{2+}/NH_3 ratio on the different CuO phases formed, as well as its effect on the catalytic activity and life-span.

2. Experimental

2.1. Synthesis of the support SBA-15 silica

Mesoporous silica (SBA-15) was synthesized according to its verified synthesis [24]. Pluronic P123 triblock copolymer (P123, molecular weight 5800 g/mol, Sigma Aldrich) was first dissolved in an 1 M aqueous solution of HCl (37 wt.%, Acros) at 30 °C. After the copolymers' dissolution, the temperature was raised to 40 °C. Subsequently, tetraethyl orthosilicate (TEOS, Sigma Aldrich) was added drop wise into the solution under vigorous stirring. The molar composition of the synthesis gel is 1.0 TEOS/0.017 P123/2.1 HCl/116 H_2O. After 24 h of stirring, the mixture was hydrothermally treated at 100 °C for 72 h. The obtained solid was filtered and washed with deionized water and dried at 60 °C overnight. Finally, the material was calcined at 550 °C for 6 h with a heating rate of 1 °C/min in ambient air.

2.2. Catalysts preparation

2.2.1. Ammonia driven deposition precipitation method

For the synthesis of CuO/SBA-15 catalysts, we modified the method described by Guo et al. and altered the Cu^{2+}/NH_3 ratio at constant pH [15,23]. Firstly, ammonia (NH_4OH, 28–30%, Sigma Aldrich) was added into the vial containing 0.19 g of copper nitrate ($Cu(NO_3)_2.3.H_2O$, >99%, Merck) in order to obtain a molar Cu^{2+}/NH_3 ratio of respectively 1/3, 1/4 and 1/6. After that, respectively 5 mL, 10 mL and 25 mL de-ionized water was added into the solutions in order to obtain a fixed pH value of 10.6 for all syntheses but with a different absolute amount of ammonia. Subsequently, 0.5 g of SBA-15 support was suspended into the solution to achieve a 10 wt.% final Cu loading. The suspensions were then stirred for 48 h at room temperature, followed by a drying step at 60 °C overnight. Finally, the dried samples were calcined at 550 °C for 6 h with a heating rate of 1 °C/min. The synthesized catalysts were denoted as CS-13, CS-14 and CS-16.

2.2.2. Wet impregnation method

As a benchmark for the catalytic activity, a CuO/SBA-15 catalyst with the same amount of CuO loading has also been prepared by the conventional wet impregnation method. 0.5 g of SBA-15 support was suspended into a 25 mL solution containing 0.19 g copper nitrate ($Cu(NO_3)_2.3.H_2O$, >99%, Merck). After 48 h stirring at room temperature, the suspension was dried at 60 °C overnight, followed by a calcination step at 550 °C for 6 h with a heating rate of 1 °C/min. The prepared catalyst was denoted as CS-WI.

2.3. Characterization

N_2-physisorption was carried out with a Quantachrome Quadrasorb SI automated gas adsorption system. Prior to the measurements, the samples were outgassed at 200 °C for 16 h. The specific area was calculated using the Brunauer-Emmet-Teller (BET) equation. For the metal loaded samples, the specific area was calculated by excluding the metal content in the total sample weight. The Barret-Joyner-Halenda method was applied to estimate the pore size distribution. The total pore volume was determined at $P/P_0 = 0.95$ while the micropore volume was obtained via the t-plot method.

Wide angle X-ray diffraction was performed using a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA, Ni-filtered CuK_{a1} radiation) and an R-AXIS IV image plate. Samples were sealed in Lindemann capillaries.

CuO dispersion of the catalysts was estimated by using the N_2O pulse titration method based on the following reaction: $2Cu + N_2O\,(g) \rightarrow Cu_2O + N_2\,(g)$ [25]. The measurement was performed in a tube furnace equipped with a Pfeiffer PrismaPlus mass spectrometer. Before the measurement, the sample was first reduced in a flow of 10% H_2/Ar (flow rate 20 mL/min) at 500 °C for 10 min. After reduction, the sample was cooled down to 100 °C and flowed with pure Ar flow for 10 min in order to remove the H_2 from the surface. Subsequently, the titration was performed at 100 °C using a 0.5% N_2O/Ar flow of 20 mL/min. The amount of active sites on the CuO surface was calculated by using the amount of N_2 produced during titration. Herein, a stoichiometric Cu:N_2 ratio of 2:1 should be taken into account. The CuO dispersion has then been determined by using the following Eq. (1):

$$\text{Dispersion}\,(\%) = \left(\frac{2 \times N_2 \text{ molecules desorbed (mol)}}{\text{Total amount ofCuin sample (mol)}}\right) \times 100 \quad (1)$$