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Promoted potassium salts based Ru/AC catalysts for water gas shift reaction

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HIGHLIGHTS

- The addition of potassium salt improved the Ru/AC activity over WGS reaction.
- CO conversion increased from 13.6% for Ru/AC to 56.1% for K_2CO_3-Ru/AC at 300 °C.
- The increase of the activity was due to the reduction temperature of the catalyst.
- The high hygroscopic ability of the salt also increased the catalyst activity.

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ABSTRACT

In this work, we have prepared several kinds of potassium salts doped Ru/AC catalysts and systematically studied their catalytic activities towards water–gas shift (WGS) reaction. Activity testing indicated that K_2CO_3 doped Ru/AC catalyst (Ru-K_2CO_3/AC) showed higher catalytic performance than KOH and KOAc doped Ru/AC catalysts, methane selectivity decreased most after doping KOH. Although the particle size of Ru nanoparticles in Ru-K_2CO_3/AC catalyst was larger than that of the parent Ru/AC catalyst, H_2-TPR indicated that RuO_x was reduced at much lower temperature, suggesting a weaker interaction between RuO_x and the surface functional group of active carbon after the doping of K_2CO_3. Thus, Ru nanoparticles interacted stronger with the reaction molecules (CO and H_2O), leading a higher catalytic activity. In addition, the doping of K_2CO_3 on the surface of Ru/AC catalyst also increased the concentration of water around Ru active site due to the hygroscopic ability. Interestingly, it was also found that the prepared method also greatly affected the catalyst activity. If the active carbon was firstly coated with K_2CO_3, followed deposition of Ru metal nanoparticles, (called Ru/K_2CO_3-AC catalyst), the activity decreased remarkably as compared to Ru-K_2CO_3/AC. The low catalytic activity of Ru/K_2CO_3-AC was mainly due to the aggregation of Ru nanoparticles.

1. Introduction

The water–gas shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$, $\Delta H = 41.2\ kJ\ mol^{-1}$) is one of the most fundamental reactions for the removal of CO and production of high purity H_2 from syngas. This reaction can be used for the upgrading of the reformed gas in fuel cells, as it is effective to reduce CO to a very low content, avoiding the poisoning of Pt electrodes [1]. In addition, WGS reaction has also played a key role in adjusting the H_2/CO ratio for Fischer–Tropsch (FT) processes [2] and providing hydrogen-rich streams for fuel cells [3]. Industrially, in order to produce high purity H_2 at the highest possible CO conversion, two-stage method is applied in WGS reaction: a high temperature shift reaction operating at 300–450 °C by the use of Fe-based catalysts (e.g., Fe_2O_3/Cr_2O_3) and a low temperature shift reaction operating at 200–270 °C by the use of Cu-based catalysts (e.g., Cu/ZnO/Al_2O_3) [4]. However, some problems still remain in the comical two-stage WGS catalysts. The catalytic activity of Fe_2O_3/Cr_2O_3 is relative low at low reaction temperatures. Furthermore, the Fe_2O_3/Cr_2O_3 contains about 1–2 wt.% hexavalent chromium (Cr^{6+}), which is highly toxic to humans, organisms and the environment [5]. The Cu/ZnO/Al_2O_3 catalysts deactivated at an oxidizing atmosphere [6]. Therefore, the need for the development of high active WGS catalysts still remains an important goal in WGS reactions.

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Some noble metals especially Pt, Pd, Au and Ru catalysts have been used as alternatives for WGS reactions to circumvent the named limitations of the commercial WGS catalysts [7–10]. Among them, supported Pt catalysts have been widely studied for WGS reaction. Compared with Pt catalysts, Ru catalysts are much cheaper, thus the use of Ru catalysts will be promising as an economical way in the industrial WGS reactions. In fact, homogeneous Ru catalysts have been used for WGS reactions for a long time, which can be operated at low temperature, achieving high equilibrium conversion. However, WGS reaction over homogeneous catalysts was mainly carried out under high CO pressures (>10 bar) and their catalytic activities were usually low. Laine et al. prepared a homogeneous $Ru_3(CO)_{12}$ catalyst and applied it in WGS reaction. A ratio of 150 mol of H_2 produced per mole of $Ru_3(CO)_{12}$ over 30 days by this system [11]. Compared with the homogeneous catalysts, the Ru based heterogeneous WGS catalysts sometimes showed even much higher high catalytic activity towards WGS reaction [12]. For example, Shinde et al. [13] prepared highly active and coke resistant $Zr_{0.93}Ru_{0.05}O_2$ catalyst, and applied it in WGS reaction. This catalyst can afforded 99% conversion of CO with 100% H_2 selectivity below 290 °C. A lack of CO methanation activity is attributed to the ionic nature of Ru species (Ru^{4+}).

In recent years, some researchers found that the catalyst activity of heterogeneous catalysts over WGS reaction could be improved by the modification of the catalyst surface with alkali additives, especially potassium salts [14–17]. For example, the catalytic activities of several kinds of Pt catalysts can be enhanced by the doping of Na^+, K^+, Li^+, Rb^+, Cs^+ [16,18]. The main role of alkali cations was claimed that it can weaken the C–H bond of formate, thus facilitating CO_2 desorption from the catalyst surface [15]. It is also believed that the introduction of alkali generated new active sites such as Pt–alkali–$O_x(OH)_y$ cluster to promote the WGS reaction [18]. Water is easily dissociated on these clusters to afford –OH, which is then reacted with CO at low temperatures. The active energy of water dissociation is higher than other steps in WGS reaction [19]. The formation of Pt–alkali–$O_x(OH)_y$ cluster can lower the active energy of water dissociation step. Besides the improvement of the catalyst activity, the alkali addition was also found to improve the Pt@SiO_2 catalyst stability in cyclic operations [20].

In our previous work, we have also found that the catalytic activity of Ru nanoparticles supported on active carbon (Ru/AC) was also greatly enhanced by the addition of K_2CO_3 [21]. Although the higher catalytic activity of Ru/AC after the doping of K_2CO_3 was obtained, many issues are still deserved to study such as the source of potassium salts and the catalyst prepared methods on the activity of Ru/AC catalyst, as well as the deep insight into the differences in these catalysts toward WGS reaction. Herein, we have prepared several kinds of potassium salts doped Ru/AC catalysts by two different methods and systematically studied their catalytic activities towards water–gas shift (WGS) reaction. More importantly, the difference in the catalytic activities of these as-prepared catalysts was also tried to be understood by various technologies.

2. Experimental section

2.1. Materials and method

30 wt.% HNO_3 was purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai China). Ethanol (99.5%), K_2CO_3 (99.9%) KOAc (99.9%), KOH (99.9%) and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai China). Ru(NO)$(NO_3)_3$ (10 wt.%) and active carbon (AC) were purchased from Alfa Aesar chemicals Co., Ltd (Shanghai, China). All of the chemical reagents except AC were used as received without further purification.

2.2. Catalyst synthesis

Ru/AC catalyst was prepared according to the method as described in our previous work with a slight modification [21]. AC was firstly treated with 30 wt.% HNO_3 at 90 °C for 4 h. For the preparation of Ru/AC catalyst, Ru(NO)$(NO_3)_3$ (0.2 g, Ru:10 wt.%) in EG solution (30 mL) and AC (1 g) was well added and dispersed in the solution with ultrasonic-assistance for 30 min. Then, the mixture was stirred at 160 °C for 6 h. After cooling to room temperature, the mixture was filtrated, washed several times by ethanol and dried at room temperature. The Ru content was 2 wt.% in theory and the catalyst was named as Ru/AC.

The alkali doping catalysts were prepared by two different methods. On method is the post-modification of the as-prepared Ru/AC catalysts. Briefly, the Ru/AC catalyst (1.0 g) was impregnated with of a certain amount of aqueous K_2CO_3 for 24 h at room temperature, and dried at 160 °C for 4 h. The catalyst was abbreviated as Ru-K_2CO_3/AC. Method for the modification of the Ru/AC catalyst with KOH and KOAc was the same as the preparation of Ru-K_2CO_3/AC, which were named as Ru-KOH/AC and Ru-KOAc/AC, respectively. In each case, the mol ratio of Ru to K was set to be 1:10. The content of K was 7.6%, 7.4% and 7.3% for Ru-KOH/AC, Ru-K_2CO_3/AC and Ru-KOAc/AC catalysts detected by ICP. The content of Ru was about 1.8% for the three catalysts detected by ICP.

On the other hand, the support was first treated with K_2CO_3 before the deposition of Ru nanoparticles. AC was first impregnated with the same amount of K_2CO_3, and then dried at 160 °C for 4 h. Then, the K_2CO_3 treated AC was added in Ru(NO$(NO_3)_3$ EG solution, and other steps were the same for the Ru/AC catalyst as described above. The as-prepared catalyst was denoted as Ru/K_2CO_3-AC.

2.3. Catalyst characterization

Fourier transform infrared (FT-IR) spectra of the samples were collected using a Nicolet Fourier transform infrared spectrometer (NEXUS 470). For the analyses, the powder samples were mixed with potassium bromide (KBr) powder and pressed into disks without any pretreatment.

H_2-temperature processed reduction (H_2-TPR) was experiments were carried out using AMI-200 from Zeton Altamira Company. The sample (50 mg) in a quartz reactor was purged with 30 ml/min Ar while heating at a ramp rate of 10°/min to 150 °C and maintaining that temperature for 1 h to remove traces of water. After cooling to 50° the sample was reduced in a flow of 10 vol.% H_2/Ar (30 ml/min) while heating from 50° to 500° at a rate of 10°/min.

BET surface area of the prepared materials was determined by physisorption of N_2 at 77 K by using a quantachrome Autosorb-1-C-MS instrument. The total pore volumes and the average pore sizes were obtained by using the Barrett–Joyner–Halenda method.

Transmission electron microscopy (TEM) images of the catalyst samples were obtained with a FEI Tecnai G20 instrument. The samples were prepared by directly suspending the catalyst in ethanol with ultrasonic treatment. A copper microscope grid covered with perforated carbon was dipped into the solution and then dried.

The ICP-AES analysis was performed on Optima 4300DV, Perkine-Elmer to determine the content of Ru and K in the iongel catalysts.

2.4. Typical procedure for WGS reaction

The activity of all prepared catalysts was evaluated in a continuous test rig with on-line analysis of the effluent gases via Agilent MicroGC 3000A GC. In a typical run, 0.4 g of the as-prepared catalyst was placed in a stainless-steel tubular fixed bed reactor and contacted with a continuous gas flow (40 mL/min) consisting of