



Aluminumphosphate molecular sieves supported Pt–Co catalysts for the preferential oxidation of CO in H₂-rich gases



ChangXu Wang, Lihong Zhang, Yutan Liu*

Tianjin Key Laboratory of Applied Catalysis Science and Engineering, Department of Catalysis Science and Technology, School of Chemical Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT

A series of aluminumphosphate molecular sieves supported platinum–cobalt catalysts were prepared and tested for the preferential oxidation of CO in H₂-rich gases. The catalysts were characterized by XRD, HRTEM, EDX, TPR and XPS techniques. The optimized catalysts were highly active and selective, CO could be purified below 10 ppm in the reaction temperature range of 110 °C–125 °C under 1% CO, 1% O₂, 12.5% CO₂, 15% H₂O, 50% H₂ in volume and N₂ balance at the space velocity of 24,000 mL g_{cat}⁻¹ h⁻¹. Pt–Co/CoAPO-5 exhibited the best catalytic performance and Pt–Co/AlPO-5 was the most active catalyst at low reaction temperature, in which particles of Pt–Co alloy were formed and the particles were highly dispersed on the surface of the support. The high activity could be attributed to the Pt–Co nano-particles with small sizes. The enlarged temperature window for CO purification should be ascribed to the loaded cobalt oxide. Substitution of cobalt ions for aluminium ions has obvious influence on the interaction between the support and platinum/cobalt species.

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1. Introduction

The hydrogen for fuel cells such as polymer exchange membrane fuel cell (PEMFC) is usually generated by reforming of hydrocarbon followed by water-gas-shift (WGS) process. The resulted H₂-rich gases contain approximately 0.5–2.0 vol.% CO, which would poison the anodic Pt electrode of PEMFC [1]. Thus, CO should be eliminated below 100 ppm before use. Among the CO removing methods, the preferential oxidation (PROX) of CO is regarded as one of the most promising ways.

So far, catalysts for CO-PROX reported include noble metal catalysts [2], such as Pt [3], Pd [4], Rh [5] and Au [6] and base metal catalysts [7], such as CuO/CeO₂ [8], cobalt oxide [9–11], LaCoO₃ with perovskite structure [12] and copper–manganese mixed oxide [13]. The base metal catalysts are cheap and highly active, while improvement on stability is needed. The Pt-based catalysts usually show good activity only at the high temperature above 150 °C [14,15]. The supported gold catalysts are reported to be very active for the PROX at low temperature, but the selectivity for CO oxidation decreases quickly at high temperature [15]. The Ru-based catalysts are recognized as the most active catalysts by Djinnovic and his co-authors. However the CO methanation, which consumes hydrogen, becomes dominated at high reaction temperatures [16].

Pt-based catalysts modified with base metal, such as Co, Ni, Fe or Sn, usually show improved catalytic performance, which is mainly owing to the formation of the base metal–platinum alloy. The support also has a marked influence on the modified Pt-based catalysts. The effects of various supports have been studied, including SiO₂ [17], CeO₂ [18], Nb₂O₅ [3], carbon nanotube [19,20] and zeolite. As for Pt–Co catalysts, supports of γ -Al₂O₃ [21], TiO₂ [22], silica aerogel [23] and yttria-stabilized zirconia (YSZ) [24] have been studied. Some supports could help to distribute the active component uniformly [19], some could interact with the active component [5] or influence the chemical state of the active component [25].

Recently, zeolite as support for CO-PROX catalyst has attracted attention. Its uniform micropores and large surface area could help the supported active species to be much highly dispersed. The zeolite supported platinum catalyst could give high activity at low reaction temperature. The reported zeolites as the supports for CO-PROX include ZSM-5 [26], zeolite Y [27], titanosilicates (ETS-10) [27], A-zeolites [29], FSM-16 [30] and mordenite [31,32].

Aluminophosphate molecular sieves (AIPOs) [33] have attracted a lot of interest in recent years. AIPO is a type of molecular sieve composed of aluminum–oxygen tetrahedron and phosphorus–oxygen tetrahedron. AIPO-5 is one of the most frequently studied AIPOs, which has one-dimensional micropore structure composed of 4, 6 and 12 ring straight channels. Aluminium ions in AIPO-5 could be partially substituted by some other transition metal ions, such as cobalt, manganese, nickel and platinum ions. The substituted AIPO-5 is generally signed as MeAPO-5, where the Me

* Corresponding author. Tel.: +86 02287401675.

E-mail address: yuanliu@tju.edu.cn (Y. Liu).

stands for the substitution metal element. It was reported that MeAPO-5 showed good activity for some oxidation reaction, for example, selective oxidation of cyclohexane by N_2O [34,35].

Different from the well studied aluminosilicate zeolites, AlPO-5 containing phosphor and the aluminium ions could be partially replaced by some transitional metal ions. Thus, it is of interest to know the catalytic behavior of AlPO-5 supported Pt-based catalyst for CO-PROX and the effect of substitution of metal ions. However, to the best of our knowledge, no research about AlPOs used in CO-PROX has been reported.

Here a series of AlPO-5 and CoAPO-5 supported Pt–Co catalysts were prepared and investigated for CO-PROX reaction to study the effect of the support and the cobalt substitution for aluminium on the catalytic performance and on the catalyst structure. The results show that the prepared catalysts are highly active and selective for CO-PROX.

2. Experimental

2.1. Preparation of catalysts

Samples of AlPO-5 were prepared according to the method stated in the literature [33]. The zeolites were prepared by direct hydrothermal synthesis. Triethylamine (TEA) was used as the template. The solution of phosphoric acid (85 wt %) was added into a pseudo-boehmite sol under violent stirring, maintained the stirring for 3 h to get a uniform sol. Then, the template was added dropwise into the sol under vigorous stirring, making a mixture with molar ratio of $Al_2O_3:P_2O_5:TEA:H_2O = 1:1:1.4:40$. After stirring for 4 h, the resulting homogeneous gel was transferred into a stainless-steel autoclave with its inner surface coated with Teflon, and was kept at 200 °C for several hours. It was then cooled and washed with deionized water, dried at 110 °C for 3 h, calcined at 550 °C for 6 h.

Samples of CoAPO-5 were prepared according to the same method with the molar ratio of $Al_2O_3:P_2O_5:TEA:Co:H_2O = 1:1:1.4:0.1:40$. Cobalt nitrate was used as the cobalt source, and it was added into the sol together with phosphoric acid.

The supported Pt catalysts were prepared by using incipient wetness impregnation method. The amount of the platinum loading was 1.0% in weight, which is platinum metal in the calcined catalyst. The support of AlPO-5, CoAPO-5 or Al_2O_3 was impregnated with chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) and it was treated with ultrasound for 1 h. Then it was dried at 110 °C for 3 h and calcined at 500 °C for 3 h.

The supported Pt–Co catalysts were prepared according to co-impregnation method with cobalt nitrate as the precursor. The other conditions were the same to that of the supported Pt catalysts. The amount of cobalt loading was 2.0% in weight which is cobalt metal in the calcined catalyst.

2.2. Catalyst characterizations

X-ray diffraction (XRD) tests were performed on a Rigaku D/max 2500v/Pc X-ray diffractometer with Ni filtered Cu-K α radiation ($\lambda = 0.15406$ nm, 40 kV, 200 mA). The XRD patterns were recorded in the 2θ range of 3–55°, with a scan speed of 4°/min.

Transmission electron microscopy (TEM) pictures were obtained on a Tecnai G² F20 micro-scope operated at 200 kV. Samples were finely grounded in a mortar to fine particles and dispersed ultrasonically in ethanol. The well dispersed samples were deposited on a grid covered by a carbon film for measurements. The energy-dispersive X-ray spectroscopy (EDX) was performed along with observation of TEM. The particle size distribution was derived according to the equalize method, about 50 particles were

counted and used to calculate the arithmetic mean value. The catalysts were reduced before TEM tests at 300 °C for 1 h in the gas mixture of 50 vol.% H_2 in N_2 .

Temperature-programmed reduction (TPR) tests were performed under 5% H_2 in Ar at a flow rate of 30 mL min⁻¹ with a heating rate of 10 °C min⁻¹. 50 mg of sample was used for each test.

X-ray photoelectron spectroscopy (XPS) experiments were performed using PERKIN ELMER PHI 1600 spectrometer equipped with a Mg K α source at a beam power of 250 W. Extended spectra (survey) were collected in the range of 0–1350 eV (187.85 eV pass energy). The binding energy (BE) was calibrated with a reference of the C1s photoelectron peak located at 284.6 eV which was the adventitious carbon.

Brunauer–Emmett–Teller (BET) specific surface areas were obtained at 77 k on an Autosorb-1 equipment with N_2 physical adsorption.

2.3. Catalytic performance test

Catalytic performance tests were carried out on a continuous flow fixed tubular quartz micro-reactor with the inner diameter of 8 mm under atmospheric pressure. In each test, the catalysts were pre-reduced at 300 °C for 1 h with 50 vol.% H_2 in N_2 . The reaction gas mixture was consisted of 1 vol.% CO, 1 vol.% O_2 and 50 vol.% H_2 with N_2 balance. For investigating the influence of CO_2 and H_2O , 12.5 vol.% CO_2 and 15 vol.% H_2O was added into the reaction gas mixture, respectively. The total flow rate was 40 mL min⁻¹. CO conversion and selectivity were obtained under steady reaction state. At each testing temperature, reaction was carried through for more than 25 min. The reaction temperature was monitored by a K-type thermocouple placed in the catalysts and controlled by a temperature controller. The effluent gases were analyzed using an on-line gas chromatograph (GC) of SP-3420 equipped with a TCD and a column packed with 5A molecular sieve. As for detecting the CO concentration at ppm level, FID was used as the detector and equipped with a methanator, thus the CO detection limit was 1 ppm. The activities were evaluated on the basis of CO conversion, which can be calculated on the basis of CO in the reactant gas and the effluent gas. The selectivity of O_2 for CO oxidation is defined as the ratio of O_2 consumption for the CO oxidation to total O_2 consumption. The following are the formulae.

$$X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

$$S_{O_2} = \frac{[CO]_{in} - [CO]_{out} - [CH_4]_{out}}{2 \times ([O_2]_{in} - [O_2]_{out})} \times 100$$

3. Results and discussion

3.1. Catalytic performance

Fig. 1 shows the CO conversion and the selectivity of O_2 for CO oxidation over AlPO-5 zeolite supported Pt–Co catalysts. Pure AlPO-5 and CoAPO-5 showed poor activity, CO conversions were lower than 10% at 170 °C, which were not shown here. Co/CoAPO-5 was a little more active than CoAPO-5, but its activity was still poor, CO conversion was 84% at the high temperature of 200 °C, as could be seen from Fig. 1. This indicated that cobalt species added by impregnation performed a better activity than that of cobalt species in the crystalline lattice of CoAPO-5. Cobalt ions added by impregnation were on the surface of CoAPO-5, i.e. outside the framework of the zeolite, which could be seen from the characterization results below.

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