



Short communication

One-step synthesis of bimetallic Pt-Pd/MCM-41 mesoporous materials with superior catalytic performance for toluene oxidation

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ABSTRACT

The catalytic performances of Pt-Pd/MCM-41 bimetallic catalysts prepared by one-step synthesis method were investigated for total toluene oxidation in this paper. The experimental results demonstrated that Pt-Pd/MCM-41 was of superior catalytic activity comparing to the monometallic Pt/MCM-41 or Pd/MCM-41 catalysts with the same metallic content, yielding an almost 100% conversion at 180 °C. The following characterization results indicated that the bimetallic catalyst possessed a higher surface Pt(0) content and smaller doped metal size owing to the synergistic effect of the two noble metals, resulting in the improvement of oxygen adsorption capacity and the reducibility.

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1. Introduction

Volatile Organic Compounds (VOCs), mainly produced from industrial processes and vehicle exhausts, are the main pollutants in atmosphere. Catalytic oxidation was considered as one of the most promising technologies for VOCs abatement [1–3]. Transition metal oxides and noble metals based catalysts were both widely used in VOCs catalytic abatement. In general, noble metals based catalysts exhibit better catalytic activity in comparison with transition metal oxides [4,5], where platinum (Pt) [6–9] or palladium (Pd) [10–12] were recognized as the most active catalysts. However, as noble metals are extremely expensive, the availability of noble metal becomes a very important factor in catalyst development. As such, numerous efforts had been conducted to improve it by increasing the dispersion of noble metals on the supports via various methods [13,14].

MCM-41 silica material with a uniform mesoporous channel structure was supposed to be a promising support in catalytic application for its huge specific surface area (over 1000 m²/g) and large pore volume (over 0.8 cm³/g) [15]. Recently, several studies had reported a new one-step synthesis method for MCM-41 modification by incorporating not only transition metals such as Ce [16], Ti [17] but also noble metals such as Pt [18], Pd [19], which suggested a well dispersion of the dopants. As such, it could be an effective way to prepare the noble metal based catalysts with highly dispersion of active phases, as the

traditional wet impregnation method normally shows some shortcomings in the stabilization and distribution of doped particles [20].

Furthermore, some literatures showed that the addition of a secondary noble metal could further increase the catalytic performance of the noble metal based catalysts. For instance, Kim et al. [21] found that bimetallic Pt-Au catalysts supported on ZnO/Al₂O₃ yielded a higher activity for complete oxidation of toluene compared to monometallic Pt or Au catalysts. In addition, Loiha et al.'s work [22] illustrated the addition of Pd onto Pt/HBEA catalyst could result in a better dispersion of Pt particles compared to the pure Pt doped catalyst.

Considering the superiorities of one-step synthesis method and the co-doping of noble metals, a series of Pt-Pd modified mesoporous MCM-41 samples as well as the pure Pt or Pd doped catalysts have been prepared via one-step synthesis method for VOCs total oxidation in this study. The main purpose of the present work is to evaluate the catalytic activity (toluene was selected as the probe molecule) of different samples and disclose the relations between physicochemical properties of the samples and the activities.

2. Experimental

2.1. Materials

All the chemicals were of analytical grade. Hydrochloroplatinic acid (H₂PtCl₆·6H₂O, Pt ≥ 37.5%), palladium chloride (PdCl₂, Pd = 59–60%), tetraethyl orthosilicate (TEOS) were purchased from Aladdin Reagent Database Inc., China. Cetyltrimethylammonium bromide (CTAB), ammonia (NH₃·H₂O, 25%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

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2.2. General synthesis

In the preparation of bimetallic Pt-Pd/MCM-41, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and PdCl_2 were used as noble metals precursors. Firstly, a certain amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and PdCl_2 were dissolved in 125 ml of deionized water together with 8 ml of aqueous ammonia. The mixture was stirred at a speed of 150 rpm. Afterwards, 2.4 g of CTAB was put into the solution. After further stirring for 25 min, 10 g of TEOS was added into the mixture drop by drop. The resulting gel was stirred for another 2 h before transferring it into a Teflon-lined steel autoclave for hydrothermal synthesis at 100 °C for 24 h. The resultant solid product was filtered and washed with deionized water, and then dried at 80 °C for 12 h. Calcination of the sample was carried out at 550 °C for 6 h in air with a heating rate of 2 °C/min. During the process of synthesis, the total content of active component (Pt + Pd wt%) was kept at a constant value (0.3 wt%). Monometallic Pt/MCM-41 and Pd/MCM-41 were synthesized in a same way by using only $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or PdCl_2 as noble metal precursor. All the samples were pretreated under hydrogen atmosphere (6% hydrogen and 94% nitrogen) at 200 °C for 2 h before the activity tests and characterizations.

2.3. Characterization

Nitrogen physisorption measurements were carried out at 77 K on a nitrogen adsorption apparatus (JW-BK132F, China), and the specific surface area was analyzed by the Brunauer-Emmett-Teller (BET) method, pore size distributions and pore volume were calculated by the Barrett-Joynew-Halenda (BJH) method. TEM analyses were conducted in a FEI Tecnai G2 F20 S-TWIN microscope (USA) to investigate the morphological structures of the samples. XPS data were recorded on a Thermo ESCALAB 250Xi (USA) spectrometer to analyze the valence states of elements. The oxygen adsorption capacity of the catalysts was measured by O_2 temperature-programmed desorption (O_2 -TPD) and reducibility properties were studied by H_2 temperature-programmed reduction (H_2 -TPR). TP experiments were conducted in a TP-5079 apparatus (China). Catalysts were heated from 30 °C to 400 °C with a heating rate of 10 °C/min in gas mixture (pure He for O_2 -TPD or 6% H_2 in N_2 for H_2 -TPR). Before the experiments, samples were pretreated at 200 °C with a flow of O_2/He and then cooled to room temperature.

2.4. Catalytic activity measurements

Catalytic activity tests were carried out in a conventional fixed bed reactor. 1 ml catalyst (particle size 0.3–0.45 mm) was loaded in an 8 mm quartz tubular reactor. The flow rate was set to maintain the gas hourly space velocity (GHSV) at 10,000 h^{-1} . The inlet gas composition was controlled as: 500 ppm toluene, 10 vol.% O_2 and balance N_2 . And the toluene catalytic activity tests were performed at a temperature range from 120 to 240 °C. At each temperature investigated, the reaction lasted 40–50 min until a stable concentration was reached. Both inlet and outlet gas composition were analyzed by Fuli 9790 gas chromatograph (China) equipped with TCD and FID.

3. Results and discussion

3.1. Toluene oxidation performances

Fig. 1 showed the light-off curves of monometallic Pt0.3 wt%/MCM-41, Pd0.3 wt%/MCM-41 and several bimetallic Pt-Pd/MCM-41 catalysts for toluene oxidation. As we can see, bimetallic Pt-Pd/MCM-41 samples showed a higher catalytic efficiency comparing to monometallic Pt or Pd/MCM-41 catalysts. Among the bimetallic catalysts, Pt0.2 wt%-Pd0.1 wt%/MCM-41 possessed the lowest light-off curve temperature and the highest oxidation activity, where the related T_{50} and T_{90} values were about 162 and 175 °C, respectively. Toluene could be completely oxidized at about 180 °C over Pt0.2 wt%-Pd0.1 wt%/MCM-41, which

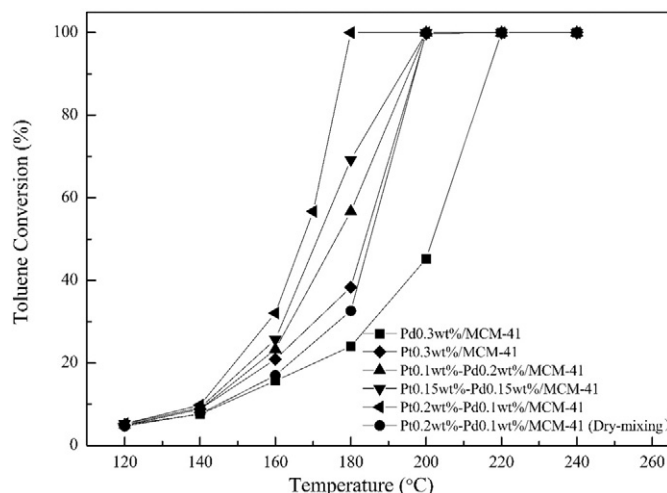


Fig. 1. Catalytic combustion of toluene over monometallic and bimetallic catalysts. (operating conditions: inlet toluene concentration = 500 ppm; $[\text{O}_2]$ = 10%; GHSV = 10,000 h^{-1}).

was lower than these on monometallic Pt0.3 wt%/MCM-41 (200 °C), Pd0.3 wt%/MCM-41 (220 °C) and the catalysts reported by other researchers [11,23]. In addition, the results also indicated that Pt species exhibited higher catalytic activity towards toluene oxidation compared with Pd species, which could be attributed to their own chemical characteristics and fitted well with the findings in the literature [5]. Moreover, the direct dry mixing of Pt and Pd doped catalysts (Pt0.3 wt%/MCM-41: Pd0.3 wt%/MCM-41 = 2:1 in weight) did not show the enhanced effect on toluene oxidation, suggesting a positive synergistic effect generated between Pt and Pd species. Similar results had been reported by Kim et al. [24] for catalytic oxidation of benzene. The catalytic activity measurements were also performed in the presence of 5 vol.% water (see Fig. S1). The toluene conversions were somewhat decreased after the addition water for all the samples, while the reaction behaviors in activity remained the same.

3.2. Physicochemical characterization of the catalysts

The specific surface area, pore diameter and pore volume of the samples were provided in Table 1. Mesoporous molecular sieve modified by noble metals via one-step synthesized method only showed slightly changes in textural properties compared to pure MCM-41 silica materials, which could be due to the partially occupation of the mesoporous pores by Pt or Pd nano-clusters [25]. This suggested that the ordered structure of MCM-41 mesoporous molecular sieves was well preserved after modification. XRD results (see Fig. S2) also confirmed it that three typical diffraction peaks corresponding to Miller indices (100), (110) and (200) [26] of MCM-41 materials were observed for all noble-metal incorporated samples with lower intensities [27]. The real loading contents of Pt and Pd in all samples were also measured by ICP-AES method and the results were given in Table S1. It could be seen that the real noble metal contents were very close to the theoretical loadings, indicating the high efficiency of one-step synthesis method.

Table 1
Textural properties of modified MCM-41 samples.

Samples	S_{BET} (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
MCM-41	1045	3.78	1.01
Pt0.3 wt%/MCM-41	970	3.62	0.92
Pd0.3 wt%/MCM-41	982	3.60	0.94
Pt0.1 wt%-Pd0.2 wt%/MCM-41	980	3.65	0.94
Pt0.15 wt%-Pd0.15 wt%/MCM-41	992	3.71	0.96
Pt0.2 wt%-Pd0.1 wt%/MCM-41	985	3.72	0.93

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