Catalytic activity of Pt catalysts promoted by MnO_x for n-hexane oxidation

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ABSTRACT

The deep oxidation of n-hexane was studied over Pt catalysts with small and large Pt crystallites, promoted by MnO_x. The Mn was deposited on the Pt/Al_2O_3 by deposition-precipitation method using two alkalis, ammonia and dimethylamine. The strength of the base influenced morphology and performances of Mn-Pt catalysts. Ammonia formed mostly spherical structure of manganese oxide, while dimethylamine created fibrous needle-like shape of MnO_x, typical for cryptomelane phase of manganese oxide. This was confirmed by XPS results that show an oxidation state of Mn close to that for cryptomelane. The Pt-Mn catalysts were more active than catalysts containing Pt only. Promoting effect of MnO_x is more pronounced for larger Pt crystallites. Among Pt-Mn samples, catalysts synthesized with dimethylamine exhibited the highest activities. Mobility and reactivity of oxygen from Pt–O–Mn sites associated with cryptomelane phase may be responsible for increased activity.

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1. Introduction

Catalytic deep oxidation is the most widely applied technology for the removal of low concentrations of volatile organic compounds (VOC) from waste gases. Typically, the active catalytic components are precious metals, platinum and palladium, supported on Al_2O_3 [1]. High price of precious metals has created a need for a cheaper replacement of this type of catalysts. Many oxides of base metals, although less active than noble metals, can be good catalysts for catalytic combustion of VOCs [2,3]. Among base metal (Fe, Cu, Ni, Co...) oxides, Mn is much studied due to its low volatility and ability to easily bind and releases oxygen [4–6]. In comparison between a metal oxide and noble metal catalysts, Lahousse et al. [7] had shown that Pt and Pd are generally the more active in the oxidation of a variety of VOCs.

The effect of addition of noble metals on the activity of transition metals catalysts has been investigated by several authors. In most cases, the better activity of promoted catalysts than noble metal catalysts has been reported [8–10]. Saqer et al. [11] reported that addition of Pt significantly improves the catalytic performance of MnO and MnO/Al_2O_3 catalysts in oxidation of toluene. Promoted MnO_x-Pd and CuO_x-Pd catalysts were found to be more active than

the pure Pd catalyst for the oxidation of methane [12,13]. Ferreira's et al. [14] found that a $Pd/V_2O_5/Al_2O_3$ catalyst was more active than Pd/Al_2O_3 for the complete oxidation of benzene. Papaefthimiou et al. [15] reported that activity of Pt and Pd catalysts in the oxidation of ethyl acetate can be significantly increased when these metals are supported on TiO_2 doped with W^{6+} cations. Regarding catalyst preparation, mostly, the promoted catalysts were synthesized by depositing of noble metal over previously supported transition metal oxide. In these catalytic systems typical transition metal oxide content is several times higher than the noble metal content [16,17].

In our previous work [18], unique method has been applied for the promoting of Pt catalyst with MnO_x. Roughly, this technique could be aligned to the deposition-precipitation method. Substantially, base metal oxide is brought into close contact with Pt by means of selective reactions with precipitation agents, previously anchored on dispersed noble metal. Such catalysts had improved performances in the deep oxidation of n-hexane.

Within this work, two different Pt crystallite sizes (1 and 15 nm) were promoted by Mn. Two alkalis, ammonia and dimethylamine (DMA), were used as precipitation agents. The doping effect of MnO_x on the catalytic activity of Pt/Al_2O_3 was tested in the reaction of deep oxidation of n-hexane. Catalysts were characterized by selective CO chemisorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR) and scanning electron microscopy (SEM).

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2. Experimental

2.1. Catalyst preparation

The Pt/Al_2O_3 catalysts were synthesized by impregnation of a $(\gamma + \theta)$ Al_2O_3 support in the form of spheres with a diameter of 3.0 ± 0.3 mm, S_{BET} of 110 $m^2 g^{-1}$, and mean pore diameter of 20 nm, using an aqueous solution of hexachloroplatinic acid. Briefly, the support was dried during 4 h at 120 °C. The concentration of hexachloroplatinic acid in the impregnating solution was 1×10^{-2} M/l and the duration of the impregnation was 3 min. After impregnation, the catalyst was air-dried at 110 °C for 2 h and reduced in a hydrogen-nitrogen mixture at 500 °C for 5 h. The platinum content determined by chemical analysis was 0.12 wt.% that is deposition in the thin outer shell of the support with shell thickness of about 100 μm. The Pt shell thickness was estimated by means of an optical microscope at a magnification of 12. The catalysts had mean Pt crystallite size of 1 nm. This sample is denoted as Pt- 1 nm in the text. In order to increase the Pt particle size, the catalyst synthesized in the previous procedure was heated in air at 700 °C for 48 h. For this sample the calculated size of the Pt crystallites was 15.5 nm (denotation: Pt- 15 nm). Calculation based on Pt dispersion, content of Pt and the surface area of Pt (275 $m^2 g^{-1}$) reveals that specific surface area of Pt are about 0.28 (small Pt crystallites) and 0.02 $m^2 g^{-1}$ (large Pt crystallites), that is only tiny part of available area of alumina support.

Deposition-precipitation method has been applied for promoting platinum catalysts with manganese, for both Pt crystallite size. This method consists of the two steps. First, immersion of dried Pt/Al_2O_3 catalysts in the alkaline solution during 10 min. Two bases as Mn precipitation agents were used – ammonia and dimethyl amine (DMA), concentrations of 1 M/l. In the second step, Pt catalysts with alkaline solutions filled up pores were brought into contact with an aqueous solution of $MnCl_2$ for 30 min. The concentration of $MnCl_2$ was 0.025 and 0.1 M/l. Catalysts were dried and calcined in air at 500 °C. In denotation of Mn-Pt catalysts, depending on the content of deposited manganese oxide and deposition precursors that is applied, the first number indicates the content of manganese oxide in wt.% (0.1 or 0.4) and the last letter describes the applied precursor, A- ammonia or D-dimethylamine.

2.2. Catalysts characterization

The CO uptake measurements were performed at a room temperature (24 ± 0.2 °C) using a pulse gas chromatographic method, home-made apparatus equipped with TCD detector (gas chromatograph Varian Aerograph-model 920). Before the measurements, the catalyst samples were treated at 400 °C in a helium flow for 1 h. After cooling in helium flow to room temperature, CO was pulsed (pulse volume 0.1 cm^3) into the helium stream (30 cm^3/min) through the adsorption cell. The catalyst adsorbed the CO pulses until saturation and the fraction of CO not adsorbed was detected by a thermal conductivity detector (TCD). The surface areas of catalysts were measured by N_2 adsorption at −196 °C, and a pore volume is measured by a Carlo Erba 2000 porosimeter.

The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG ESCALAB II electron spectrometer under a base pressure of 1×10^{-8} Pa. The photoelectron spectra were obtained using un-monochromatized Al Kα radiation ($h\nu = 1486.6$ eV) with a total resolution of 1 eV. The C 1s line of adventitious carbon at 285.0 eV was used as internal standard to calibrate the binding energies. The photoelectron spectra were corrected by subtracting a Shirley-type background and were quantified using the peak area and Scofield's photoionization cross sections. The surface morphology of the samples was examined by scanning electron microscopy (SEM) using a JEM-200CX electron microscope (Japan) equipped with an ultrahigh resolution scanning system (ASID-3D) in a regime of secondary electron image (SEI). The accelerating voltage was 120 kV, I ~100 mA. The pressure was ~10^{-6} Torr. Temperature-programmed reduction (TPR) measurements were carried out with a home-made apparatus, consisting of continuous-flow gas lines attached to a thermal conductivity detector (TCD). The sample (40 mg) was pretreated with 30 ml/min of He during 1 h at 300 °C to eliminate possible contaminants, and then cooled to room temperature in He gas flow before reduction was performed. After cooling to room temperature, a 10 °C/min heating program up to 400 °C was applied while measuring the H_2 consumption from a 3% H_2/Ar current, flowing at 30 mL/min. TPR analysis was conducted on samples with 0.4 wt.% of Mn, assuming that Mn content does not influence TPR data.

2.3. Catalytic activity

The experiments of n-hexane deep oxidation were performed in a fixed bed catalytic reactor made of a stainless steel tube having 6 mm o.d., 4 mm i.d. and 115 mm in length. The catalysts were placed in the middle of reactor, housed on a quartz wool holder, with thermocouples on the top and bottom of the catalyst bed. The reactor was loaded with 100 mg of catalysts, corresponding to a volume of 0.135 cm^3. In order to load the integral reactor, the whole catalysts spheres were completely homogeneously crushed down to 0.05 mm and palletized. In this manner egg shell macrodistribution of active components is destroyed and homogeneous mixture of active catalytic components, Pt and Mn, and pure alumina was obtained. The tablets were ground and various granulations of catalyst were separated. Catalytic tests were performed with catalysts particles smaller than 0.25 mm mean diameter. Liquid n-hexane is contained in temperature controlled saturator. A mass flow-controlled air stream passes through the saturator to give the desired partial pressure of n-hexane. The applied air flow rates through the catalyst bed corresponded to a space velocity of 17,500 h^{-1}. The inlet and outlet concentrations of hydrocarbons were analyzed by an FID detector using a stainless steel column, 6.5 ft. long and 1/8 in. in diameter, containing 23% SP 1700 on chromosorb PAW. CO and CO_2 were analyzed using a TCD detector. The investigated temperature range was between 50 and 400 °C, at a constant n-hexane inlet concentration of 1500 ppm in the air. The temperatures were maintained with an accuracy of ± 0.2 °C. The concentrations of reactants were determined with an accuracy of ± 0.2%. The reproducibility of the results was verified by performing each test several times.

3. Results and discussion

The applied catalysts preparation method does not change the surface area and pore structure of the starting Al_2O_3 support. The Pt/Al_2O_3 and Pt-Mn promoted catalysts have a surface area of 110 ± 3 and 100 ± 2 $m^2 g^{-1}$ for the catalysts with small and large Pt crystallites size, respectively (Table 1). Smaller specific surface area of samples with large crystallites of platinum should be attributed solely to sintering of alumina support due to heat treatment at 700 °C for 48 h.

Platinum parent catalyst with different crystallite size was used as starting materials for preparation of Pt-Mn catalysts. The first step of the catalysts preparation consisted of filling pores of the catalyst with precipitation agents, ammonia or DMA. Dried Pt catalysts were immersed in the alkali solutions of the precipitation agents during 10 min. Within first of about 15 s a transport of the liquid into the pores as a consequence of capillary forces proceeded. When penetration has been ceased further introduction of precipitation agents into the pores proceeds only by diffusion. After 10 min it is consider that steady state is established and concen-