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Effect of group IB metals on the dehydrogenation of propane to propylene over anti-sintering Pt/$MgAl_2O_4$

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ABSTRACT

Anti-sintering platinum-based catalyst for propane dehydrogenation (PDH) is promising to avoid corrosive oxychlorination re-dispersion of sintered Pt during coke combustion. Herein, we report an anti-sintering Pt/$MgAl_2O_4$ catalyst and optimizations on its activity for PDH with group IB metals (Cu, Ag and Au). Using a suite of characterizations including BET, H_2 chemisorption, XRD, STEM, CO-DRIFTs, XANES, XPS, TG/DTA, TPO, C_3H_6-TPD and TPSR of C_3H_6 with H_2, we reveal that Cu and Ag dilute the surface Pt atoms and donate electron to Pt while the case for Pt-Au is inverse. As a result, significant enhancements in propane conversion and propylene selectivity were obtained on the Pt-Cu/$MgAl_2O_4$ and Pt-Ag/$MgAl_2O_4$ catalysts. The Pt-Cu/$MgAl_2O_4$ exhibited excellent C_3H_6 yield and regeneration stability, presumably due to the formation of intermetallic compounds and little phase segregation during cyclic dehydrogenation-regeneration runs.

1. Introduction

Production of propylene via propane dehydrogenation (PDH) has drawn renewed attention with increasing propane supply from vast exploration of shale gas [1–3]. PDH is a highly endothermic reaction so that high reaction temperature (>550 °C) is essential for high propane conversion [4]. However, high temperature also favors undesired reactions, such as cracking, hydro-cracking and coking which result in low propylene selectivity [3]. Supported platinum based catalysts are highly active for PDH while susceptible to deactivation by coke deposition [5]. Frequent regenerations of deactivated catalyst by coke combustion are required in practice during which irreversible sintering of highly dispersed Pt species occurs under the high-temperature and oxidizing conditions [6,7]. Oxychlorination is usually adopted to re-disperse the sintered Pt particles while which causes severe equipment corrosion [8]. Thus, anti-sintering Pt based catalyst that is stable during cyclic coke combustion and no need of oxychlorination regeneration is highly desired as coke deposition seems thermodynamically inevitable under PDH operation conditions [5].

Extensive efforts on optimizing support materials and modulating electronic property of Pt have been performed to improve the catalyst's stability and propylene selectivity. Based on the discovery that coordinatively unsaturated pentacoordinate Al^{3+} centers are anchoring sites for Pt [9], Shi et al. [10] prepared raft-like Pt-Sn clusters over pentacoordinate Al^{3+} ions rich Al_2O_3 nanosheet that exhibits much better durability than conventional PtSn/Al_2O_3 catalyst under relatively low propane partial pressure. By introducing Pt during the synthesis of γ-Al_2O_3 via sol-gel chemistry, Im et al. [7] constructed partially entrapped Pt@γ-Al_2O_3 structure which has improved regeneration stability in twenty consecutive regeneration cycles. Confining Pt in the channels of Na-[Fe]ZSM5 zeolite built selective and stable catalyst for dehydrogenation of diluted propane [11]. Doping Al_2O_3 with Mg or Zn and forming $MgAl_2O_4$ or $ZnAl_2O_4$ spinel enhances the capability of stabilizing Pt during PDH reactions, [12,13] presumably because the formation of epitaxial lattice matched metal-oxide interfacial structure at (1 1 1) between Pt and spinel [14–16]. Sn is a typical additive that can increase Pt dispersion by forming Pt-Sn alloy [17] and can also serve as nucleation sites to redisperse sintered Pt during regeneration process [6]. Some oxides like CeO_2 and PdO are able to trap volatile PtO_2 at high temperatures, benefiting the stabilization and regeneration of Pt [18,19]. In addition to serving as structural stabilizers, the additives, such as Sn [6,20], Ga [2,21] and Zn [22,23], also modulate the electronic properties of Pt to improve the propylene selectivity when they are in metallic state and forming alloy with Pt [24,25]. Group IB metals (Cu, Ag and Au) which have much stronger metallic character are also candidates as

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modulators [26]. Han et al. [27] presented that Cu can well interact with Pt and improve the propylene selectivity of Pt/Al_2O_3 by weakening the adsorption of propylene on Pt. Different electronic modulating effects of group IB metals have been demonstrated on Pd which indeed adjusted the adsorption strength of ethylene [28,29]. With our recent advance in improving the stabilization efficiency of Pt over $MgAl_2O_4$, [14,15] further modulating the electronic property of anti-sintering Pt/$MgAl_2O_4$ would be promising for constructing highly durable and selective PDH catalysts.

In this work, we report the preparation of highly stable and active PDH catalysts by integrating the stabilization capability of $MgAl_2O_4$ and the electronic modulation effect of group IB metals on Pt. We demonstrated that the Pt/$MgAl_2O_4$ catalyst indeed exhibited excellent regeneration stability during cyclic dehydrogenation-regeneration operations albeit the propylene selectivity was inferior. With addition of Cu, Ag and Au, the stable yields of propylene are all improved with the propylene selectivity in an order of Pt-Cu > Pt-Ag > Pt > Pt-Au. Meanwhile, the regeneration stability is further enhanced after group IB metals modification, especially for Pt-Cu/$MgAl_2O_4$ sample. We further provide insight on the influence of group IB metals on the catalyst structure and catalytic behaviour by using a suite of characterization techniques.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of Pt/$MgAl_2O_4$ and Pt/Al_2O_3 catalysts

$MgAl_2O_4$ support was prepared by hydrolysis of aluminum isopropoxide with magnesium nitrate hexahydrate in ethanol as previously reported [14]. γ-Al_2O_3 (>99.5%) was purchased from Shandong Aluminum Industry. Incipient wetness impregnation method was adopted for the catalyst preparation. 3.0 g of $MgAl_2O_4$ or γ-Al_2O_3 was impregnated in aqueous $H_2PtCl_6{\cdot}6H_2O$ (>99.99%, Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd) solution containing Pt of 0.030 g under room temperature for 24 h. Impregnated samples were dried at 60 °C overnight and then calcined in ambient air at 500 °C for 5 h with a heating rate of 5 °C·min^{-1}. Pt/$MgAl_2O_4$ and Pt/Al_2O_3 catalysts were obtained after reduction of the calcined samples in flowing H_2 at 600 °C for 2 h.

2.1.2. Synthesis of M/$MgAl_2O_4$ (M = Cu, Ag and Au) and Pt-M/$MgAl_2O_4$ catalysts

M/$MgAl_2O_4$ (M = Cu, Ag and Au) catalysts with 1 wt% were also prepared for comparison via the same procedures to preparing Pt/$MgAl_2O_4$. The precursors are $Cu(NO_3)_2{\cdot}3H_2O$ (>99.5%, Tianjin Damao Chemical Reagent Technologies Co., Ltd), $AgNO_3$ (>99.8%, Tianjin Tiangan Chemical Reagent Technologies Co., Ltd) and $HAuCl_4{\cdot}4H_2O$ (>99.99%, Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd), respectively. Incipient wetness co-impregnation method was applied for the synthesizing Pt-M/$MgAl_2O_4$ (M = Cu, Ag and Au) catalysts by using $H_2PtCl_6{\cdot}6H_2O/Cu(NO_3)_2{\cdot}3H_2O$, $Pt(NH_3)_4(NO_3)_2$ (>99.99%, Alfa Aesar)/$AgNO_3$ and $H_2PtCl_6{\cdot}6H_2O/HAuCl_4{\cdot}4H_2O$ as corresponding precursors. The nominal weight loadings of Pt and M were both 1.0 wt% and the real contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Similar impregnation and thermal treatment procedures to preparing Pt/$MgAl_2O_4$ were conducted to synthesize Pt-M/$MgAl_2O_4$ catalysts.

2.2. Catalyst characterization

Surface areas were measured on a Micromeritics ASAP 2460 using N_2 adsorption isotherms and BET analysis method. All of the samples were degassed under vacuum at 300 °C for 5 h before the adsorption measurements.

X-ray diffraction (XRD) patterns were recorded on a PANalytical PW3040/60 X′ Pert PRO diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm), operating at 40 kV and 40 mA.

The actual contents of the metals in these samples were determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS intrepid II XSP instrument (Thermo Electron Corporation).

High resolution TEM analysis was performed using a JEOL JEM-2100F operated at 200 keV with a specified point-to-point resolution of 0.19 nm and a lattice resolution of 0.10 nm. This instrument is equipped with a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) detector and the resolution is 0.2 nm. TEM specimens were prepared by depositing a suspension of the powdered sample on a lacey carbon-coated copper or nickel (for cupper containing samples) grid. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed by an Oxford Instruments ISIS/INCA energy-dispersive X-ray spectroscopy (EDS) system with an Oxford Pentafet Ultrathin Window (UTW) Detector in HAADF-STEM mode.

Pt dispersions were measured by pulse adsorption of H_2 on a Micromeritics AutoChem II 2920 automated characterization system at 50 °C. Approximately 50 mg of the sample was loaded in a U-shaped quartz tube and heated to 600 °C for 30 min under pure H_2 of 30 mL·min^{-1}, and then switched to pure Ar of 30 mL·min^{-1} for 1 h before cooled to 50 °C. H_2 pulse (10 vol% H_2/Ar) was introduced by switching the six-way valve. Pt dispersions were estimated by assuming the adsorption stoichiometry of H_2 to Pt to be 0.5.

IR spectra were collected in a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) mode using a Bruker EQUINOX 55 spectrometer, equipped with an MCT detector and operated at a resolution of 4 cm^{-1} for 64 scans. Before each experiment, the sample (~40 mg) was reduced in situ in pure H_2 at 500 °C in a DRIFTs cell (HC-500, Pike technologies). Then under flowing He, the temperature was cooled to 30 °C and hold for 60 min. After that, a background spectrum was recorded for the sample, which was then subtracted automatically from the subsequent spectra. The corresponding gas for CO adsorption (10 vol% CO/He) was introduced into the reaction cell consequently and the spectrum was recorded as a function of time until saturation. He was then switched on to purge the gaseous CO. All the total flow rates involved were 20 mL·min^{-1}.

X-ray adsorption spectroscopy (XAS) at the Pt L_3-edge was collected at the beamline 14 W of Shanghai Synchrotron Radiation Facility (SSRF) in China. The output beam was selected by Si(1 1 1) monochromator. Energy calibration was undertaken by using Pt foil. The spectra were recorded at room temperature under the fluorescence mode with a solid-state detector. Prior to the experiments, the samples were reduced at 600 °C for 2 h. After it was cooled to room temperature, the reactor was evacuated and transferred to the glove box without exposure to air. Then, all of the samples were sealed in Kapton films in the glove box. The Athena software package was used for the data analysis.

X-ray photoelectron spectroscopy (XPS) data were collected using a Thermofisher ESCALAB 250 spectrometer with a monochromatized Al Kα X-ray source (1486.6 eV) and an applied power of 150 W. C_{1s} (binding energy 284.6 eV) was used as the reference.

Thermal gravity (TG) analysis was performed on a TGA Q600 (TA Instruments). Approximately 15 mg of sample was placed in an alumina crucible and heated at a rate of 10 °C·min^{-1} in air atmosphere (flow rate: 100 mL·min^{-1}) up to 850 °C.

Raman spectra of the spent catalysts were collected on a LabRAM HR 800 Raman spectrometer with a 532 cm^{-1} Ar-ion laser