



Catalytic hydrodechlorination of 1,2,4-trichlorobenzene over Pd/Mg(Al)O catalysts

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ABSTRACT

Catalytic hydrodechlorination (HDC) is an efficient way to remove chloride species from chlorinated hydrocarbons. Hydrodechlorination reaction of 1,2,4-trichlorobenzene was studied over a series of palladium (1 wt.%) catalysts supported on calcined Mg/Al hydrotalcite-like materials (HT) prepared with different Mg/Al ratios. The fresh catalysts were characterized using ICP-OES, XRD, N₂-physisorption, H₂-chemisorption, TPR, and TEM. It has been observed that the activity, stability and selectivity of the catalysts in the hydrodechlorination reaction of 1,2,4-trichlorobenzene were strongly dependent on the Mg/Al molar ratio in the Mg(Al)O support. The sample with Mg/Al ratio of 4 exhibited the highest activity and selectivity towards total hydrodechlorination reaction giving benzene. Rehydration of the calcined hydrotalcite catalyst resulted in an enhancement of the hydrodechlorination performance. The spent samples were characterized by TPO/MS, TGA and ESEM-EDS techniques. Based on our results it was revealed that catalyst deactivation was mainly due to coke formation. The amount of coke decreased with the base character of the support. The amount of coke formed during the reaction can be eliminated by combustion recovering the initial activity.

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1. Introduction

Organohalogenated compounds are hazardous pollutants contained in various waste oils and organic liquids. They have been used widely in the manufacture of refrigerants, herbicides, dyes, wood protectors, plant growth regulators, dye carriers, pesticide intermediate, heat-transfer medium and dielectric fluid in transformers. The options of their disposal include incineration, pyrolysis, catalytic steam reforming, biological treatment and catalytic oxidation. However all these processes are associated with drawbacks like high toxic emissions for instance formation of dioxins [1], low conversion and high energy expense. Catalytic hydrodechlorination (HDC) is then becoming an attractive method for the treatment of chlorinated organic wastes [2–4]. HDC operates at low temperature and pressure, forms no harmful side-products and could eventually be selective towards chloride removal [5]. This process is efficiently catalyzed by noble metal catalysts on various supports under mild conditions. The best catalytic systems contain palladium [4]. A characteristic of HDC is the occurrence of fast deactivation, observed with most substrates.

Catalytic decay in gas-phase hydrodechlorination has been linked to different phenomena such as poisoning of the active phase by the HCl formed in the reaction [6–9], particle sintering [10], and coke deposition [11,12].

Particle sintering and coke formation are expected to be affected by the choice of the support. The common supports employed for HDC are activated carbon, MgO, SiO₂, and Al₂O₃. The acido-basic character of the support has an influence on the catalytic properties of the metal for the conversion of chlorobenzene to cyclohexane: Hashimoto et al. reported a higher selectivity towards cyclohexane for Pd supported on chlorinated aluminas [13], and on silica–alumina [13]. The effects of the modification of Pd/C by basic additives have been linked to chloroarene dissociation and surface charge effects [14]. A different charge at the Pd surface has been evidenced by the shift of the infrared band of CO in the case of Pd and Pt supported on hydrotalcites [15–17]. Indeed a clear effect of basic supports has been reported on the catalytic properties for reactions involving arylchlorides, such as Heck reactions, in which the reactivity increases when hydrotalcites [18] or MgLa mixed oxides [19] are used as supports. An effect on deactivation is also expected to change: an increase of the electron density at the surface induced by the support should decrease the adsorption of Cl which is an electro-donor. Moreover coke formation catalyzed by acido-basic mechanisms should also be

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affected. Surprisingly basic supports have scarcely been used for dechlorination, probably because they were expected to be neutralized by the HCl produced by the reaction. We report here the hydrodechlorination reaction of 1,2,4-trichlorobenzene over hydrotalcite-like supported Pd. The activity of palladium supported on calcined Mg/Al hydrotalcites with different basic character was studied. The effect of rehydration–reconstruction of the supports together with Pd catalyst was investigated on the catalytic activity and stability. Finally the source and nature of deactivation on spent catalysts were studied. The activity and stability of the catalyst was also assessed with the meixnerite-like phase obtained by rehydration of calcined hydrotalcite.

2. Experimental

2.1. Preparation of the support

The hydrotalcite-like (HT) compound was prepared by coprecipitation of suitable amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mg/Al molar ratio of 2, 3 and 4) with solutions of NaOH (2.0 M) as stated elsewhere [20]. HT was prepared with constant stirring maintaining the pH 10. The addition of the alkaline solution and pH were controlled by pH-STAT Titrino (Metrohm). The suspension was stirred overnight at room temperature. The resulting gel was centrifuged and washed several times thoroughly with distilled water ($\text{Na} < 100$ ppm) until the pH of the centrifuged material is neutral and also to remove any free sodium ions. The sample was dried in an oven overnight at 393 K and then heat-activated in air flow at 723 K for 6 h (heating rate: 1 K min^{-1}) to yield the Mg(Al)O mixed oxide. Calcined hydrotalcites with different Mg/Al molar ratios of 2, 3 and 4 prepared were labeled as HT-21, HT-31 and HT-41, respectively. The chemical compositions of the samples were determined by ICP-OES in a PerkinElmer Plasma 400.

2.2. Catalyst preparation

The palladium Mg(Al)O catalysts were prepared by two procedures. Pd (II) acetylacetonate ($\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$) was used as Pd precursor. In the first one, the calcined solid was introduced in a toluene solution of palladium (II) acetylacetonate for 12 h, dried at 398 K under vacuum, and calcined in air flow at 673 K for 2 h. The calcined material was reduced at 623 K under hydrogen flow for 2 h before reaction. The palladium catalysts were denoted as Pd-HT-41, Pd-HT-31 and Pd-HT-21. In the second procedure 250 mg of calcined Pd-HT-41 catalyst was first reduced at 623 K under hydrogen flow ($60 \text{ cm}^3 \text{ min}^{-1}$) and then rehydrated in gas-phase at 373 K using argon (flow 40 ml min^{-1}) saturated with deionized water for 18 h in situ. This catalyst hereafter was named as Pd-HTR-41.

2.3. Catalyst characterization

2.3.1. ICP-OES

The chemical composition of the samples was determined by ICP-OES with a PerkinElmer Plasma 400 instrument.

2.3.2. Powder X-ray diffraction patterns

The XRD analysis of the materials were recorded using Siemens D5000 diffractometer (Bragg-Bentano parafocusing geometry and vertical θ - θ goniometer) fitted with a grazing incident ($\omega = 0.52^\circ$) attachment for thin film analysis and scintillation counter as a detector. The samples were dispersed on Si (5 1 0) sample holder. The angular 2θ diffraction range was between 5° and 90° . The data were collected with an angular step of 0.03° at 12 s per step and sample rotation. Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) was obtained

from a copper X-ray tube operated at 40 kV and 30 mA. The crystalline phases were identified using the JCPDS files.

2.3.3. N_2 -physisorption adsorption–desorption isotherms at 77 K

It was measured using Micromeritics ASAP 2000 surface analyzer and BET surface areas were calculated. Before analysis, all the samples were degassed in vacuum at 393 K for 6 h.

2.3.4. Hydrogen-chemisorption

The analysis was performed under static volumetric conditions with a Micromeritics ASAP 2010 apparatus. Prior to the measurement, the sample was evacuated at 373 K for 1 h, treated in flow pure hydrogen ($30 \text{ cm}^3 \text{ min}^{-1}$) at 623 K for 3 h, evacuated at 623 K for 1 h, cooled down to 373 K and evacuated for 30 min. Finally the chemisorption analysis was performed at 373 K. The double isotherm method was used to determine the amount of irreversible adsorbed hydrogen which allows calculating the apparent metallic dispersion (H/Pd) assuming an adsorption stoichiometry of H:Pd = 1:1. From the first isotherm the total volume of hydrogen adsorbed was obtained. The sample was evacuated (about 10^{-6} Torr) again at the chemisorption analysis temperature for 10 min for back sorption measurements in order to obtain the volume of hydrogen reversibly adsorbed. The linear zone of each isotherm was extrapolated to zero pressure in order to estimate the volume of the strong hydrogen adsorbed.

2.3.5. Transmission electron microscopy (TEM)

TEM operated at 80 kV (JEOL JEM-2000EX II) was taken to analyze the morphology and dispersion of our catalysts. Samples were dispersed in alcohol in an ultrasonic bath and a drop of supernatant suspension was poured onto a holey carbon-coated grid and dried completely before the measurements were taken.

2.3.6. H_2 -temperature-programmed reduction (TPR)

TPR studies were performed in a ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector (TCD). The catalysts were treated in O_2 for 1 h at 573 K before TPR analysis. The samples were then purged with argon flow before the TPR analysis. The analysis was carried out using a 3% H_2/Ar gas flowing at 20 ml min^{-1} by heating from room temperature to 823 K with a ramp of 10 K min^{-1} . Water produced during TPR was trapped in $\text{CaO} + \text{Na}_2\text{O}$ (Soda lime) before reaching the TCD.

2.3.7. CO_2 -TPD

The basic properties of the materials were also determined by TPD of CO_2 using a TPDR 1100 (Thermo Finnigan), equipped with a programmable temperature furnace and a TCD detector. The catalysts were first purged using He 373 K for 45 min. The CO_2/He (3%) adsorption was carried out by heating the sample from 303 to 373 K flowing at 20 ml min^{-1} . Finally the weakly adsorbed CO_2 were purged using He flowing at 100°C for 45 min. Typically, ca. 150 mg of sample were placed between plugs of quartz wool in a quartz reactor, and the desorption of CO_2 was measured by heating the sample from room temperature to 1123 K at 10 K min^{-1} under a He gas flow ($20 \text{ cm}^3 \text{ STP min}^{-1}$).

2.3.8. Temperature-programmed desorption and oxidation (TPDO/MS)

It was carried out for spent catalysts (washed with ethanol) in ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector. Previously we have seen that no effect in reactivation of the spent catalyst by washing with ethanol. Before analysis the catalysts were pretreated using He-TPD/MS heating from room temperature to 623 K at 20 K min^{-1} and maintained for 30 min at this temperature to remove ethanol and other species.

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