



Performance of alkali modified Pd/Mg(Al)O catalysts for hydrodechlorination of 1,2,4-trichlorobenzene

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ABSTRACT

Alkali-modified Pd (wt%)/HT catalysts, where HT is calcined Mg/Al hydrotalcite (Mg(Al)O), were studied for the HDC reaction of 1,2,4-trichlorobenzene at mild conditions (atmospheric pressure and 373 K) using a continuous reactor. Characterization of the alkali-modified Pd/HT catalysts by H₂-chemisorption, N₂-physisorption, SEM, HRTEM and CO₂-TPD analysis revealed different textural, metallic and basic properties depending on the type of alkaline metal and precursor. The hydrodechlorination reaction of 1,2,4-trichlorobenzene was strongly dependent on the type of alkaline additives (Li, Na or Cs) and alkaline precursors (OH⁻ or NO₃⁻). The basic properties of the catalysts showed a predominant role in activity, selectivity and stability of the catalysts. Furthermore the HDC catalytic activity is highly dependent in the intrinsic property of alkali metal species. The affinity of the chloride produced during the reaction to the strong basic alkali surface contributes for the higher stability of the alkali-modified catalyst. Calcination–reduction and reduction treatments were employed to regenerate the catalyst. The initial catalytic activity was recovered when the used sample was regenerated by reduction treatment.

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1. Introduction

Despite their numerous applications in industry as, for example, refrigerants, herbicides, dyes and pesticides, polychlorinated aromatic compounds are carcinogenic and mutagenic. These toxic compounds are environmentally stable and can undergo bioaccumulation in fatty tissues [1]. A convenient dechlorination of organohalogenated compounds is an alternative for halogenated waste handling. Unlike techniques such as pyrolysis and incineration, catalytic hydrodechlorination (HDC) enables hazardous chlorinated wastes to be transformed into null toxic commercial products or easily destructible compounds with non-toxic emissions [2–5]. Moreover, HDC is simple and efficient. Also, it is known to be promoted by VIII noble metals. Palladium is considered the best catalyst to selectively replace chlorine atoms with hydrogen and is the least affected by the catalyst-poisoning properties of the halide ions released [5–8]. However, the deactivation of the catalyst is a great problem associated with HDC reaction. This occurs through the release of the hydrogen chloride co-product

and/or the formation of carbonaceous deposit on the catalyst active sites [2–4,6–10]. Another issue is the decrease of reactivity upon electron withdrawing groups substitution on the aromatic ring, e.g. with polychlorinated arenes. These two drawbacks can be partially circumvented by the addition of alkali to the reaction medium (mainly in liquid phase) [6–10], or the use of promoters and supports with “electron donating” properties [11–15]. The beneficial effect of basic promoters and supports can be understood owing to some mechanistic aspects of the HDC reaction. Although the mechanism of the HDC of chloroaromatic compounds is still unclear, an electrophilic effect has been proposed to explain the HDC reaction of different chloroaromatic compounds over nickel and palladium catalysts [4,7,16–26]. On that account, HDC activity may be promoted owing to the electron donor character of additives, promoters and supports that activate the aromatic compound, thus providing an electron-rich environment for hydrogen scission of the C–Cl bond. Moreover, an “electron-rich” metal site will be less prone to be deactivated by chlorine interaction. These behaviours were nicely put in evidence by using the HDC of chlorinated benzenes in both gas and liquid phases [9,10,15]. In particular, we reported in a previous study dealing with the HDC of 1,2,4-trichlorobenzene (124TCB) on a series of Pd catalysts supported on several MgAlO_x mixed oxides, that the palladium catalyst

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Table 1
Some characteristics of the catalysts.

Sample	Composition (wt/wt%)		BET surface (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	CO ₂ desorption ^a		Pd H ₂ -uptake (H/Pd%)	Pd size from TEM
	Pd	Alkali			(mmol g ⁻¹)	(μmol m ⁻²)		
Pd/HT	1.1	–	151	0.40	3.7	25	18	4.8
Pd/HT(LiOH)	1.0	1.2	115	0.20	8.3	72	19	4.9
Pd/HT(LiOH) _{0.24}	1.0	0.24	118	0.21	–	–	18	5.0
Pd/HT(LiOH) _{0.12}	1.0	0.12	117	0.20	–	–	17	4.9
Pd/HT(NaOH)	0.98	4.9	21	0.06	6.7	320	5.5	5.0
Pd/HT(CsOH)	0.97	23	12	0.04	6.0	500	2.3	5.1
Pd/HT(CsOH) _{4.6}	1.0	4.6	25	0.06	–	–	5	5.0
Pd/HT(CsOH) _{2.3}	1.1	2.3	28	0.09	–	–	7	4.9
Pd/HT(LiNO ₃)	1.2	1.2	92	0.33	3.8	29	24	5.0
Pd/HT(NaNO ₃)	1.0	5.0	70	0.20	5.1	73	16	4.9
Pd/HT(CsNO ₃)	0.99	22.8	70	0.18	5.8	83	6.4	4.8

^a Obtained by deconvolution of CO₂-TPD profiles.

with higher basicity of the support gave the uppermost activity and stability [15]. The best HDC performances were obtained for a Mg/Al molar ratio of 4. The MgAlO_x supports were derived from hydrotalcite precursors (HT). It was also shown that catalyst deactivation at high temperature reaction (473 K) was mainly due to coke formation, which decreased as the basic character of the support increased.

It is well known that the basic properties of an inorganic oxide can be boosted by using alkaline additives. For instance, the Na- and K-doped MgO showed a large increase in the generation of super base sites by an induction effect of the electron released from the alkali metal [27,28]. On that account, the enhancement of the basic properties of Mg(Al)O mixed oxides may be expected upon addition of alkaline promoters. Indeed, a clear effect of alkaline-doping agents on the catalytic activity of hydrotalcite-like compounds has been observed for the aldol condensation reaction [29]. One may thus anticipate that the same effect should be beneficial for the HDC catalytic properties of alkaline-promoted Pd/MgAlO_x catalysts. With this view the present work addresses to the HDC of 1,2,4-TCB as a model reaction on Pd/MgAlO_x promoted by Li, Na and Cs that comes from nitrates and hydroxides salts. The study focuses on activity, selectivity and stability in relation with the basic properties of the promoted mixed oxides. A low reaction temperature (273 K) has been chosen to study the deactivation and the regeneration of the catalysts.

2. Experimental

2.1. Preparation of the supports and catalysts

Full details of the support synthesis were given previously [15]. In brief, the hydrotalcite-like compound was prepared by co-precipitation of suitable amounts of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O (Mg/Al molar ratio of 4) with NaOH 2 M at pH 10. The resulting gel was washed thoroughly several times with deionized water to remove any remaining free sodium ions. The sample was dried and calcined in flowing air at 723 K for 12 h (heating rate: 1 K min⁻¹) to yield the MgAlO_x mixed oxide (HT). For the alkali-doped HT, 1 g of this MgAlO_x was impregnated with the appropriate amount of an aqueous solution of the alkali hydroxides or nitrates to obtain the desired alkali loading (see Table 1). The solids were dried and calcined at 723 K (for alkali hydroxides) or 873 K (for alkali nitrates) for 12 h. The supports thus obtained were labelled HT(AOH) and HT(ANO₃) (A = Li, Na and Cs; and OH and NO₃ indicate the type of alkali precursor).

These supports were used to prepare the metal catalysts by depositing palladium by the incipient wetness impregnation method [15]. The metal precursor used was Pd(II) acetylaceto-

nate (Pd(acac)₂). A solution of Pd(acac)₂ in toluene was used to impregnate the corresponding alkali-doped mixed oxide support. The nominal Pd content in all samples was 1 wt%. The samples were then dried and calcined in air at 623 K for 3 h. The catalysts were reduced in situ at 623 K for 2 h before starting the reaction. The final catalysts were labelled Pd/HT(AOH) and Pd/HT(ANO₃).

2.2. Textural, structural and morphological characterizations

The chemical composition of the samples was determined by atomic absorption spectroscopy with a Perkin–Elmer Plasma 400 instrument.

Textural properties of the solids were obtained from N₂ adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2000 surface analyzer. Before analysis, all the samples were degassed in vacuum at 393 K overnight. BET surface areas and average pore diameters were thus determined. The XRD analysis of the materials was recorded using a Siemens D5000 diffractometer (Bragg–Bentano for focusing geometry and vertical θ – θ goniometer) with an angular 2θ -diffraction range between 5° and 70°. The samples were dispersed on a Si(5 1 0) sample holder. The data were collected with an angular step of 0.03° at 5 s per step and sample rotation. Cu K α radiation ($\lambda = 1.54056$ Å) was obtained from a copper X-ray tube operated at 40 kV and 30 mA. The crystalline phases were identified using the JCPDS files. The morphologies of the catalysts were observed by SEM with a JEOL JSM-35C scanning microscope operated at an acceleration voltage of 15 kV. A small portion of each sample powder was coated on a metallic disk holder and covered with a thin gold layer before SEM analysis. High-resolution transmission electron microscopy (HRTEM) was carried out at 200 kV with a JEOL JEM 2100 instrument equipped with a LaB₆ source. The point-to-point resolution of the microscope was 0.20 nm. Samples were deposited on holey-carbon-coated Cu grids from alcohol suspensions. For each sample, particle-size distribution histograms were obtained.

2.3. Characterization of the basic properties

The basic properties of the materials were characterized by TPD of CO₂ using a ThermoFinnigan (TPORD 110) apparatus equipped with a programmable temperature furnace and a TCD detector. Typically, 20 mg of catalyst was placed between plugs of quartz wool in a quartz reactor. The sample was first purged using pure He (flowing at 20 cm³ min⁻¹) at 393 K for 30 min. After the temperature was cooled to room temperature, CO₂/He (3/97, vol/vol%) mixture was contacted with the sample (flowing at 20 cm³ min⁻¹). The temperature was raised to 353 K with a rate of 20 K min⁻¹ and kept at 353 K for 60 min. Then the weakly adsorbed CO₂ was then

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