

Effect of tin and potassium addition on the nature of platinum supported on silica[☆]

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Abstract

The effects of tin and potassium addition on the catalytic properties of Pt/SiO₂ catalysts were studied by diffuse reflectance UV–vis spectroscopy, temperature programmed reduction (TPR), CO chemisorption and isobutane dehydrogenation. Pt/SiO₂, Sn/SiO₂ and Pt–Sn/SiO₂ catalysts were prepared by incipient wetness impregnation with aqueous solutions of H₂PtCl₆ and SnCl₂. Pt–Sn/SiO₂ catalysts were prepared by coimpregnation and sequential impregnation. A part of these catalysts was then impregnated with an aqueous solution of KOH. Fresh and calcined catalysts were studied. [PtCl₂(SnCl₃)₂]²⁻ complex was only detected in (PtSn/SiO₂) and Sn(Pt/SiO₂) catalysts. The proximity between Pt and Sn species favoured the formation of Pt–Sn ensembles or alloys after the reduction treatment that provided stability and selectivity for the isobutane dehydrogenation. The addition of potassium to fresh Pt–Sn/SiO₂ did not change the activity, but it improved the dehydrogenation selectivity, which reached values of almost 100%. Surface Pt–Sn species changed by the calcination treatment, causing the segregation of Pt and Sn oxide species. This treatment caused a decrease of CO/Pt ratio, activity and selectivity of Pt–Sn catalysts. In calcined Pt–Sn–K catalysts, the activity seemed to be a function of K–Pt–Sn interactions.

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1. Introduction

Recently, the dehydrogenation of light paraffins has acquired importance due to the growing demand of light olefins such as propene and isobutene [1]. In these processes, supported Pt–Sn catalysts have shown advantages because of their lower deactivation rate and high selectivity for dehydrogenation reactions. The effect of tin has been explained in terms of geometric effects [2]: tin decreases the size of platinum ensembles; reducing hydrogenolysis and coking that require large ensembles of platinum. A second explanation is the modification of the electronic density of Pt, either due to a charge positive transfer from Snⁿ⁺ species or to the different electronic structures in Pt–Sn alloys [3].

Nowadays, several studies are being carried out to evaluate the modification of the stability, selectivity and activity of metallic catalysts by the addition of some alkali metals such as Li, Ba, K, Ca and others [4–9]. The use of alkaline ions has been reported for Pt/Al₂O₃ and PtSn/SiO₂, [4] Ni/SiO₂ [5], Pd/SiO₂ [6] and Cr/Al₂O₃ [7]. Siri et al. [8] studied isobutane dehydrogenation in a series of Pt and Pt–Sn catalysts, modified by the Li addition, prepared by incipient wetness impregnation and surface organometallic chemistry on metal (SOMC/M) techniques. The incorporation of Sn and Li improved light-paraffin dehydrogenation and inhibited isomerization and cracking reactions. Siri et al. [4] also found selectivities of 98% toward isobutene and a good performance in deactivation–regeneration cycles on Pt–Sn/Al₂O₃ catalysts modified with magnesium, calcium and barium.

The effect of potassium on Pt and Pt–Sn supported on silica, prepared by ion-exchange method, was studied by Cortright et al. [9] for isobutane dehydrogenation. They found that the addition of tin and potassium diminishes the size of the surface platinum ensembles, suppressing

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the hydrogenolysis, isomerization and coking reactions. In K–Sn–Pt/SiO₂ catalyst, dehydrogenation rate increased either due to an increase in the number of sites available for hydrogen removal from adsorbed isobutane or to the stabilization by potassium of molecular adsorbed isobutane.

This study aimed to examine the effects of tin and potassium addition on the catalytic properties of Pt/SiO₂. Temperature programmed reduction (TPR), UV–vis spectroscopy by diffuse reflectance (DRS) and CO chemisorption were used to characterize these catalysts. The activity of the catalysts was determined for the isobutane dehydrogenation.

2. Experimental

Pt/SiO₂, Sn/SiO₂ and Pt–Sn/SiO₂ catalysts were prepared by incipient wetness impregnation, using aqueous solutions of H₂PtCl₆ and SnCl₂ in 1 M HCl. Pt–Sn/SiO₂ catalysts were prepared by coimpregnation and sequential impregnation, adding first Pt and then Sn and vice versa. A commercial SiO₂ (Baker), crushed to a size of 60–80 mesh, was used as support. The volume of the impregnation solution was 2.4 cm³ g⁻¹ silica. A part of these catalysts was then impregnated with an aqueous solution of KOH. The metal contents in the catalysts were 0.5% Pt, 0.6% Sn and 0.3% potassium. Fresh and calcined catalysts were studied. The catalyst preparation methods are listed in Table 1.

The catalysts were studied by diffuse reflectance UV–vis spectroscopy at atmospheric conditions in a Perkin-Elmer model Lambda 2 spectrometer equipped with a diffuse reflectance accessory. The wavelength range varied from 190 to 700 nm. Temperature programmed reduction (TPR) was performed using a 5% H₂/Ar mixture at a heating rate of 10 °C min⁻¹ from 25 to 700 °C. Prior to the TPR experiments, samples were dried in Ar at 120 °C for 1 h; then calcined catalysts were obtained by heating in air at 500 °C for 1 h. The hydrogen consumption was monitored with a thermal conductivity detector (TCD). Dynamic CO chemisorption measurements were carried out by sending 46 μL pulses of CO at room temperature, the gas carrier was H₂ with a flow of 30 cm³ min⁻¹, samples were dried in Ar at 120 °C for 1 h, and then treated under H₂ flow at 500 °C for 2 h.

The isobutane dehydrogenation activity was carried out in a stainless steel apparatus designed to work either by pulses or continuous flow. The reactor was a U-shaped Vycor tube, 6 mm OD. The switching of gases was done without mixing or access of air. The reaction was done at atmospheric pressure and 500 °C. Eighty milligrams of catalyst were used for each reaction test, samples were dried in Ar at 120 °C for 1 h and then reduced in H₂ at 500 °C for 2 h. The reaction mixture contained H₂, i-C₄H₁₀, and He, with a 3:1 hydrogen:isobutane ratio. A total flow of 100 cm³ min⁻¹ and a WHSV of 28.8 h⁻¹ was used. The exit gases were analyzed in a Perkin-Elmer GC, equipped with an Alumina F1 packed column and a flame ionization detector (FID).

3. Results and discussion

3.1. UV–vis

Diffuse reflectance spectra of Pt/SiO₂, PtSn/SiO₂, Sn/SiO₂ and SiO₂ catalysts are shown in Fig. 1. The spectrum of calcined silica (Fig. 1a) presents a band at 226 nm, which also has been reported by other authors [10,11]. The absorption band at 220 nm observed in the spectrum of the Sn/SiO₂ sample is mainly attributed to the contributions of the silica.

In the Pt/SiO₂ spectra, the three bands at 260, 353 and 460 nm have been attributed to the (PtCl₆)²⁻ anion adsorbed on the support [12], which could be anchored on the surface by a ligand exchange of silanol (OH)⁻ groups of the silica. Due to the low OH⁻ density of the silica, a large fraction of (PtCl₆)²⁻ could be mobile on the support surface.

Jackson et al. [13] by NMR found that Pt adsorbs on alumina both as (PtCl₆)²⁻ and [PtCl₅(OH)]²⁻, the latter species is produced by the deprotonation of [PtCl₅(H₂O)]⁻ present in the initial solution. The ratio of (PtCl₆)²⁻/[PtCl₅(OH)]²⁻ depends on the pH of the impregnating solution, the support pretreatment and impregnation time [14]. Lietz et al. [12] and Alerasool et al. [15] proposed that the reaction of ligand exchange begins with the water adsorbed on the support. Choren et al. [10] proposed the following scheme for the

Table 1
Precursor and preparation method of the Pt/SiO₂, Sn/SiO₂ and Pt–Sn/SiO₂ catalysts

Catalyst nomenclature	Precursors	Preparation method
Pt/SiO ₂	H ₂ PtCl ₆ ·6H ₂ O	Incipient wetness impregnation
Sn/SiO ₂	SnCl ₂ ·2H ₂ O	Incipient wetness impregnation
(Pt–Sn)/SiO ₂	H ₂ PtCl ₆ ·6H ₂ O + SnCl ₂ ·2H ₂ O	Coimpregnation
Sn–(Pt/SiO ₂)	H ₂ PtCl ₆ ·6H ₂ O/SnCl ₂ ·2H ₂ O	Successive impregnation 1st Pt, 2nd Sn
Pt–(Sn/SiO ₂)	SnCl ₂ ·2H ₂ O/H ₂ PtCl ₆ ·6H ₂ O	Successive impregnation: 1st Sn, 2nd Pt
K–/SiO ₂	KOH	Impregnation
K–Pt/SiO ₂	H ₂ PtCl ₆ ·6H ₂ O + KOH	Successive impregnation: 1st Pt, 2nd K
K–(Pt–Sn)/SiO ₂	(H ₂ PtCl ₆ ·6H ₂ O + SnCl ₂ ·2H ₂ O) + KOH	Coimpregnation and then addition of K
K–Sn(Pt/SiO ₂)	H ₂ PtCl ₆ ·6H ₂ O/SnCl ₂ ·2H ₂ O/KOH	Successive impregnation: 1st Pt, 2nd Sn, 3rd K
K–Pt(Sn/SiO ₂)	SnCl ₂ ·2H ₂ O/H ₂ PtCl ₆ ·6H ₂ O/KOH	Successive impregnation: 1st Sn, 2nd Pt, 3rd K

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