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Dehydrogenation of n-butane over Pd–Ga/Al_2O_3 catalysts

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ABSTRACT

Dehydrogenation of n-butane over alumina-supported Pd and Pd–Ga catalysts was studied. Catalysts were prepared by incipient wetness impregnation with a Pd content of 0.66 wt% and atomic Ga/Pd ratios from 0 to ∞, using aqueous solutions of $PdCl_2$ and $Ga(NO_3)_3$. Fresh (uncalcined) and calcined catalysts were characterized by X-ray fluorescence spectroscopy (XRF), N_2 adsorption, temperature programmed reduction (TPR), CO and H_2 chemisorptions and O_2/H_2 titrations. n-Butane dehydrogenation reaction was carried out at 500 °C, atmospheric pressure and a H_2/C_4H_{10} ratio of 10. An increase in the Pd dispersion with increasing Ga content was observed for the fresh catalysts, according to CO chemisorption results. H_2 chemisorption and H_2/O_2 titrations were not reliable methods to determine the Pd dispersion in the fresh catalysts. For the calcined catalysts with low Ga contents, the CO/Pd, H/Pd and O/Pd values were very similar, but different for those with the higher Ga contents. These differences were explained based on the presence of chlorine. Coke deposition produced the deactivation of the catalysts and inhibited hydrogenolysis reactions on Pd, favoring the dehydrogenation selectivity. In the fresh catalysts, the Ga addition caused an effect similar to that produced by coke, reducing the activity and increasing the dehydrogenation selectivity. In the calcined catalysts, the effect of Ga addition on activity was diminished by the calcination treatment. The combination of calcination and high Ga content led to a catalyst with enhanced activity and very high dehydrogenation selectivity.

1. Introduction

The importance of catalytic dehydrogenation of paraffins to olefins has been growing due to the demand for these unsaturated hydrocarbons. Light olefins, such as butenes, are essential raw materials used to obtain polymers, gasoline additives and other chemical products. Butenes can be obtained in plants of n-butane catalytic dehydrogenation, as secondary products in steam cracking and catalytic cracking units, among other processes. Catalytic dehydrogenation of paraffins is a selective method to produce alkenes. However, the conversion of paraffins to the corresponding olefins is limited by thermodynamics restrictions due to the strong endothermic character of the reaction. High temperatures (530–730 °C) are required to reach conversions of nearly 50% for paraffins C_2–C_6 [1]. The dehydrogenation temperatures are higher for light paraffins than for heavy ones. Consequently, lateral reactions of cracking to lighter hydrocarbons and coking are favored at these high temperatures, causing a decrease in the selectivity towards desired products.

Alumina-supported Pt catalysts have been used in the dehydrogenation of light paraffins, being very active but little selective and strongly deactivated by the formation of coke. For this reason, the catalytic stability and selectivity of this system can be improved with the incorporation of a second metal, such as Sn [2,3]. A catalytic system based on Pd can be an alternative to the more expensive metals, such as Pt. The use of Pd/Al_2O_3 catalysts for the dehydrogenation of a hydrocarbon was first reported in 1973 to produce benzene from cyclohexane [4]. Recently, the dehydrogenation of propane was used to study supported Pd catalysts, which without modifications presented the same problems mentioned for Pt/Al_2O_3 catalysts, and the addition of a second metal (Sn) improved the catalytic properties of these systems [5]. In literature, it has been reported an enhancement in the selectivity towards propylene when Ga is added to Pt/Al_2O_3 catalysts [3] and ZSM-5 zeolites [6].

The objective of this work is to study the effects of the addition of Ga and calcination treatment on the catalytic behavior of Pd/Al_2O_3 catalysts in the n-butane dehydrogenation reaction. Catalysts were characterized by X-ray fluorescence spectroscopy (XRF), N_2 adsorption, temperature programmed reduction (TPR), CO and H_2 chemisorptions and O_2/H_2 titrations.

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2. Experimental

2.1. Catalyst preparation and characterization

The monometallic Pd/Al_2O_3 and Ga/Al_2O_3 catalysts were prepared by incipient wetness impregnation of γ-Al_2O_3 (supplied by IFP) with a hydrochloric solution of $PdCl_2$ (>99%, Fisher) and an aqueous solution of $Ga(NO_3)_3 \cdot xH_2O$ (>99.9%, Alfa), respectively. The wet solids were dried at 70 °C in a rotavapor and then at 120 °C overnight in a furnace. Before impregnation, the γ-Al_2O_3 support (60/80 mesh) was calcined at 700 °C for 2 h. The bimetallic Pd–Ga/Al_2O_3 catalysts were prepared by impregnation of the Pd/Al_2O_3 catalyst with the appropriate amounts of an aqueous solution of $Ga(NO_3)_3 \cdot xH_2O$ to obtain Ga/Pd atomic ratios of 0.2, 0.5, 1 and 2. The catalyst samples dried at 120 °C were designated as "fresh catalysts", and those calcined at 550 °C as "calcined catalysts". These designations did not change for the reduced catalysts. The Pd and Ga contents were measured by energy dispersive X-ray fluorescence spectroscopy (EDX) using a Shimadzu EDX-700HS spectrometer. The chemical compositions of the catalysts used in the present study are given in Table 1, along with the Ga/Pd atomic ratios.

The BET surface areas of the support and the catalysts were determined from the N_2 adsorption isotherms at −196 °C using an automatic Micromeritics ASAP 2010 apparatus after the samples were outgassed at 120 °C overnight. The specific surface areas of all the catalysts are also listed in Table 1.

TPR experiments were carried out using a stainless steel apparatus provided with a TCD, using a gaseous mixture of 5% H_2/Ar (Praxair) at a flow of 30 ml/min (reducing gas) and a catalyst sample of 100 mg. The sample was dried at 120 °C or calcined at 550 °C for 1 h in a flow of air (30 ml/min) and then was cooled to −80 °C using a cold trap (isopropyl alcohol and liquid nitrogen). At this temperature, the reactor was purged with flowing Ar, and the TCD signal was stabilized in the flow of the reducing gas before starting heating. The sample was spontaneously heated from −80 °C to RT by removing the cold trap and then to 700 °C at 10 °C/min using a furnace.

The measurements of CO and H_2 chemisorptions were determined at RT and 80 °C, respectively, by the pulse method, using the same TPR apparatus, which was equipped with a gas injection valve (Valco). The catalyst sample was dried or calcined as explained before, and then reduced in a flow of H_2 (20 ml/min) at 500 °C for 1 h. Then, the reactor temperature was kept at 300 °C in an Ar flow (H_2 chemisorption) or a He flow (CO chemisorption) for 30 min to remove the adsorbed hydrogen. The pulses were sent to the reactor until reaching the saturation. O_2/H_2 titrations were carried out after H_2 chemisorption at 80 °C. O_2 pulses were sent to the reactor to titrate the chemisorbed hydrogen. Then, H_2 pulses were sent to the reactor to titrate adsorbed oxygen.

2.2. Catalytic activity measurements

The n-butane dehydrogenation reaction was carried out in a fixed bed reactor at 500 °C and 1 atm under differential conditions. A feed with a H_2/n-C_4H_{10} molar ratio of 10 was used. The catalyst sample (20 mg) was dried or calcined and reduced, as explained before. The analyses were performed in a Perkin-Elmer Auto-System gas chromatograph, equipped with a 0.19% picric acid/Carbograph packed column and FID detector.

Table 1
Chemical composition (wt%) and surface area of the catalysts.

Catalyst	% Pd	% Ga	Ga/Pd	S_{BET} [m^2/g]
Pd(C)	0.66	0	0	180
Pd0.07Ga(C)	0.66	0.07	0.15	176
Pd0.16Ga(C)	0.66	0.16	0.36	176
Pd0.29Ga(C)	0.66	0.29	0.68	176
Pd0.72Ga(C)	0.66	0.72	1.68	146
0.34Ga(C)	0	0.34	∞	170
Al_2O_3	–	–	–	167

3. Results and discussion

The TPR profiles of the fresh catalysts are shown in Fig. 1. The monometallic Pd catalyst (Pd(F)) shows a reduction peak at 153 °C, which is ascribed to the reduction of $PdCl_2$. This assignment differs from that proposed by Chandra et al. [7], who detected HCl at *ca.* 150 °C during the TPR run of a fresh Pd/Al_2O_3 catalyst. They considered that the reduction of $PdCl_2$ on alumina occurred at room temperature and the formed HCl appeared to be adsorbed on alumina surface at lower temperatures and then desorbed at 150 °C. In the present work, no H_2 consumption was observed at temperatures below 150 °C for the mentioned catalyst and, therefore, the formation and desorption of HCl occurred simultaneously at 153 °C as a result of $PdCl_2$ reduction at this temperature. In order to support this statement, an additional TPR experiment was carried out using a 0.35%Pd/SiO_2 catalyst prepared by impregnation with a $PdCl_2$ solution. Again, an only reduction peak also centered at 153 °C was observed, and the H_2 consumption (expressed as a H_2/Pd ratio) was 1.06, as expected for the reduction of this Pd salt.

The monometallic Ga catalyst shows a reduction peak at 393 °C (Fig. 1). This peak can be attributed to the reduction of $Ga(NO_3)_3$. In the fresh Pd–Ga/Al_2O_3 catalysts, the temperature of the peak attributed to the $PdCl_2$ reduction increased with the smaller dose of Ga to 174 °C and then decreased for higher Ga contents up to 131 °C, while the peak intensity increased continuously with the Ga content. These results can be attributed to the simultaneous reduction of $PdCl_2$ and $Ga(NO_3)_3$, where Pd^0 catalytically assisted the reduction of the Ga salt. An additional catalyst (Pd0.49Ga(F)) was prepared in order to confirm the observed tendencies in the reduction temperature and peak intensity.

The TPR profiles of calcined catalysts are showed in Fig. 2. The calcination treatment produced the segregation of the palladium

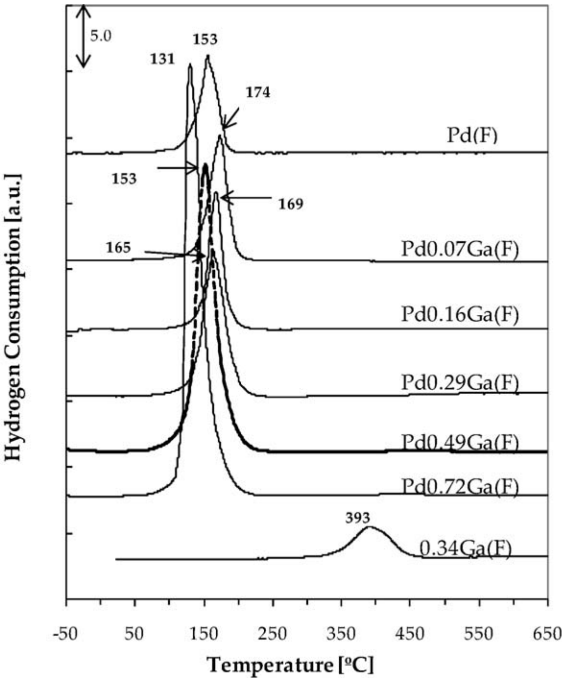

Fig. 1. TPR profiles of the fresh Pd, Ga and Pd–Ga catalysts.