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Microporous and Mesoporous Materials 77 (2005) 245–255

MICROPOROUS AND MESOPOROUS MATERIALS

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Influence of catalyst treatments on the adsorption properties of γ-Al_2O_3 supported Pt, Rh and Ru catalysts

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Received 26 July 2004; received in revised form 10 September 2004; accepted 13 September 2004
Available online 21 November 2004

Abstract

The influence of different treatments (reduction with hydrogen, oxidation with air and treatment with inert gas) of alumina supported Pt, Rh and Ru catalysts on the adsorption of different *n*-alkanes, cycloalkanes, aromatics and chlorinated compounds was studied. The effect of these treatments is twofold: change in the oxidation state of the active metal, and the presence of adsorbed hydrogen or oxygen, which affects the adsorption of the organic compounds. The first effect was characterized by temperature-programmed reduction (TPR) and oxidation (TPO) of catalyst samples, whereas the strength of the O_2 and H_2 adsorption was determined by temperature-programmed desorption (TPD). Inverse gas chromatography (IGC) was used to characterize the adsorption of five *n*-alkanes (C_6–C_{10}) in the 200–230 °C temperature range. Moreover, heats of adsorption, entropies of adsorption and free energy of adsorption, are also reported. Interaction parameters of polar molecules (benzene, chloroform, trichloroethylene, etc.) with the stationary phase have also been determined and compared with those for the *n*-alkanes. It was observed that catalyst treatment affects the adsorption capacity, strength and nature of the studied catalysts.

Keywords: Inverse gas chromatography; Platinum; Rhodium; Ruthenium; Adsorption

1. Introduction

Most of the catalysts used nowadays for the abatement of pollutants from automotive or industrial exhausts are based on noble metals such as platinum, palladium or rhodium. In addition to cleaning up pollutants, these catalysts usually play a key role in industrial processes, which are used to manufacture chemicals and refine crude oil into higher value products such as gasoline, diesel, and jet fuel.

Platinum supported on alumina carriers is widely employed for the combustion of non-halogenated volatile organic compounds [1,2]. Particularly, platinum-based catalysts are highly active for oxidative removal of small amounts of hydrocarbons from gaseous or liquid streams. Except in the case of palladium for the oxidation of alkanes lighter than pentane, platinum is considered to be the most active metal for hydrocarbon oxidation [3]. Rhodium is a widely used noble metal catalyst; one of its most important applications is the manufacture of automobile catalytic converts [4]. Rh/Al_2O_3 is an active catalyst for ammonia and carbon monoxide oxidation and nitric oxide removal [5]. Likewise, rhodium catalysts were successfully used for hydrogen production by steam reforming of alcohols [6]. On the other hand, ruthenium is among the best catalysts for hydrocarbon oxidation [7,8], this metal also being used as a catalyst in several industrial processes such as the Fischer–Tropsch synthesis of paraffins or methanation of carbon dioxide [9].

Supported metal catalysts are generally activated and rejuvenated by alternative cycles of oxidation and

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1387-1811/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2004.09.008

reduction until the system reaches a steady state characterized by thermally stable metal particles and by high and reproducible reaction rates. Oxidation/reduction cycles not only remove carbonaceous deposits but may also induce significant alterations of the catalytic system, as well as its adsorption properties. Studies of catalytic activity of Pt/Al_2O_3 after oxidation/reduction treatment have been carried out [10–12]. In the same way, variations of support properties due to RhO_x species formed on supported rhodium samples were exhaustively studied [5]. However, comparative studies of the adsorption of hydrocarbons on supported metals—key factor in the catalytic process—, as well as the influence of the oxidation state in adsorption capacities are non-existent, to our knowledge.

In our previous work [13], the role of the oxidation state of palladium supported over alumina was analyzed by studying the variations in the adsorption of different hydrocarbons over the oxidized and reduced catalysts. Furthermore, γ-Al_2O_3 is an active catalytic support because it has a high specific surface area (more than $100\,m^2/g$), and marked chemical surface properties. So, its adsorption properties have been compared to those of Pd/Al_2O_3. It was noted that the adsorption characteristics of the palladium catalyst is largely influenced by the sorption properties of the γ-Al_2O_3, whereas a marked influence of the oxidation state of the metal was also observed to be determinant, the reduced Pd catalyst showing the highest adsorption capacity.

Adsorption properties have been evaluated, as in previous works [13,14], by inverse gas chromatography (IGC), a technique extensively used in applications such as characterization of synthetic and biological polymers, copolymers, polymer blends and adsorbents [15,16], fibers [17], coals, foods [18] and carbon blacks [19].

The present research is focused on the relationship between the adsorption properties of different hydrocarbons and the chemical state (oxidation state, presence of adsorbed molecules), of the active metal for alumina-supported Pt, Rh and Ru catalysts. In order to achieve this goal, heats of adsorption, free energy of adsorption and surface free energy, as well as its specific and dispersive components, of different hydrocarbons are reported for the three catalysts in their oxidized and reduced forms.

2. Experimental section

2.1. Materials

Three commercial catalysts, kindly supplied by Engelhard, were used in this work. The commercial catalysts were Pt, Rh and Ru on Al_2O_3, whose textural characteristics (measured by nitrogen adsorption with a Micromeritics ASAP 2000 apparatus) and composition (given by the manufacturer) are listed in Table 1. Catalysts were crushed and sieved to obtain particle sizes between 250 and 355 μm.

Table 1
Chemical and morphological properties of the catalysts used in this work

	Pt/Al_2O_3	Rh/Al_2O_3	Ru/Al_2O_3
Metal loading (%, w/w)	0.5	0.5	0.5
Surface area (BET) (m^2/g)	116	117	118
Mesopore volume (BJH desorption) (cm^3/g)	0.49	0.49	0.50
Average pore diameter (nm)	17	16.5	16.8

All *n*-alkanes (C_6–C_{10}) and the other chemicals (cyclohexane, cycloheptane, benzene, and tetracholoethylene) were of analytical grade (purity at least 99%), supplied by Sigma-Aldrich and used as received. Samples were injected with a 1 μL Hamilton syringe.

2.2. Equipment

Temperature programmed oxidation (TPO) and temperature programmed reduction (TPR) experiments were carried out in a Micromeritics TPD/TPR 2900 apparatus connected to an MS detector (Glaslab 300). The oxidation was conducted by flowing an O_2/He mixture (2% O_2) through the samples, whereas the reduction was carried out by flowing a H_2/He mixture (10% H_2) through them. In both cases, the temperature was increased with a constant rate of 10 °C/min from 50 °C to 900 °C and the flow rate was kept at $50\,cm^3$/min. Oxidation and reduction temperatures were obtained from TPO and TPR, respectively. In order to establish the conditioning temperature for each catalyst, temperature programmed desorption (TPD) was carried out. TPD experiments were carried out in the aforementioned apparatus. Samples of 50 mg of catalyst were heated from 50 to 900 °C at 10 °C/min in a stream of He with a flow rate of $50\,cm^3$/min.

Chromatographic measurements were carried out in a Varian 3800 gas chromatograph equipped with a thermal conductivity detector (TCD). About 4 g of catalyst, with diameters between 255 and 350 mm, were filled into a Supelco Premium grade 304 stainless steel column of a 30 cm length, with passivated inner walls and an inside diameter of 5.3 mm (1/4 in. OD). The columns were packed with the catalyst particles under vacuum and mechanical vibration, analysis of the air flowed through a 15 μm filter prevents the formation of fines. The two ends of the column were plugged with silane-treated glass wool. The columns, packed with commercial catalyst, were then stabilized in the GC system at the temperature considered overnight under a helium flow rate of 30 mL/min. In order to avoid detector contamination, the outlet of the column was not connected to the detector during this period. Measurements were carried out in