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Effect of pretreatment conditions on the catalytic performance of Ni–Pt–W supported on amorphous silica–alumina catalysts
Part 1. Catalysts prepared by a sol–gel method

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Abstract

In this work, the catalytic behavior of Pt–Ni–WO_x supported on amorphous silica–alumina catalysts, prepared by means of a sol–gel technique was tested by hydroisomerization of *n*-hexane in a continuous fixed-bed reactor operating at atmospheric pressure. Temperature-programmed desorption of ammonia (TPDA), temperature-programmed reduction, BET and atomic absorption spectroscopy techniques were used to characterize the catalysts. The results revealed that both catalytic activity and surface acidity of these solids is strongly dependent on their calcination and reduction temperatures. Besides, the collected data showed that platinum interacts with tungsten and this interaction depends on the pretreatment conditions.

Keywords: Platinum; Tungsten oxide; Nickel; Isomerization; Reduction; Acidity

1. Introduction

Environmental and public health reasons are motivating the production of transportation fuels with increase amount of high octane number branched alkanes [1]. These compounds are made by alkylation and by isomerization of straight-chain alkanes. The drawback of these two processes is that they employ harmful and potentially polluting catalysts, such as H_2SO_4, and HF [2]. Nowadays, most working isomerization plants use Pt/Cl–Al_2O_3 catalysts, that have good activity and selectivity at relatively low temperatures (T_{reac} = 110–135 °C) [3]. These catalysts are however candidates for replacement because of their corrosiveness and potential for pollution. Active, stable solid acid catalysts that might replace chlorinated alumina are the halid-free solid acid catalysts. Among them, the best candidate was sulfated zirconia, this latter is actually used in industry [4], but it is said that it may undergo sulfur loss during reaction [5] leading to structural modifications. Therefore, the amelioration or the replacement of this solid by some other superacid catalyst of higher stability, especially for hydrocarbons heavier than butane, is currently desired. Recently bulk tungsten oxide-based catalysts have attracted considerable attention, these solids seems to be potential catalysts for skeletal rearrangements of hydrocarbons [6–10]. The presence of noble metals (Pt or Pd) in such solids was expected to improve their stability but also to activate the isomerization toward saturated hydrocarbons [11–13]. However it was mentioned that, when introducing noble metals directly to bulk tungsten oxides, the metallic function was very sensitive to hydrocarbon poisoning, leading to catalyst deactivation toward saturated alkanes. Thus the necessity to stabilize the bulk oxide and metallic active phases was mentioned and the use of a support seemed to be a potential way [10]. Based on these facts, it would be said that tungsten catalytic performance can be largely modified upon dispersing on oxide supports, where variables such as calcination temperature, nature of the supported phase and surface acidity–basicity as well as the nature of the support used are of paramount importance [14,15]. As mentioned by Maciej and Zbigniew [16], catalytic behavior of supported metals in the conversion of saturated hydrocarbons can be influenced by components, metal and support. The relative contribution of the

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support to the overall reactivity is generally attributed to its surface acidity which could be enhanced by thermal treatments. These thermal pretreatments are related to the catalyst preparation method. Several methods for the preparation of supported metal oxide catalysts have been reported in the literature: mechanical mixing of metal compound and support, ion exchange processes, coprecipitation of metal oxides and support, impregnation and incipient wetness processes [17–21], solid–solid wetting [22] and grafting of metal alkoxide precursors onto a metal oxide support alkoxides [23–26].

A great deal of attention in the last two decades has been given to the use of sol–gel method which is a homogeneous process resulting in a continuous transformation of a solution into hydrated solid precursor (hydrogel). The gelation route (sol–gel process) has several promising advantages over the conventional techniques. It offers better control of the texture, composition, homogeneity and structural properties of the final solids [27–29].

In a previous paper, we have used the latter method to synthesize catalysts based on nickel–tungsten oxide supported on silica–alumina [30] and we have demonstrated that these materials can exhibit an interesting behavior in catalytic hydroisomerization (up to 79.2% and 70% selectivity to isomers in the case of *n*-hexane and *n*-heptane, at 24% and 29% conversions, respectively) [30,31] and dewaxing (the selectivity to isomers, in the case of *n*-decane, amounts to 55% at a conversion of 42.3%) [32] if the rate of hydrogenolysis can be diminished. In this aim, the objective of our work was the incorporation, by different methods, of platinum in Ni–WO_x/SiO_2–Al_2O_3 catalysts and the attempt to study the effect of pretreatment conditions on the activity of the prepared solids. This issue seems important in light of common practice of using alkanes (*n*-hexane) as test molecules for probing the state of metal in supported catalysts. In this first part, we decided to study the catalytic behavior of $(Ni_xPt_y)_{BC}$ samples, prepared by sol–gel method where the platinum was incorporated before calcination.

2. Experimental

2.1. Catalyst preparation

We studied the effects of the pretreatment conditions on the activity of Ni–Pt–WO_x/SiO_2–Al_2O_3 catalysts for *n*-hexane hydroisomerization. In this order, nine catalysts were prepared and were treated with different conditions. The prepared solids noted $(Ni_xPt_y)_{BC}$ (Table 1), where *x* and *y* indicate the percentage of nickel and platinum in the catalyst, and BC indicate that the incorporation of Pt was done before calcination, having the same amount of tungsten (10%) and a constant SiO_2/Al_2O_3 ratio (1.83), were prepared using a sol–gel method.

A sol was obtained by mixing, under vigorous stirring, an aqueous solution of nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) preliminarily acidified by nitric acid with the required amounts of aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$), sodium tungstate ($Na_2WO_4$) and hexachloroplatinic acid (H_2PtCl_6) solutions. To the sol obtained, under vigorous stirring, an aqueous solution of sodium silicate (Na_2SiO_3) was added. Next, ammonium sulfate was used to activate the prepared gel at 60 °C (liquid to solid ratio equal to 30), under reflux conditions in a thermostat and over a period of 48 h (this unit operation was repeated several times). Then the solid was washed with hot water (60 °C), dried at 120 °C for 4 h and finally calcined in the temperature range 300–700 °C for 5 h. A heating rate of 10 °C/min was used.

Table 1
Chemical composition of the $(Ni_xPt_yW/ASA)_{BC}$ samples (noted $(Ni_xPt_y)_{BC}$)

Catalyst	%Ni	%Pt	%W	SiO_2/Al_2O_3
$Ni_{12}Pt_0$	12	0.0	10	1.83
$(Ni_{12}Pt_{0.1})_{BC}$	12	0.1	10	1.83
$(Ni_{12}Pt_{0.4})_{BC}$	12	0.4	10	1.83
$(Ni_{12}Pt_1)_{BC}$	12	1.0	10	1.83
$Ni_{15}Pt_0$	15	0.0	10	1.83
$(Ni_{15}Pt_{0.1})_{BC}$	15	0.1	10	1.83
$(Ni_{15}Pt_{0.4})_{BC}$	15	0.4	10	1.83
$(Ni_{15}Pt_1)_{BC}$	15	1.0	10	1.83
$Ni_{17}Pt_0$	17	0.0	10	1.83
$(Ni_{17}Pt_{0.1})_{BC}$	17	0.1	10	1.83
$(Ni_{17}Pt_{0.4})_{BC}$	17	0.4	10	1.83
$(Ni_{17}Pt_1)_{BC}$	17	1.0	10	1.83

For comparison purposes, Pt-free catalysts containing 12%, 15%, 17% Ni and 10% of tungsten supported on amorphous silica–alumina were prepared as described in Ref. [31].

2.2. Catalyst characterization

The specific surface area of the catalysts was determined by the BET method. The adsorption isotherm was measured at the temperature of liquid nitrogen. Before the adsorption was measured, all samples were degassed at 350 °C for 30 min, and then reduced at 430 °C, with hydrogen, for 1 h. The tungsten, nickel and platinum concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The surface species reducibility was determined by temperature-programmed reduction (TPR) using an Ohkura TP 2002 S equipped with a thermal conductivity detector. After loading, samples were pretreated at 500 °C in an air flow for 3 h and afterward cooled at room temperature. Next, they were stabilized in an Ar/H_2 (95/5 volumetric ratio) flow. The temperature and detector signals were then continuously recorded while heating at 5 °C/min to 600 °C.

The acidic properties of samples were studied by means of temperature-programmed desorption of ammonia (TPD of NH_3). Prior to TPD experiments, the sample was pretreated, for 3 h at the desired calcination temperature, with an oxygen flow, then purged by flowing helium at 300 °C, and then reduced, at 430 °C for 2 h, in a hydrogen flow. After reduction, the sample was further dried in flowing He at 300 °C for 1 h and then cooled to room temperature. When the system become steady, ammonia was adsorbed at 100 °C for 30 min (using a 10% NH_3/He carrier gas) and then the sample was subsequently purged, at the same temperature, by flowing He (100 ml/min) for 1 h to remove the excess and physically adsorbed NH_3. The TPD