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Effect of the impregnation order on the nature of metal particles of bi-functional Pt/Pd-supported zeolite Beta materials and on their catalytic activity for the hydroisomerization of alkanes

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Abstract

A series of mono- and bi-metallic (Pt and/or Pd) impregnated zeolite Beta samples have been prepared, characterized using a number of experimental techniques and catalytically tested for the hydroisomerization of a mixture of light paraffins. In particular, the effect of the order of Pt and Pd impregnation on the type/structure of the metallic species of the zeolite support and on the catalytic activity has been studied. Studied samples included a zeolite Beta in which both Pt and Pd (0.5 wt% of each) were simultaneously impregnated (and subsequently calcined and reduced) and two equally metal-loaded samples where the metals were sequentially impregnated (samples Pt*–Pd/Beta and Pd*–Pt/Beta, in which Pt and Pd were impregnated first, respectively). Mono-metallic samples were also prepared for comparison. TPR, DR–UV–visible, TEM, and XAS studies confirm that the order of impregnation plays a key role in the formation of metallic particles, influencing aspects as decisive in their catalytic behavior as their size, their dispersion and their composition (e.g., mono- or bi-metallic). The initial impregnation of Pd and subsequently of Pt produces a higher number of hetero-metallic (Pt–Pd) bonds than the simultaneous co-impregnation and especially for the impregnation in reverse order, which does not produce Pt–Pd bonds in a detectable amount. Based on the results from the different characterization techniques, a model of the metal distribution and composition of the particles was proposed for each bi-metallic sample. In good agreement, the order of the catalytic activity was found to be Pd*–Pt/Beta > Pd–Pt/Beta > Pt/Beta > Pt*–Pd/Beta > Pd/Beta, making clear that not only the presence of both metals, but also an adequate preparation method generating a high number of hetero-metallic bonds must be taken into account to improve the catalytic properties in relation to the mono-metallic samples.

Keywords: Platinum; Palladium; Bi-metallic catalysts; Zeolite Beta; Hydroisomerization; EXAFS; TPR; Diffuse-reflectance UV–visible

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1. Introduction

Octane ratings in gasoline are conventionally boosted by addition of aromatic and oxygenated compounds. However, as a result of increasingly stringent environmental legislation, the content of these compounds in gasoline is being restricted and thus industry has been forced to investigate alternative processes to reach the required octane levels. The hydroisomer-

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ization of light linear paraffins, such as n-hexane and n-heptane, to produce the corresponding branched isoparaffins, is a viable alternative [1]. Indeed, the isomerization of such linear alkanes results in an outstanding increase of the research octane number (RON). For instance, this value is only 25 for n-hexane, while it is 74 for the average of its mono-branched isomers and even higher (98) for the multi-branched ones.

These reactions are commercially performed using bi-functional catalysts consisting of a metal supported on either chlorinated alumina or zeolites [2–5]. Their bi-functionality originates from the acidity of the support and the hydrogenation–dehydrogenation activity of finely dispersed metal particles. The isomerization mechanism requires an initial dehydrogenation of a n-paraffin (generating the corresponding n-olefin) over a metal site, followed by an isomerization via a carbocationic intermediate in an acid site, giving rise to the iso-olefin which is finally hydrogenated on a metal site to form an iso-paraffin [1]. Although alumina supported catalysts are more active at low temperatures, they are highly sensitive to poisoning by both water and sulfur and therefore require constant regeneration with chlorine which is hazardous and can potentially alter the structure of the precious metal. Consequently, enormous research effort has focused on using the more stable and environmental-friendly zeolite-based catalysts, since they possess the necessary acidity, internal structure and pore size distribution to be catalytically active and selective for these hydroisomerizations [6–18].

The most suitable zeolite catalysts for hydroisomerization are those containing Pt- or Pd-supported on zeolites mordenite or Beta [5,6]. It is well known that the final conversion and selectivity depend on a number of parameters including the acidity and pore structure of the zeolite, the nature and dispersion of the supported metal, and operating conditions such as temperature and contact time [7,19–21]. The maximum isomer yield is reached when the metal and acidic functions of the catalyst are well balanced [22]. The nature of the metal clearly affects the final product distribution, which can be understood in terms of the type of mechanisms involved in the reaction. For example, Blomsma et al. [23] showed that the n-heptane conversion to iso-heptanes over Pd/H-Beta and Pt/H-Beta mainly occurs via the classical mono-molecular mechanism, although parallel mechanisms take place: a bi-molecular mechanism (dimerization–cracking) mainly in Pd/H-Beta catalyst, and a cracking mechanism (hydrogenolysis) in the case of the Pt/H-Beta catalyst, because of the higher activity of Pt in hydrogenation processes.

The catalysts being bi-functional, the improvement of their activity involves the modification of either the properties of the zeolitic support or alternatively the properties of the supported metal. In this sense, the optimization of the preparation conditions, such as calcination/reduction temperature or heating rate, has been extensively studied [24–27]. Concerning the supported metal, significant improvements on the catalytic performance have been reached by alloying with a second metal. The structures of the resultant bi-metallic species are far from being well-understood, mainly due to the fact that they are composed of very small and well-dispersed particles. Among others, bi-metallic Pt–Pd catalysts have been deeply studied for isomerization reactions [23,28]. Blomsma et al. [23] described how the addition of up to a 20 wt% of Pd over Pt/H-Beta (expressed as percentage of the Pt load) improved the metallic dispersion and reduced the above-mentioned side cracking mechanisms. Furthermore, the use of the bi-metallic Pt–Pd-supported catalyst has been reported to enhance the sulfur tolerance in isomerization and hydrogenation processes by increasing the number of electron-deficient metal sites and thus inhibiting the irreversible adsorption of sulfur [28–32]. In addition, its hydrogenation activity increases with respect to a mono-metallic catalyst [33–35]. A parallel study on this sulfur tolerance with the catalysts obtained in this work is in preparation.

Here we focussed our attention to the issue of the order of impregnation of Pt and Pd over zeolite Beta, which to our knowledge has not been previously addressed, by preparing catalysts via simultaneous and sequential impregnation of Pt and Pd. The bi-metallic Pt–Pd-supported catalysts have been characterized by temperature-programmed reduction (TPR), diffuse reflectance (DR) UV–visible spectroscopy, X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM) and their results compared with those of the mono-metallic ones. The structural properties deduced from these techniques have been correlated with their performance in the hydroisomerization of a feed composed of n-hexane, cyclohexane, and n-heptane.

2. Experimental

2.1. Synthesis

Mono-metallic Pt- and Pd-supported (0.5 wt%) zeolite samples were prepared by the incipient wetness method, using Pt(II) or Pd(II) tetraamine nitrate (99%, Sigma–Aldrich) as metal sources and a H-Beta zeolite with a SiO_2/Al_2O_3 ratio of 25 (CP814-E, purchased from Zeolyst Int.) as support. Bi-metallic catalysts (0.5 + 0.5 wt%) were also prepared according to the following three different procedures:

(a) Co-impregnation of H-Beta zeolite with a solution of both metal salts: sample Pt–Pd/Beta.
(b) Impregnation of Pd over a reduced (in H_2 at 400 °C) Pt/Beta sample: sample Pt*–Pd/Beta (the asterisk indicates the metal impregnated first).
(c) Impregnation of Pt over a reduced (in H_2 at 400 °C) Pd/Beta sample: sample Pd*–Pt/Beta.

The solids were loaded into the catalytic reactor (see reactor details below) and subsequently calcined in situ before being reduced prior to use in the reaction. Calcination was performed using an O_2 stream at a flow-rate of 20 ml min^{-1} at 400 °C for 30 min (heating from room temperature at a rate of 5 °C min^{-1}). After flushing with N_2 at 20 ml min^{-1} at 400 °C for 15 min, the sample was reduced in an H_2 stream at 20 ml min^{-1} at the same temperature for 1 h.