Pt–Re–Ge/Al₂O₃ catalysts for n-octane reforming: Influence of the order of addition of the metal precursors

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ABSTRACT

Trimetallic Pt–Re–Ge supported catalysts for naphtha reforming were prepared by successive impregnation of suitable precursors on gamma alumina. The order of addition of these precursors was varied and its influence on the catalytic properties was assessed by means of the model reaction of n-octane reforming. It was found that the order of addition of the metal precursors greatly affects the performance and properties of these systems, which in turn is closely related to the first impregnated metal. When platinum is impregnated before rhenium and germanium the metals are reduced separately resulting in catalysts with high dehydrogenation activity and low hydrogenolysis activity. On the other hand, the impregnation of germanium before the other metals leads to the production of catalysts with low activities for dehydrogenation and high activity for hydrogenolysis, as a consequence of the strong interactions among the metals. By adding rhenium before the other metals, catalysts with intermediate behavior are produced. For all catalysts, platinum interacts more strongly with rhenium than with germanium. The order of addition does not modify the acidic properties of the support but germanium and rhenium seem to change the acidity of the support in the vicinity of the metals, causing differences in the selectivity to aromatic compounds and paraffinic isomers. These features can be used to tailor catalysts with high selectivity for the production of aromatics or isoparaffins, depending on the purpose of the reforming process. The RePtGe catalyst has the highest selectivity to branched isoparaffins and then can be used to produce isoparaffins-rich gasoline while a reformate rich in aromatics can be obtained by using the GeRePt catalyst.

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1. Introduction

Catalytic naphtha reforming is by far the main commercial route for producing aromatics, high value intermediates used in the manufacture of plastics, nylon, rubbers and polyester fibers, among others. This process is also used to convert linear hydrocarbons into branched ones in order to improve the octane number of gasoline. Hydrogen is obtained as a by-product, which is mainly used in hydrotreating processes such as hydrodesulfurization and hydrogenation. According to the current environmental laws, the aromatic content in fuels should be even lower than the previous values. The benzene content in American gasolines should be at maximum 0.62 vol.% by 2015, according to the new regulations of the US Environmental Protection Agency (MSAT II). The restrictions for benzene, the major supplier of octane number to gasoline pool, make important its replacement by other compounds of high RON and with no nosxious environmental impact, such as branched isoparaffins.

The huge and complex network of chemical reactions occurring in the catalytic reformer is basically made of only two kinds of reactions: acid-catalyzed and metal–catalyzed ones. Therefore, naphtha reforming catalysts must be bifunctional. The metal function is usually supplied by platinum metal particles highly dispersed on a porous carrier, typically chlorided gamma–alumina. Platinum provides the essential sites for hydrogenation and dehydrogenation. The acid function is supplied by the support itself. While gamma-alumina is amphoteric, the addition of chlorine promotes its acidity and gives to the support the ability to catalyze isomerization and cyclization reactions [1].

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