



# In<sub>2</sub>O<sub>3</sub>-doped Pt/WO<sub>3</sub>/ZrO<sub>2</sub> as a novel efficient catalyst for hydroisomerization of *n*-heptane

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## ABSTRACT

A series of Pt catalysts supported on In<sub>2</sub>O<sub>3</sub>-doped (In/Zr molar ratio = 0.01–0.04) WO<sub>3</sub>/ZrO<sub>2</sub> (9–24 wt.% WO<sub>3</sub>) have been tested for the hydroisomerization of *n*-heptane at 473 K. Several techniques including X-ray diffraction, N<sub>2</sub> adsorption, CO chemisorption and X-ray photoelectron spectroscopy were applied to characterize the physicochemical properties of the as-synthesized materials. The catalytic activity is strongly dependent on the surface WO<sub>3</sub> loading and In/Zr ratio. The maximum activity was observed for the sample with a In/Zr molar ratio of 0.02, which gave 72% *n*-heptane conversion and 96% C<sub>7</sub> isomer selectivity at 473 K, and can be kept constant over 80 h under reaction reactions. The incorporation of small amounts of In<sub>2</sub>O<sub>3</sub> into Pt/WO<sub>3</sub>/ZrO<sub>2</sub> increases the activity significantly (from 37% to 72%) and improves the isomerization selectivity moderately (from 90% to 96% at a conversion of 72%). The results of cumene cracking reveal that the remarkable activity and selectivity of the In<sub>2</sub>O<sub>3</sub>-promoted catalysts are caused by an enhancement in the number of Brønsted acid sites under reaction conditions and in the hydride transfer reaction rate of isomerized carbenium ions with hydride ions originating from hydrogen molecules.

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## 1. Introduction

Under the pressure of more stringent environment protection regulations, the specifications for diesel and gasoline impose strong restrictions on sulfur and aromatic compounds, and there has been a sharp rise in the demand for processes that can produce clean fuels with non-aromatic hydrocarbons and high octane numbers [1,2]. The isomerization of C<sub>7+</sub> *n*-alkanes (C<sub>7</sub> and higher paraffins) to their branched isomers with high octane number as octane-enhancing components is among the most effective routes to compensate for the loss of octane number caused by removal of aromatics, thus it has aroused new interest [3–5]. Paraffin isomerization processes to C<sub>4</sub>–C<sub>6</sub> *n*-alkanes have already been commercialized using three types of catalysts, i.e. Pt/Al<sub>2</sub>O<sub>3</sub>-Cl, Pt/zeolite and Pt/SO<sub>4</sub><sup>2–</sup>/ZrO<sub>2</sub> [6]. However, there exist no commercial hydroisomerization processes for the *n*-alkanes composed of 7 carbon atoms and higher. During C<sub>7+</sub> *n*-alkanes isomerization, cracking by β-scission easily occurs, resulting in a low selectivity for isomerization. It is thus desired to develop the catalysts that can minimize cracking while achieving high yields of branched isomers for the isomerization of *n*-heptane and larger paraffins.

Various catalysts have been explored in the isomerization of *n*-heptane, mainly base on Pt- or Pd-bearing catalysts supported on SAPO molecular sieves [7,8], zeolite [9–12], heteropolyacid [13,14], SO<sub>4</sub><sup>2–</sup>/ZrO<sub>2</sub> [15–17] and WO<sub>3</sub>/ZrO<sub>2</sub> [18–23]. Among all the studies catalysts, Pt/WO<sub>3</sub>/ZrO<sub>2</sub> has recently emerged as the most promising of a new generation of catalyst due to its high catalytic efficiency [5]. Compared with the traditional Pt/zeolite catalysts, Pt/WO<sub>3</sub>/ZrO<sub>2</sub> exhibits higher activity at lower temperature due to its stronger acidity [5,20]. Iglesia and co-workers [18,19] reported that Pt/WO<sub>3</sub>/ZrO<sub>2</sub> showed a high selectivity for *n*-heptane isomerization than Pt/SO<sub>4</sub><sup>2–</sup>/ZrO<sub>2</sub>, which is due to the fact that the desorption of branched carbenium ions as isomer products from the former catalyst is faster than that from the latter one, resulting from a high availability of surface hydrogen on Pt/WO<sub>3</sub>/ZrO<sub>2</sub>. Tungstated zirconia (WO<sub>3</sub>/ZrO<sub>2</sub>), first reported by Hino and Arata [24], has drawn increasing interest in the last years due to their promising application in acid-catalyzed reactions of industrial importance, such as *n*-alkanes isomerization and esterification [23,25–28]. Hua and Sommer [29] found that the addition of small amounts of Al<sub>2</sub>O<sub>3</sub> to the Pt/WO<sub>3</sub>/ZrO<sub>2</sub> system enhanced significantly the catalytic activity for *n*-heptane isomerization. This promoting effect of Al<sub>2</sub>O<sub>3</sub> on Pt/WO<sub>3</sub>/ZrO<sub>2</sub> was later confirmed by Xu and Ying [30]. Liu et al. [31] reported that adding an appropriate amount of ZnO additives to Pt/WO<sub>3</sub>/ZrO<sub>2</sub> can stabilize the tetragonal phase of ZrO<sub>2</sub> and affect acidity, thus enhance moderately the selectivity and yield of C<sub>7</sub> isomers for *n*-heptane isomerization.

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