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Kinetics of bifunctional isomerization over carbides (Mo, W)

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Abstract

Kinetics of isomerization of *n*-heptane was studied over three types of catalysts: a W_2C-type carbide and two composites of molybdenum carbide and tungsten oxide. The precursors were carburized using ethane (10 vol.% C_2H_6/H_2) following a temperature programmed reaction up to 863 K. The catalytic test conditions were as follows: total pressure of 1 or 6 bar, temperature range between 543 and 623 K, and H_2/nC_7 molar ratio equal to 14.8. The selectivity towards isomers was at least equal to 89% for the full range of conversion. The global consumption of *n*-heptane is a first order reaction to the reactant. By simulating the global kinetics of the reaction, the experimental curves lead us to calculate rate constants. We show that, at conversion higher than 60%, the reaction becomes a two-way process. The $2mC_6/3mC_6$ molar ratio was close to 1, corresponding to a bifunctionnal isomerization. Isomerization mechanism can be explained by three cycles: the first cycle, corresponding to the dehydrogenation of the *n*-alkane on metallic sites, is closed to equilibrium; the second corresponds to the isomerization of *n*-alkene into *iso*-alkene on acidic sites; finally, the third cycle corresponds to the hydrogenation of *iso*-alkene into *iso*-alkane on metallic sites. We showed that the global kinetics of the reaction only occurs on acidic sites.

Keywords: Carbides; Bimetallic; Isomerization; *n*-Heptane; Two-way process

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1. Introduction

New constraints on the octane number of the unleaded gasoline, as well as health and environmental protections, lead to new targets. It is necessary to develop processes allowing to obtain reformulated gasolines, in order to decrease harmful emissions, while maintaining the properties necessary to the correct operation of engine.

Transition metal carbides are well known to have catalytic properties similar to those of group VIII metals [1].Transition metal oxides and carbides have been found to be potential materials for hydroisomerization [2,3]. It has been shown that they can become two-way catalysts with a dioxygen treatment at high temperature. In this paper, the synthesis of carbides were performed in order to limit the carburization process and to preserve a high content of oxygen atoms from the initial oxide, so as to control the acidic function owing to these residual oxygen species. One way consists in carburizing the oxide precursor at low temperature, using ethane as carburizing agent [4].

Isomerization of *n*-heptane was chosen as a model reaction to test the reactivity of the catalysts in hydroisomerization of paraffins. Molybdenum carbide [5], as well as supported noble metal, follows a metallic like isomerization process, the major route being alkane hydrogenolysis, resulting in a poor selectivity in isomerization. In the presence of zeolite or acidic materials, acidic isomerization process takes place, cracking being the major route.

Tungsten oxynitrides [6] or Pt/WO_x–ZrO_2 [7] present a two-way isomerization behavior, where the two functions, metallic and acidic, are present.

Only a few papers have been dedicated to the kinetics of bifunctional isomerization over carbide materials. The present paper deals with the design of bifunctional catalysts

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and with the global kinetics of isomerization of *n*-heptane over these materials.

2. Experimental

2.1. Materials

Molybdenum oxide (MoO_3, Aldrich, 99.99%), tungsten oxide (WO_3, Acros, 99.995%) and ammonium metatungstate ($(NH_4)_6W_{12}O_{39}\cdot xH_2O$), Aldrich, 99.99%) were used as precursors.

Commercial gases employed (C_2H_6, Ar, O_2 and H_2), *n*-heptane (Aldrich, 99+%) and hydrochloric acid (Carlo Erba, 37%) were used as received.

2.2. Catalyst preparation

A W_2C-type catalyst was prepared using ammonium metatungstate as a precursor: 1.5 g of $(NH_4)_6W_{12}O_{39}\cdot xH_2O$ was introduced into a tubular quartz reactor and a 10 vol.% C_2H_6 in H_2 (total flow rate = 10 L/h) was passed through the reactor. The temperature was increased from room temperature (RT) up to 500 °C (773 K) at 240 °C/h and then from 500 °C (773 K) up to 590 °C (863 K) at 60 °C/h, the reactor was kept at 590 °C for 1.5 h. The reactor was then rapidly cooled to RT under a pure dihydrogen flow. Then, the flow was switched to pure argon and the reactor was purged during 10 min. The passivation step has been performed in 1 vol.% O_2 in argon, during 1 h.

The material was analyzed by X-ray diffraction (XRD) (Fig. 1) and by elemental analysis. The nominal composition was $WC_{0.8}O_{0.7}$.

The Mo_2C–WO_2 catalyst was prepared by crushing a mixture of MoO_3 and WO_3 (W/Mo molar ratio equal to 1) in a mortar. Ethanol was added to increase dispersion [8], and subsequently evaporated at room temperature. The carburization procedure was the same as for the W_2C-type catalyst.

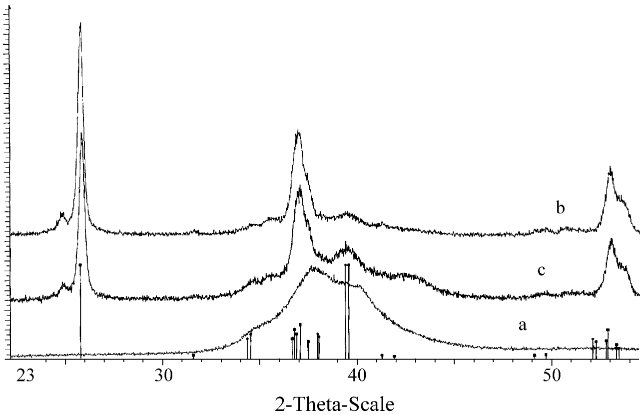

Fig. 1. XRD diffractograms for W_2C (a), Mo_2C–WO_2 (b) and $H_xMoO_yC_z$–Mo_2C–WO_2 (c). (♦) 00-035-0787 Molybdenum carbide MO_2C; (■) 00-032-1393 tungsten oxide WO_2; (●) 00-035-0076 tungsten carbide W_2C.

The temperature was raised from RT to 600 °C (873 K) at 60 °C/h and kept at this temperature for 2 h. The material was also submitted to a passivation step. It was analyzed by XRD (Fig. 1) and submitted to elemental analysis. The nominal composition was $MoWC_{0.5}O_{0.6}$.

The molybdenum bronze was synthesized using a method described elsewhere [9]. WO_3 powder was added in the same time as MoO_3 powder. The carburization step was exactly the same as for Mo_2C–WO_2 catalyst. The material was characterized by XRD (Fig. 1) and elemental analysis gave the nominal composition $HMoWO_{1.7}C_{0.5}$.

2.3. Standard reaction conditions

The isomerization of *n*-heptane was carried out in a flow reactor at either 300 °C (573 K) and 1 bar on composite materials ((Mo,W)C) or 350 °C (623 K) and 6 bar on W_2C-type catalyst. The *n*-heptane was introduced either by a high-pressure pump (Gilson) or by saturating flow of H_2 with *n*-heptane.

Temperature programmed analyses were carried out on two HP 5890 chromatograph equipped with a PONA or an Al_2O_3–KCl column, respectively.

Before reaction, (Mo,W)C materials were pretreated in situ at 500 °C in flowing H_2 (18 cm^3/min). The W_2C-type catalyst was pretreated as follows: 150 °C, 6 bar of dihydrogen, 150 cm^3/min, for 1 h.

The H_2/*n*-heptane feed ratio was set to 14.8. Contact times were calculated as the ratio between the catalyst volume (cm^3) and the total flow rate (hydrogen and *n*-heptane, cm^3/min).

3. Results

Fig. 2A shows the consumption of nC_7 and the formation of single-branched (SB) and multi-branched (MB) isomers, versus contact time, over the W_2C-type catalyst, at 350 °C (623 K) and under a total pressure of 6 bar. Similarly, the consumption of nC_7 and the production of single-branched and multi-branched isomers over $MoWC_{0.5}O_{0.6}$ and $HMoWO_{1.7}C_{0.5}$ catalysts, at 300 °C (573 K) and atmospheric pressure are reported in Fig. 2B and C, respectively. Fig. 3 shows the linear transforms of the disappearance of *n*-heptane over the three catalysts, corresponding to a global first order reaction.

On the W_2C-type catalyst, the first order reaction is observed up to a conversion of 60%. The conversion in single-branched isomers reaches a maximum and then decreases. Their concentrations go through a maximum for a contact time close to 0.27 s (Fig. 2A). At low contact time, the concentrations of multi-branched products are weak.

The reaction product distribution is given in Table 1. In all cases, the selectivity towards isomers products (defined by the percentage of nC_7 converted to *iso*-heptanes) is at least equal to 89%. The major products are monomethylhexanes