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Isomerization of *n*-hexane on heteropolyacids supported on SBA-15. 1. Monofunctional impregnated catalysts

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ABSTRACT

Monofunctional hybrid materials based on Keggin-type heteropolyacids supported on mesostructured silica were used in isomerization of *n*-hexane. The heteropolyacids, namely $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, were immobilized onto SBA-15 type silica by incipient wetness impregnation. The resulting catalysts were thoroughly characterized by N_2 adsorption–desorption isotherms, XRD, ^{31}P NMR, TGA and FT-IR. These hybrid materials were active for the gas-phase isomerization of *n*-hexane. Various reaction parameters and catalyst features were investigated: tungsten loading, reaction temperature, contact time, pressure and nature of the polyanion. All results could be explained by a competition of the mono- and bimolecular mechanisms. Supported tungstosilicic acid was intrinsically more selective than phosphotungstic counterpart and should be preferred for applications in isomerization of alkanes. A deactivation of the catalysts was observed due to the poisoning of acid sites by coke formation.

1. Introduction

The isomerization of alkanes, such as *n*-hexane, is one of the best procedures to achieve high quality of clean gasoline. It allows the formation of branched alkanes, which is an interesting option to increase the research octane number (RON), hence improving the performance of vehicle motors. This reaction also satisfies the specifications of gasoline production, such limited amount of aromatic compounds, olefins or methyl tert-butyl ether (MTBE) which is known to be a potential carcinogenic [1–3]. One of the current challenges is to obtain a catalyst capable of high global conversion of *n*-hexane with high selectivity into its four branched isomers: 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (2,2DMB) and 2,3-dimethylbutane (2,3DMB), without catalyst deactivation. In particular, the main objective of the present study was to achieve the highest selectivity for the di- branched isomers, 2,2-DMB and 2,3-DMB, as they have the highest octane number.

Currently, bifunctional catalysts are used in the industrial isomerization processes [4]. One function is an acid catalyst while the other is a hydrogenation-dehydrogenation catalytic system (typically a transition metal). Typical examples are based on platinum catalysts supported either on chlorinated alumina [5] or mordenite [6], the last ones being considered as the new generation of catalysts. They have the advantage to be easy to use and to be less sensitive to the presence of poisons such as sulfur and water in the feedstock allowing for longer lifetimes. Nevertheless, they have some disadvantages such as a low improvement in octane number, high operating temperatures, high hydrogen pressure and lower acidity [4,7,8]. As a consequence, the development of new acid catalyst avoiding these problems is highly required.

Heteropolyacids (HPAs) have unique acid–base and redox properties, which render them valuable in a number of applications [9]. Their strong acidity makes them attractive candidates to tackle the current challenges in alkanes isomerization. However, a main drawback is their low surface area ($1–10\,m^2/g$). In order to overcome this problem, two main methods have been described in the literature: the immobilization of HPAs onto large surface area supports to improve the dispersion of the active phase or the direct synthesis of acidic porous salts [10,11].

In the past few years, some catalytic studies were undertaken to confirm the HPAs ability to perform the skeletal isomerization of *n*-alkanes, such as *n*-butane, *n*-pentane, *n*-hexane or *n*-decane [12–16]. In particular, Keggin-type HPAs, namely $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW), were tested in the acid-catalyzed isomerization of *n*-hexane [17]. A. V. Ivanov et al. showed that HPW supported on ZrO_2 was highly active in *n*-hexane isomerization [18]. N. Essayem et al. observed a high selectivity toward

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isomerization with HPAs catalysts and a higher activity than with mordenite [19]. Hubaut et al. observed a better performance of HPW/SiO_2 compared to the $HSiW/SiO_2$ system for *n*-hexane isomerization when used in combination with mixed Ce–Pd oxides [20]. A. Gherib et al. confirmed that silica-supported heteropolyacids were active in isomerization, but the catalysts were very easily deactivated by coke deposition [21].

In view of these challenges, our first approach was to synthesize monofunctional hybrid materials containing only the acid function. For this purpose, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were immobilized onto SBA-15 silica via the classical impregnation method. SBA-15 type silica is well-suited as a support for immobilizing functional groups. Its large, uniform pore diameter (~6 nm) provides ample room for reactant and product diffusion, and its thick walls provide hydrothermal stability. The main goal of this work was to study the activity and selectivity of these systems in *n*-hexane isomerization and determine the optimal catalyst features to achieve higher performance.

2. Experimental

2.1. Synthesis of the catalysts

The synthesis of the SBA-15 was performed following the protocol described by Zhao et al. [22–24]. The triblock copolymer Pluronic 123® (P123) was used as organic structure directing agent (SDA) and 16 g of this material were dissolved in 500 mL of a 1.9 M HCl solution at 40 °C. After dissolution of the P123, 32.64 g of the silica precursor, tetraethoxysilicate (TEOS), were added dropwise and the solution was left under vigorous stirring for 20 h at 40 °C. The suspension was then introduced in an autoclave and aged for 20 h at 100 °C. After the hydrothermal treatment, the resulting solid was filtered and washed carefully with distilled water. The remaining organics were then calcined under flowing air at 490 °C for 16 h.

The monofunctional hybrid materials were synthesized by the wetness impregnation method. The desired amount of HPA ($H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$) was dissolved in 30 mL of methanol. The solution was added drop by drop over 3 g of calcined SBA-15 slightly agitated. After evaporation of the solvent, the powder was dried overnight in an oven at 80 °C. The resulting materials are denoted **HPW/SBA-15** and **HSiW/SBA-15** in the following.

2.2. Characterization of the catalysts

FT-IR spectra were recorded from KBr pellets, in the 400–4000 cm^{-1} range, on a Nicolet 5700 spectrometer in the absorbance modes. The ^{31}P MAS NMR spectra were recorded on a Bruker DSX-500 spectrometer operating at 202.40 MHz with a classical 4 mm probehead allowing spinning rates up to 10 kHz. A total of 3000 scans was acquired for each sample. The x-ray diffraction patterns of samples were recorded on a Bruker D5005 diffractometer by using the Cu Kα monochromatic radiation (($\lambda = 1.54184$ Å). N_2 adsorption–desorption were performed on a Micromeritics ASAP 2020 system. The samples were evacuated at 350 °C for 12 h before the experiment. The surface area was obtained from the BET equation and the pore size distribution was calculated by the BJH method applied to the desorption branch of the nitrogen adsorption/desorption isotherm. Elemental analyses were made by ICP-AES with an ICP spectroflamme-D from a solution obtained by treatment of the solid catalyst with a mixture of HF, HNO_3 and H_2SO_4 in a Teflon reactor at 150 °C. Thermogravimetric analysis was performed on a Mettler Toledo TGA DSC 1 apparatus. The samples were heated from room temperature to 1000 °C at a rate of 3 °C min^{-1}.

2.3. Catalytic experiments at atmospheric pressure

The reaction at atmospheric pressure was carried out in a fixed bed dynamic flow reactor. The synthesized hybrid material was weighted and charged into a stainless steel ½" cylindrical reactor (diameter 1 cm and length 20 cm). The catalyst bed was 5 cm. The reactor was then placed in an oven into a hot box. Before allowing the *n*-hexane feed to pass through the reactor, the catalyst was activated to remove the remaining water molecules. This was made by treatment under argon (flow rate 5 mL·min^{-1}) during 2 h at 200 °C. After activation of the catalyst, the gas mixture (5 mL·min^{-1} of argon flow in contact with liquid hexane (>99% provided by Sigma–Aldrich), at 25 °C, partial pressure of *n*-hexane = 151 torr, ratio hexane/argon = 0.25) was allowed to pass through the reactor at the desired temperature. The experiment was conducted during 12 h. The reaction products were analyzed online by Gas Chromatography (GC) equipped with a flame ionization detector (FID) and a nonpolar capillary column KCl/Al_2O_3 (Varian Capillary column; 50 m × 530 μm × 15 μm).

2.4. Catalytic experiments at high pressure

The experiments were performed in a PID Eng & Tech® reactor, placed in an oven into a hot box. The operational pressure was controlled by a micrometric regulating valve at 4 or 15 bar. The reactants could be introduced as gas or liquid into the system. The introduction of gas (argon in this case) was monitored by a Bronkhorst® mass flow-meter. *n*-hexane was introduced in liquid state via a high pressure liquid syringe from Top Industrie® PMPH 50-500 and vaporized in the hot box (at 200 °C) before reaching the catalyst bed. The catalysts were charged into a stainless steel ½" cylinder reactor (inner diameter 1 cm, total length 20 cm, catalyst amount: 1 g). After connection to the gas lines and extensive purging with argon, the temperature and pressure were increased to the desired values at a rate of respectively 2.5 °C min^{-1} and 0.1 bar min^{-1}. After reaching the reaction conditions, a mixture of *n*-hexane in argon (5 mL·min^{-1} total flow, ratio hexane/argon = 0.25) was passed through the catalytic bed. The reaction products were analyzed online by Gas Chromatography (Agilent technologies 7890A) equipped with a nonpolar capillary column KCl/Al_2O_3. The quantification was performed with a FID detector.

3. Results and discussion

3.1. Characterization of the catalysts

The catalysts were characterized by various physicochemical and spectroscopic methods: FT-IR and MAS NMR analyses were used to provide information on the molecular state of the catalyst. While powder x-ray diffraction and nitrogen sorption measurements allowed the determination of the catalyst structures.

Three catalysts with various HPW loadings (17.7, 24.7 and 40.3 wt. % based on tungsten) were prepared and characterized by means of ^{31}P MAS NMR. Whatever the HPW loading, the ^{31}P NMR spectrum showed only a sharp peak at −15 ppm (Fig. 1) which could be attributed to the Keggin-$[PW_{12}O_{40}]^{3-}$ anion [9]. Only a small broadening of the signal was observed for the highest loading, the line width increasing from 35 to 60 Hz. A careful observation of the spectrum showed that this was due to an additional component at −15.3 ppm. This second peak is probably related to the presence of bulk heteropolyacid as observed on Aerosil silica for high loadings [25]. The most important feature which can then be deduced from these experiments is that the Keggin structure was retained upon impregnation.