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Comparative study of transformation of linear alkanes over modified mordenites and sulphated zirconia catalysts: Influence of the zeolite acidity on the performance of *n*-butane isomerization

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ABSTRACT

Zeolite mordenite was dealuminated by steam treatment followed by acid leaching and further impregnated with 1 wt.% of iron or sulphated. The various solids were characterized by XRD, ^{29}Si and ^{27}Al NMR, IR of adsorbed pyridine as well as ammonia adsorption calorimetry and evaluated in *n*-butane isomerization. BET surface area of non-dealuminated mordenite was 462 $m^2\,g^{-1}$ and this value showed marked decreases if compared with the dealuminated (310 $m^2\,g^{-1}$), iron impregnated (302 $m^2\,g^{-1}$) and sulphated mordenite (247 $m^2\,g^{-1}$). It suggested the pore plugging or blocking by EFAL species, further confirmed by NMR experiments. The dealuminated mordenite showed Brønsted and Lewis acid sites with medium strength. The sulphated modified mordenite showed highest acidity strength, however its isomerization activity remains modest. The activity in the transformation of *n*-butane to isobutane was markedly improved by dealumination and subsequently iron impregnation (from 4×10^{-9} to 2×10^{-7} $mol\,s^{-1}\,g^{-1}$); a significant initial activity was observed at a temperature as low as 200 °C. At higher temperatures, the conversion level did not change. The positive effect of iron impregnation could be related to the increase in acid strength and/or to the participation of the redox properties of iron to the initial activation step of the reaction. Nevertheless, sulphated zirconia, used as a reference catalyst, presented the highest performance (7×10^{-7} $mol\,s^{-1}\,g^{-1}$) in comparison with modified mordenites.

1. Introduction

The isomerization of light paraffins is an important process for producing high-octane blending components in gasoline, with environmental regulations. As a typical acid-catalyzed reaction, the chlorinated alumina, heteropolyacid-based materials, sulphated zirconia and tungsten oxide on zirconia containing platinum have been shown to be active for carrying out the transformation of light alkanes [1]. However, owing to their acid properties and their shape selectivity and stability, zeolites promoted with Pt are the catalysts extensively used for the skeletal isomerization of light alkanes. Thus, over H-mordenite-based catalysts, the promotion with platinum improves considerably the activity, selectivity and stability with time on stream in the isomerization of light alkanes (C_4–C_6) [1,2]. Indeed, it is well known that light alkanes isomerization over non-modified Mordenite requires relatively high temperature to proceed via a monofunctional acid mechanism. Over Pt/zeolite, light alkanes isomerization occur more rapidly at moderate temperature, via a bifunctionnal metal-acid mechanism. The dehydrogenation abilities of the metallic sites generates olefins which are readily protonated over the Brønsted acid centers and converted into carbenium ions. Then , the isomerization process may proceed via classical acid catalyzed elementary steps.

A similar improvement in isomerization activity might be expected, if new active sites are generated nearby the zeolites Brønsted sites. These new sites should be able to generate a pool of carbocationic species by a pathway which would be energetically less demanding.

To reach that objective, it appeared interesting to evaluate two other directions. First, we assume that the presence of sites of highest strength might promote the zeolite isomerization activity, since the generation of the first carbocationic species might be favored. For that, we tentatively promoted Mordenite with sulphate groups. Second, since it is well known that the presence of re-dox sites could generate cationic radicals and then the required initial carbocationic species, we tentatively modified mordenite with iron.

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Mordenite was chosen according to its knwon efficiency in light alkane isomerization; this molecular sieve is a large pore 12-membered ring (MR) zeolite with a one-dimensional pore system [3–6]. The channel geometry consists of two types of pores parallel to one another one with a diameter of 2.6 Å × 5.7 Å and the other one with a diameter of 6.5 Å × 7.0 Å [3]. These two channels do not intersect, but small channels are accessible from the large ones by 8-rings windows. Also, mordenite has a total pore volume of approximately 0.2 mL g^{-1}. The specific pore geometry and the medium acidity make this zeolite potentially interesting for a variety of hydrocarbon conversion reactions such as isomerization [6], alkylation of aromatics [7], disproportionation [8] and transalkylation [9]. Among them, isomerization of *n*-butane to isobutane is a reaction that is generally carried out over strong Brønsted acidic materials like H-mordenite, sulphated zirconia or heteropycompounds [10]. The reaction of *n*-butane isomerization is represented by:

$$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10} \qquad \text{(I)}$$

It is generally accepted that the reaction occurs via a bimolecular mechanism over mordenite, involving a C_8^+ carbenium ion as intermediate [10,11]. Intramolecular rearrangement of *n*-C_4 alkane would require the formation of an unstable primary carbenium ion, which requires superacid sites. However, different routes have also been proposed, depending upon the reaction temperature and the concentration of the acid sites [6,12].

Generally, the main problem associated with the use of strongly acidic zeolites as isomerization catalysts is the fast rate of deactivation. Using hydrogen or water as additives into the feed stream combined with the modification of the zeolite with noble metals can partially circumvent this problem. The additives are used to prevent the formation of polymeric hydrocarbons or to help their decomposition and desorption.

In order to improve their isomerization activity, strong solid acids such as sulphated zirconia were successfully modified with low amounts of transition metals like Fe and/or Mn. These metals were proposed to promote a bifunctional mechanism, where the redox properties of the transition element could initiate the alkane conversion [13]. Although enormous work has been reported on the isomerization properties of mordenite zeolite, very little information has been reported in open literature on the modification of this zeolite with sulphated groups or transition metals such as Fe and Mn in the *n*-butane transformation [2,12–14], in order to enhance its catalytic activity.

The present study focuses on the use of modified mordenite for the *n*-butane isomerization. Mordenite was first dealuminated and then impregnated with iron or sulphate. Dealumination is a well-known method for enhancing the acidity and accessibility of active sites in zeolites [15]. Iron compounds are extensively used as catalysts in industrial processes due to their chemical properties and low cost. Both the dealumination and iron incorporation were expected to enhance the mordenite performance in the *n*-butane isomerization. It was also shown that sulphated mordenites are active for catalytic reactions involving bulky organic compounds, showing different activities and selectivities, depending on their acidity and active sites accessibility [16]. Therefore, the structural changes resulting from the mordenite modifications as well as the acid properties of the catalysts were studied and correlated with the *n*-C_4 isomerization activity.

2. Experimental

2.1. Samples preparation

Na-mordenite was obtained from Societé Chimique Grande Paroisse with a Si/Al ratio of 6.3, a BET surface area of 450 m^{-2} g^{-1} and a sodium content of 3.2 wt.%. The sodium modernite was converted into the acidic form by treatment with a 0.5 mol L^{-1} HCl solution at 80 °C for 1 h. The solid was then dried at 80 °C and calcined at 500 °C under nitrogen/air flow. The protonic mordenite sample was labelled M. Dealumination was performed on the exchanged solid as proposed by Almanza et al. [6] by using a steam partial pressure of 12.5 kPa, for approximately 9 h. The solid was then refluxed in hydrochloric acid (3 mol L^{-1}) at 80 °C for 1 h and subsequently washed in order to remove chloride species. A final calcination was performed under air at 500 °C for 2 h, leading to the dealuminated mordenite sample, labelled M1.

An iron impregnated mordenite was prepared from M1 by using a 0.1 mol L^{-1} iron nitrate solution to obtain a concentration of Fe of 1 wt.%. Iron impregnation was carried out under stirring for 1 h, followed by vacuum filtration and drying at 80 °C. The solid was then calcined under air flow at 500 °C for 2 h, leading to sample FeM1 (iron impregnated dealuminated modernite).

A sulphated mordenite (SO_4M1) was prepared by treating 1 g of M1 with a 0.1 mol L^{-1} sulphuric acid solution (50 mL of solution for 1 g of M1). The impregnation of M1 with the sulphate was carried out under stirring during 4 h, with a buffer (pH 3–5) followed by vacuum filtration and drying at 80 °C. The solid was then calcined under air flow at 500 °C for 2 h. Following each step, the crystallinity of the solids was evaluated by X-ray diffraction.

A sulphated zirconia (SO_4Z) was synthesized according to the literature [17], by using zirconium hydroxide with a 0.2N sulphuric acid solution. This solid was used as control catalyst. Its specific surface area (BET) is equal to 100 m^2 g^{-1}. The protonic density drawn from NH_3 adsorption at 373 K is equal to 22×10^{17} H^+ m^{-2} [1].

2.2. Characterization

All solids were characterized by XRD, chemical analysis, nitrogen adsorption at 77 K, microcalorimetry adsorption of ammonia, pyridine adsorption, NMR and *n*-butane isomerization as a test reaction.

The chemical analyses were performed on a Carry AAS/ICP OES instrument. Each sample was dissolved in HF:HCl solutions, before measurement of the chemical composition.

X-ray diffraction (XRD) patterns were colleted on a Bruker (Siemens) D5005 diffractometer by using the Cu Kα radiation, at a work voltage of 40 kV and current was 40 mA.

BET measurements were recorded on a Micromeretics ASAP 2002 equipment. Samples were first treated in vacuum to remove the gaseous impurities (300 °C, 6 h, 10^{-3} Torr) and the textural features were studied by using nitrogen adsorption at 77 K.

NMR experiments were carried out on a Bruker DSX 400 spectrometer. Samples were spun at 10 kHz in 4 nm zirconia rotors. ^{27}Al and ^{29}Si chemical shifts were referenced to $Al(H_2O)_6{}^{3+}$ and tetramethylsilane (TMS), respectively.

2.3. Acidity measurements

Pyridine adsorption–desorption was monitored by infrared spectroscopy (IR). Self-supported wafers of 20 mg and 18 mm diameter were evacuated *in situ* in an infrared glass vacuum cell equipped with calcium fluoride windows. The cell was then connected to a vacuum system and the samples were degassed under 10^{-5} Torr at 450 °C for 4 h. IR spectra were recorded before as well as after pyridine adsorption at room temperature. Pyridine was then desorbed at increasing temperatures (150, 250, 350, and 450 °C) in dynamic vacuum and spectra were recorded on a Bruker Vector 22 (IRFT) spectrometer.

Calorimetry of ammonia adsorption was performed in a tubular cell preliminary heated at 400 °C under vacuum for 2 h. The cell