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Nickel-doped small pore zeolite bifunctional catalysts: A way to achieve high activity and yields into olefins

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ABSTRACT

The present study deals with the modification of mordenite (HMOR) and ferrierite (HFER) zeolites by nickel. XRD, XRF, nitrogen adsorption, TPR, XANES, EXAFS were used to thoroughly characterize the materials. The metal level was set to 1 wt% for all catalysts and nickel was introduced by cationic exchange following either conventional thermal heating or in the presence of microwave radiation (HFER). The metal exchange methods employed ensured to maintain the structural integrity of the zeolites. However nickel was predominantly distributed as small NiO particles on HFER for both catalysts. The rate of both *n*-hexane and isobutane cracking increased when nickel was introduced under microwave radiation for HFER zeolite. Likewise, the selectivity toward ethylene and propylene was enhanced by nickel presence in *n*-hexane cracking reaction, while no effect on selectivity was observed in isobutane cracking. These results confirm that a new bifunctional system was obtained, since both metallic and Brønsted acid sites are acting in a synergetic manner within the zeolite catalyst.

1. Introduction

The first generation of petrochemical products, propylene and ethylene are of prime importance worldwide [1,2]. The high market prices of these key building blocks compared to gasoline and diesel led to several important developments in the FCC technology [3]. The FCC process itself is responsible today for nearly 30% of total propylene production [4,5], whereas ethylene is obtained via a thermal cracking process [6]. Several improvements are therefore expected in the FCC process, mainly in the catalyst formulation. Other processes may also be coupled to a FCC petrochemical unit in order to process particular hydrocarbon streams. Recently a comprehensive review was presented on metal-doped ZSM-5 catalyst [7]. In addition, many studies devoted to nickel-promoted ZSM-5 catalysts have been published [8–10].

The chemical inertness of starting alkanes can be generally overcome using high temperatures and strongly acidic catalysts, such as proton exchanged zeolites [11]. Recently a longstanding controversy about the initial step of hydrocarbon activation over industrial catalysts such as acidic zeolites has been solved [12]. These experiments using isotopic labeled D-zeolites have shown that σ_{C-H} bond and σ_{C-C} bond are directly protonated by zeolite Brønsted acid sites, thus leading to the formation of HD and CH_3D as primary products, respectively [12]. The limitations related to the small zeolite pore openings, as exhibited for instance by MFI zeolites, improve the formation of cracking products by favoring the direct protolysis of alkanes [13,14]. Nevertheless, a lower accessibility within the MFI framework is observed [15]. In contrast, large pore size zeolites (FAU-type) favor secondary and tertiary reactions involving carbocations such as alkylations and β-scissions [16,17].

The presence of a dehydrogenation metallic site in the catalyst strongly influences the chemistry aforementioned. Recently a huge increase in isobutane cracking activity was observed over NiHZSM-5 catalyst, whilst such effect could not be evidenced for linear hydrocarbons [9]. The higher concentration of olefins encompasses the rate-limiting protolysis of the alkane σ-bond, since olefins are more basic than corresponding alkanes. In addition, olefins favor bimolecular reactions, such as alkylation that undergo β-scissions of oligomerized products. The increased toward ethylene selectivity for NiHZSM-5 catalyst compared to pristine HZSM-5 was ascribed to the aforementioned reactions.

Hence, the aim of the present study is to investigate and to extend the nickel effect observed for ZSM-5 zeolites to FER (small pore) and also to MOR zeolites (larger pores) in *n*-hexane and

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Table 1
Metal content, SSA and number of Brønsted acid sites of as-prepared Ni-FER and Ni-ZSM-5 catalysts.

Catalysts	BET (m^2/g)	A_{ext}	mmol OH/g_{cat}	Metal amount (%)	Cristallinity
HFER	317	68	2.26	0	40
HFERM60	334	58	1.73	0	49
NiHFER	305	42	2.13	0.70	48
NiHFERM60	309	40	1.63	0.90	86
HZSM-5	392	n.d.	1.58	0	n.d.
NiHZSM-5EX	340	n.d.	1.06	0.83	n.d.
NiHZSM-5IMP	332	n.d.	1.43	1.00	n.d.
HMOR	448	n.d.	n.d.	0	n.d.
NiHMOR	444	n.d.	n.d.	0.78	n.d.

isobutane cracking reactions. Finally, the methodology pursued for Section 1 of Ni^{2+} cation in HFER zeolite was also investigated.

2. Experimental

2.1. Preparation of nickel-promoted zeolites

Nickel was introduced in mordenite and ferrierite zeolites based on metal exchange method as described elsewhere [18]. Nickel nitrate aqueous solution was added to zeolites and vigorously stirred during 2 h at 70–80 °C, filtered and washed with distilled water at 65 °C. A further drying at 120 °C for 12 h and calcination at 600 °C for 3 h in air were successively performed. In addition, the ionic exchange method with nickel salt was also conducted in the presence of microwave radiation for HFER zeolite. An aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ was heated under continuous stirring in order to maintain a constant temperature at 150 °C for 1 h or for 10 min under microwave. The catalyst HFERM60 was treated for 1 h and the catalyst HFERM10 was treated for 10 min. This procedure involving conventional heating for nickel introduction in HFER was repeated five times to achieve the same metal amount obtained in microwave-mediated synthesis. The samples named M30 or M60 were prepared during 30 min or 60 min under microwave radiation, respectively.

2.2. Characterization of the catalysts

The Si/Al ratio was determined by chemical analysis. Specific surface areas (SSA) and external surface (A_{ext}) of as-prepared materials were measured using nitrogen adsorption–desorption isotherms (BET method) in Micromeritics equipment (GEMINI 2375). Brønsted acid sites quantification of the FER materials was done by H/D isotope exchange technique [19]. The temperature-programmed reduction (TPR) was performed in a glass reactor as reported elsewhere [20]. The profile was obtained under a 60 mL/min flow of 1.5% hydrogen in argon. Hydrogen consumption was monitored from room temperature up to 1000 °C with a heating rate of 10 °C/min and staying at this temperature for 1 h. The measurements were monitored on-line by mass spectrometry (MKS able to measure $m/z = 100$). XANES and EXAFS measurements were carried out at the D08B XAS beamline at the National Laboratory of Synchrotron Radiation, operating at 1.37 GeV, with maximum ring current of 120 mA. The spectra were collected in the K edge of Ni (8333 eV) in the fluorescence mode, using a Ge multi-element detector. Details of all these characterizations can be found elsewhere [10].

Relative crystallinity expressed in percentage was determined by the sum of the more intense reflexions for each catalyst (multiplied by 100) and divided by the sum of these reflexions for FER catalyst, which exhibits the higher crystallinity set arbitrarily to 100.

2.3. Cracking experiments

Isobutane and *n*-hexane cracking reactions were performed in a high throughput unit. Eight parallel quartz tubular reactors (187 mm in length and 6 mm internal diameter) were used. The catalyst was placed in the middle of the reactor. The temperature was measured by means of a thermocouple located at the center of each reactor; temperature differences among the reactors are smaller than 2 K. All experiments were conducted at 1 atm (open reactor) in a continuous down flow fixed-bed micro reactor. Prior to catalyst evaluation, all the catalyst were heated simultaneously under N_2 flow from room temperature to the desired temperature (773 K), at a rate of 10 K/min. Then isobutane or *n*-hexane was carried with N_2 (60 mL/min) containing 10% v/v of alkane for all catalytic tests. A typical run was carried out with 0.01 g to 0.1 g of catalyst (the amount of catalyst was adjusted to keep alkane conversion lower than 10%). Since catalyst's weight varied between 0.01 g and 0.1 g at constant flow (60 mL/min), W/F values were comprised between 1.6×10^{-4} and 1.6×10^{-3}. Reaction products were analyzed on-line after three distinct times on stream (3 min, 17 min and 32 min) by gas chromatography using a Shimadzu GC-2010. The set-up details as well as chromatographic conditions were already reported [10]. The activities and selectivities were presented as the average result obtained after 17 min and 32 min on stream. Detailed catalytic results are given in supplementary information. It is noteworthy that these values only differed by less than 5% and 2% in activity and selectivity, respectively. Ethylene and propylene selectivities were calculated dividing the formed amount (in w/w) by the total alkane consumption (conversion in w/w). Butenes selectivity includes 1-butene, *cis*-butene, *trans*-butene and isobutene. Pentene selectivity takes into account all pentenes. The catalysts showed small deactivation, i.e.; the catalytic activity measured after 3 min on stream differed by less than 5% when compared to the one measured after 32 min), despite this small deactivation the first injection (at 3 min) was not used neither in the activity nor in the selectivity calculations.

3. Results and discussion

The textural properties and metal loadings for as-synthesized catalysts are presented in Table 1. The data related to pristine and Ni-exchanged HZSM-5 zeolites are also included for the sake of comparison [10]. Mordenite and NiHMOR exhibit the same BET area (which suggest that nickel is distributed as a compensation cation of the zeolite framework). The presence of microwave radiation itself slightly raises the catalyst area and decreases the amount of acid sites present in FER zeolite, yet relative crystallinities increased from 40% to 49% for HFER and HFERM60, respectively. Furthermore, a shorter time under microwave radiation led to increase the crystallinity to 56% (as presented in Table S1).

Regarding the methodology for nickel introduction in HFER, five successive cationic exchange steps were necessary to achieve the same metal loading in HFER zeolite under conventional heating,