C. R. Chimie 18 (2015) 330–335

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

GeCat 2014: Advances and prospects in heterogeneous catalysis

Catalyst optimization for enhanced propylene formation in the methanol-to-olefins reaction

Pit Losch [a], Marilyne Boltz [a], Benoît Louis [a,*], Sachin Chavan [b], Unni Olsbye [b]

[a] Laboratoire de synthèse réactivité organiques et catalyse, Institut de Chimie, Université de Strasbourg, UMR 7177 CNRS, 4, rue Blaise-Pascal, 67000 Strasbourg cedex, France
[b] inGAP Center of Research Based Innovation, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo, Norway

ARTICLE INFO

Article history:
Received 21 May 2014
Accepted after revision 27 June 2014
Available online 5 January 2015

Keywords:
MTO
Propylene
ZSM-5 zeolite
Catalyst design
HF replacement

ABSTRACT

ZSM-5 zeolites possessing different chemical compositions, acidities and crystal sizes, were synthesized and characterized by XRD, SEM and FTIR. Those as-prepared acid catalysts were tested in the conversion of methanol into light olefins at 673 K under atmospheric pressure. Propylene-to-ethylene ratios above 5 were achieved over ZSM-5 zeolite catalyst prepared via the fluoride route. This promising methanol-to-propylene (MTP) catalyst was designed both at the molecular scale, *exhibiting low Brønsted acid site density*, and at the microscopic level since *large crystals (25 μm) with few defects* were obtained. Aiming in a possible industrial application, the synthesis medium has to be seriously modified, thus avoiding harmful hydrofluoric acid use. Hydrochloric and phosphoric acids were therefore chosen as alternatives and resulted in the same ZSM-5 crystal morphologies and similar catalytic performance.

RÉSUMÉ

De nos jours, les procédés de conversion du méthanol en oléfines légères (MTO) et plus particulièrement du méthanol en propylène (MTP) sont considérés comme des voies attractives et viables pour la valorisation des ressources en gaz naturel. Notre stratégie est de développer un catalyseur zéolithique de type ZSM-5, *via la synthèse en milieu fluorure*, ayant des propriétés désirées pour la réaction MTP effectuée à 400 °C. Un catalyseur présentant une densité de sites acides faible et une taille de cristal de 25 μm a démontré des performances intéressantes. De plus, nous avons été en mesure de substituer l'acide fluorhydrique par de l'acide phosphorique dans le gel de synthèse et ainsi développer une voie plus écocompatible pour le design du catalyseur.

1. Introduction

The transformation of methanol to hydrocarbons (MTH) to produce high-octane gasoline [1] represents a valuable process involving zeolite or zeotype catalysts, which received considerable industrial interest [2–5]. Besides the Mobil Oil methanol-to-gasoline (MTG) process, Lurgi's methanol-to-propene (MTP) [6], Norsk Hydro/UOP's methanol-to-olefins (MTO) and Haldor Topsøe TIGAS processes [7] are also commercialized [8,9].

The MTO reaction is a competitive option for the valorization of stranded gas reserves. Several studies

* Corresponding author.
E-mail address: blouis@unistra.fr (B. Louis).

http://dx.doi.org/10.1016/j.crci.2014.06.007
1631-0748/

devoted either to the reaction mechanism or to the technology were therefore undertaken [9–17]. In addition, the worldwide market demand in ethylene and propylene is gradually raising and projected growth rates in coming decades are further expected to remain high [18]. ZSM-5 zeolite catalysts are often employed and several strategies targeting to achieve an improved selectivity toward light olefins have been tempted: operating conditions, change in reactor configuration [19], proper tailoring of catalyst Brønsted acidity [20], development of structured catalyst [12,21].

We have recently investigated the influence of both Brønsted acid sites density and crystal size on activity/selectivity in the MTO reaction [22]. The main goal was to raise and then maintain a high selectivity toward propylene, hence to develop a simple strategy for designing a MTP catalyst with the MFI structure. With these promising results in hand, it was decided to further optimize ZSM-5 zeolites synthesized under fluoride conditions. Indeed, hydrofluoric acid has to be replaced to warrant industrial catalyst implementation. This study will therefore focus on the design of a novel MTP-catalyst generation, synthesized in the absence of HF.

2. Experimental

2.1. Catalyst preparation

Several ZSM-5 zeolites were synthesized via fluoride-mediated syntheses to investigate different parameters: density of Brønsted acid sites, crystal size, chemical composition. One ZSM-5 zeolite prepared via the classical alkaline route was used as the reference material and named MFI-R [22]. MFI-F catalyst was prepared via the fluoride-mediated route according to our previous studies [23]. The same procedure was followed while substituting hydrofluoric acid by either hydrochloric acid or phosphoric acid to maintain a neutral pH (Table 1). These samples were named MFI-FCl and MFI-FP, respectively. All ZSM-5 samples obtained in either NH_4- or Na-form were either ion-exchanged and calcined or simply calcined. Cationic exchange was repeated three times, using 20 mL of a 1.0 M aqueous NH_4NO_3 solution per gram of catalyst. The solution was kept at 348 K for 2 h before catalyst separation by centrifugation. The solid was dried overnight in an oven at 373 K and further calcined in static air during 6 h at 823 K.

2.2. Characterization

Specific surface areas (SSA) of the materials were determined by N_2 adsorption-desorption measurements performed at 77 K employing the BET-method (Micromeritics sorptometer Tri Star 3000). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer, with a Ni detector side filtered Cu Kα radiation (1.5406 Å) over a 2θ range of 5° to 60°. Scanning electron microscopy (SEM) micrographs were acquired on a JEOL FEG 6700F microscope working at a 9 kV accelerating voltage. The Si/Al ratios of the materials were determined by EDX analysis coupled with the SEM chamber.

Infrared spectroscopy (FTIR) spectra were recorded in controlled atmosphere at 2 cm^{-1} resolution on a Bruker Vertex 80 FTIR spectrophotometer, equipped with a MCT detector and using a homemade IR cell. FTIR spectra were collected in transmission mode on a thin film prepared by deposition of a zeolite water suspension on a silicon wafer. The difference in the Brønsted acid strength of these samples was derived from CO adsorption. In order to compare the IR band intensities, spectra were normalized to the overtone mode at 2005 cm^{-1}.

2.3. MTO reaction

Prior to use, the catalysts were activated at 823 K with a gradient of 15 K/min in static air. The zeolites were sieved and particles < 250 μm were used in the following experiments. Sixty milligrams of zeolite were introduced in a tubular quartz reactor and packed between quartz wool plugs. A constant nitrogen flow, of 20 mL/min was flown through a methanol saturator, cooled at 273 K, to achieve a WHSV = 1.12 g_{MeOH}/g_{cat} * 1/h. The reactant was subsequently fed to the reactor containing the catalyst at 673 K. GC analysis was performed on a HP GC5890 equipped with a 50-m capillary column (PONA) and a flame ionization detector (FID). The activity of the catalysts was expressed in terms of methanol and dimethylether conversion, calculated from the difference between inlet and outlet concentrations of methanol (DME is considered as an intermediate). The selectivity was defined as the mole ratio of each product referred to the moles of

Table 1
Textural properties and catalytic performances of as-prepared catalysts.

Entry	Catalyst	pH-gel	Si/Al/(P)-gel	MeOH conversion[a] [%[	S_{C2}[b] [%]	S_{C3}[b] [%[	S_{C2-C4}[b] [%[
1	H-ZSM-5R	10	25	14	15	27	56
2	H-ZSM-5F	6–7	67	98	7	36	66
3	H-ZSM-5FCl	6–7	100	64	26	35	78
4	H-ZSM-5FP	6–7	100/1/11	0	–	–	–
5	H-ZSM-5FP	7	100/1/1	13	33	35	83
6	H-ZSM-5FP	7	100/3/2	54	32	33	78

[a] After 48 h on stream.
[b] After 15 min on stream at complete methanol conversion.