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Catalytic behavior of hybrid Co/SiO$_2$-(medium-pore) zeolite catalysts during the one-stage conversion of syngas to gasoline

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ABSTRACT

The catalytic properties of 10-MR (membered ring) zeolites (ZSM-5, MCM-22, IM-5, ITQ-2, all with a similar Si/Al ratio of ca. 15) in hybrid Co/SiO$_2$-zeolite catalysts for the direct conversion of syngas to mainly high-octane gasoline-range hydrocarbons has been studied under typical Fischer-Tropsch (FT) conditions: 250 °C, 2.0 MPa, and $H_2/CO = 2$. Special emphasis has been given to the deactivation behavior and the characterization of the amount and nature of the carbonaceous deposits formed by a combination of techniques (elemental analysis, TGA (thermogravimetric analyses), GC–MS, and DR (diffuse reflectance) UV–vis spectroscopy). The presence of the medium-pore zeolite increases the gasoline yield by about 20–50%, depending on the particular zeolite, and enhances the formation of branched products with respect to the base Co/SiO$_2$ catalyst, which is explained by the promotion of isomerization and cracking of long-chain (C_{13+}) *n*-paraffins formed on the FT component. The initial zeolite activity is mostly determined by the surface acidity rather than by the total amount of Brønsted acid sites, pointing out to the existence of limitations for the diffusion of the long-chain *n*-paraffins through the 10-MR channels under FT conditions. Thus, ITQ-2 bearing the largest surface area presents the highest initial yield of branched gasoline-range products, followed by ZSM-5, IM-5, and MCM-22. All zeolites experience a loss of activity with TOS, particularly during the initial reaction stages. This deactivation is governed by the morphological and structural properties of the zeolite, which finally determine the amount and location of the coke species, and not by the acidity.

1. Introduction

High-quality sulfur-free liquid fuels can be produced from alternative sources to petroleum, such as natural gas, coal, and biomass, via syngas ($CO + H_2$) through the well-known Fischer-Tropsch (FT) process using either iron or cobalt based catalysts [1]. The FT reaction follows a polymerization-type kinetics resulting in a nearly statistical hydrocarbon distribution known as the Anderson–Schulz–Flory (ASF) distribution, which can be represented by the parameter α, the chain growth probability [2]. Such a distribution introduces a limit to the maximum selectivity that can be attained to a given hydrocarbon fraction in a conventional (one-stage) FT process. In addition to the selectivity limitation, the linear structure of the FT hydrocarbons determines a too poor quality of the synfuels directly produced in the FT reaction, thus requiring further processing in order to improve the octane and cold flow properties of the gasoline and diesel fractions, respectively. The concentration of branched hydrocarbons could be increased, for instance, through selective isomerization of the linear components [3]. In order to overcome the selectivity limitation, the FT process is typically operated under conditions that maximize the formation of long-chain *n*-paraffins (waxes) in the presence of a Co-based catalyst and then subjecting the waxes to downstream (hydro)-cracking and/or (hydro)isomerization steps [4]. The benefit of using FT waxes as a potential feedstock for FCC units to produce high-octane *iso*-paraffin rich gasoline and light olefins for petrochemical applications has also been studied recently [5,6].

An interesting approach to circumvent the above two-stage processing and thus to significantly reduce the overall investment cost of the synfuel production would be to use hybrid or composite catalyst formulations combining, preferably in separate particles, the active FT component (Co or Fe) with a co-catalyst active for

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converting the primary FT products into the desired compounds in a single stage operation. An obvious requirement of such a modified FT process is that the co-catalyst must be active at the reaction conditions typically applied for FT synthesis. For instance, hybrid catalysts comprising an iron-based FT catalyst displaying high selectivity to light α-olefins and oxygenates and an acidic zeolite, such as HY [7] or HZSM-5 [8–11], were shown to enhance the selectivity to hydrocarbons in the gasoline-range while increasing the concentration of high-octane *iso*-paraffins and aromatics. On the other hand, by combining a Co-based FT catalyst (i.e. Co/SiO_2) with an acidic or bifunctional (metal/acid) zeolite co-catalyst, the heavy *n*-paraffins produced on the former can be selectively cracked/hydrocracked on the zeolite into mainly gasoline or diesel-range *iso*-paraffins with little formation of aromatics [12–14], a less desired component of reformulated gasolines.

A serious concern of such hybrid systems is the gradual deactivation of the acid component in the hybrid catalyst (i.e. zeolite) with time-on-stream (TOS) due to the accumulation of carbonaceous deposits. However, very little effort has been devoted to investigating the deactivation behavior of zeolite co-catalysts during a modified FT operation using hybrid catalysts. In a recent work, we have shown that the amount and nature of the carbonaceous deposits formed on the zeolitic component of Co/SiO_2 + zeolite composites, and thus the deactivation rate, depended mainly on the zeolite structure rather than on acidity [15]. Under typical FT conditions (250 °C, 2.0 MPa, $H_2/CO = 2$), large-pore tridirectional zeolites (USY, beta) produced higher amounts of aromatic-type coke and deactivated faster than the large-pore unidirectional mordenite, while the medium-pore ZSM-5 displayed the highest stability with TOS. This latter zeolite produced low amounts of (poly)aromatic-type coke as their formation is hindered inside the narrow 10-membered ring (MR) channels, thus retaining a higher number of acid sites for isomerization and cracking of the primary long-chain *n*-paraffins at larger TOS than the 12-MR zeolites [15].

The above results constituted the main motivation for extending the study to other 10-MR zeolites with different structural characteristics. According to our previous work, the dimensions and connectivity of the 10-MR channels as well as the presence of large cages should have an affect on the zeolite activity but especially on its stability with TOS. Thus, in the present work we compare the catalytic behavior of hybrid catalysts comprising Co/SiO_2 (20 wt% Co) as the FT component and ZSM-5, MCM-22, ITQ-2, and IM-5 zeolites as acidic co-catalysts. The well-known ZSM-5 is constituted by a bidirectional 10-MR pore system with apertures of ca. 5.1–5.6 Å in diameter, one of the channels being straight and the other sinusoidal. MCM-22 consists in two non-interconnected 10-MR channel systems, one of which is tridimensional and contains 12-MR supercages (7.1 Å × 7.1 Å × 18.4 Å) which are only accessible through small 10-MR apertures (4.0 Å × 5.5 Å), and the other is a bidimensional sinusoidal 10-MR system (4.1 Å × 5.1 Å). ITQ-2 is obtained by delamination of the layered MCM-22 precursor through treatment with an appropriate swelling agent and separation of the layers by ultrasonication, as described in [16]. Thus, a completely delaminated ITQ-2 material would consist of thin sheets of 2.5 Å in height with a very high external surface area (typically above 600 m^2/g) containing large hemi-cavities (7.0 Å × 7.1 Å × 7.1 Å) arising from the truncation of the 12-MR supercages present in MCM-22. The sheets also contain the sinusoidal 10-MR system of MCM-22. Finally, IM-5 is a relatively new zeolite whose catalytic properties have been scarcely studied in the literature [17,18] since it was synthesized for the first time in 1998 [19]. Though previous catalytic and adsorption studies classed IM-5 as a multidimensional 10-MR zeolite [20–23], its complex structure having an unusually large unit cell size could not be definitively elucidated until very recently [24]. The structure of IM-5 can be described as consisting in an unusual bidirectional 10-MR pore channel system with pore widths ranging from 4.8 to 5.5 Å and having a limited third dimension. The peculiarity of this structure comes from the 2D (two-dimensional) channel systems running perpendicular to the *b* axis that are connected to one another to form a ~2.5 nm thick pore system. This pore topology gives IM-5 the character of a 3D zeolite structure while retaining the effect of a 2D one with long range diffusion restricted to just 2D [24].

In this investigation we have placed especial emphasis in addressing the deactivation behavior of the different 10-MR zeolites under FT conditions, and to relate it with the amount, nature, and location of the carbonaceous deposits formed by using a combination of characterization techniques.

2. Experimental

2.1. Preparation of catalysts

The hybrid catalysts were prepared by physically mixing 1.0 g of a Co/SiO_2 (20 wt% Co) FT catalyst and 1.0 g of zeolite previously pressed and crushed to a particle size of 0.25–0.42 mm. The Co/SiO_2 component (base) was prepared by wet impregnation of a commercial amorphous SiO_2 (Fluka, silica gel 100, BET = 387 m^2/g, PV = 0.8 cm^3/g) with an aqueous solution containing the required amount of $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich, 98%), followed by drying and calcination at 300 °C for 10 h.

All the zeolites used had similar Si/Al atomic ratios of ca. 15 (Table 1). The ZSM-5 was a commercial sample (CBV3020, Zeolyst Int.) which was already in the protonic form and used as received. The layered precursor of MCM-22 was synthesized using hexamethylenimine (HMI), silica (Aerosil 200, Degussa), sodium aluminate (56% Al_2O_3, 37% Na_2O, Carlo Erba), sodium hydroxide (98%, Prolabo), and deionized water. Thus, a gel of the following molar composition:

$$SiO_2 : 0.033Al_2O_3 : 0.10OH : 0.18Na : 44.9H_2O : 0.50HMI$$

was prepared and crystallized in Teflon-lined stainless steel autoclaves at 150 °C for 9 days. After crystallization, the solids were washed with deionized water and dried at 100 °C to produce the layered precursor MCM-22(P). A part of this precursor was calcined at 540 °C for 3 h to produce the MCM-22 zeolite. Another part of the layered precursor was swelled by mixing the solid with an aqueous solution of cetyltrimethylamonium bromide (CTABr) and an aqueous solution of tetrapropylamonium hydroxide (TPAOH, 40 wt%), and the resulting solution was refluxed for 16 h at 80 °C. The layers were forced apart by placing the slurry in an ultrasound bath (50 W, 40 kHz) for 1 h. The solid was separated by acidification of the medium with concentrated hydrochloric acid (HCl, 37%) until the pH was below 2, followed by centrifugation. Then the material was calcined at 540 °C to yield the ITQ-2 sample [16].

The IM-5 zeolite was prepared by hydrothermal synthesis in Teflon-lined stainless steel autoclaves at 175 °C under rotation

Table 1
Chemical composition and textural properties of H-zeolites

Zeolite	Si/Al ratio	S_{BET} (m^2/g)	S_{microp} (m^2/g)	S_{ext} (m^2/g)	V_{microp} (cm^3/g)
ZSM-5	15	379	322	58	0.16
MCM-22	15	451	310	141	0.16
ITQ-2	14	560	239	321	0.12
IM-5	14	350	315	35	0.15