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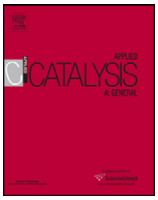

Study of the selectivity in FCC naphtha hydrotreating by modifying the acid–base balance of CoMo/γ-Al_2O_3 catalysts

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ABSTRACT

CoMo catalysts supported on a commercial γ-Al_2O_3 modified with B, Na or K were prepared in order to analyze the effect of acid–base characteristics on the FCC naphtha hydrotreatment. Catalysts were characterized by NH_3 TPD, IR of pre-adsorbed pyridine and CO_2, XPS, Raman, and XRD. In general, with either boron or alkaline metal modification the HDS/HYDO selectivity did not significantly improve. However, it is remarkable that when the alumina was modified to be either more acidic (B) or more basic (K, Na), improvements in the ratio between the HDS and the conversion of the internal branched olefin as well as in the ratio double-bond isomerization to HYD of linear olefins were observed. For both modifications, this fact was related to the promotion of the double-bond isomerization reaction from external to internal positions. For alkaline-doped catalysts, it was found that the double-bond isomerization was related to the existence of basic sites. For the boron, there is a range of boria content (2–3 wt.%) where the double-bond isomerization was promoted selectively over the cracking and alkylation reactions because only weak Brönsted acid sites are present. Additionally, both modifications (Boron or alkaline metals) of alumina led to a decrease in the HDS activity, which was found to be related to changes in the distribution of Co and Mo species in the oxide state. Alkaline metal introduction led to the formation of alkaline metal molybdates, whereas boron introduction increased the proportion of octahedral polymeric Mo species, consequently, decreasing the dispersion of the Mo phase.

1. Introduction

The development of catalysts highly selective to the HDS reaction is the key to meet the environmental regulations regarding sulfur content in gasoline while preserving octane number [1]. Among the attempts to meet this purpose, support modification appears to be a good approach to obtain more selective catalysts [1–10]. In this sense, most works claim that an increment in the hydrodesulfurization/hydrogenation of olefin (HDS/HYDO) selectivity can be observed using less acidic [1,2,9,10] carriers than classical γ-alumina. However, some successful works can be found using more acidic catalysts [3,8,9]. Thus, the particular influence of the acid–base properties of catalysts on selectivity is not yet clear. For instance, Mey et al. [2] found some selectivity improvements, using K doped CoMo/γ-Al_2O_3 catalysts, which were attributed to the modification of the catalysts acid–base properties. K introduction poisons the acid sites, where the double-bond isomerization from internal to terminal positions is carried out [2]. Avoiding this reaction is a way to inhibit the hydrogenation because internal olefins are harder to hydrogenate than terminal ones [2,11]. On the other hand, in another work, it is claimed that with support modifications the catalysts selectivity is more affected by the changes in the CoMo sulfided phase morphology than by changes in catalysts acidity [7]. However, in this last work, a real feed was used and there is not information about the reaction schemes and the yields of the individual reactions involved in the reaction system [7]. Thus, with these contradictions in the literature, it is not clear if the modification of the acid–base properties is the principal factor affecting the HDS/HYDO selectivity in the HDT of fluid-catalytic-cracking (FCC) naphtha.

A fact that could account in some way for the contradictory results in literature is the use of different kinds of feeds in the catalytic evaluation for the different works. On the one hand, there are authors who used model feeds and based their explanations proposing some kind of reaction schemes, but they used only one kind of olefin either linear or branched [2,3,6,8,12]. On the other hand, there are authors who used real feeds and try to follow the

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[1] IMCN and MOST are new research entities emerging from the reorganization of the Université catholique de Louvain, and integrating the laboratory formerly known as Unité de catalyse et chimie des matériaux divisés.

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reactivity of the different kinds of olefins, but due to the complexity of working with real feeds, it was difficult to propose reliable reaction schemes [4,7,9,10]. Thus, it is necessary a detailed study of the support effects on the HDT of FCC naphtha using model feeds with different kinds of olefins. It is also necessary to include in this study the effect of support modification on the acid–base properties and the CoMo phase morphology.

In this work, the Co and Mo were supported on alumina modified with B, Na and K in order to obtain CoMo catalysts with a wide range of acid–base properties. The catalytic performance of these catalysts in the HDT of a synthetic FCC gasoline (2-methylthiophene and different kinds of olefins dissolved in n-heptane) was studied in detail. In order to elucidate which are the important factors for enhancing the HDS/HYDO selectivity, the acid–base properties of the catalysts along with the distribution of the different Mo and Co species in the oxide state were determined.

2. Experimental

2.1. Catalyst preparation

CoMo catalysts containing 10% MoO_3 and 2% CoO supported on a commercial γ-Al_2O_3 *Procatalyse* (BET surface area: 210 $m^2\,g^{-1}$, pore volume: 0.6 $cm^3\,g^{-1}$, pore diameter: 109 Å) modified with either B, Na or K were prepared. The dopant (B, Na or K), Mo and Co were deposited by successive incipient wetness impregnation. An initial impregnation step was performed either with a solution of H_3BO_3 (Merck) in methanol or an aqueous solution of either $NaNO_3$ or KNO_3 (Merck). Subsequently, the solids were impregnated with an aqueous solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Merck), and finally the solids were impregnated with an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich). After each impregnation step, solids were dried under air flow at 393 K for 12 h, and finally, air calcined at 773 K for 4 h. A CoMo catalysts supported on pure alumina *Procatalyse* was also prepared in the same way as a reference catalyst (named here CMA). The nominal content of B_2O_3 was 2, 3, 5 and 8 wt.%. In the case of Na and K nominal contents of 1, 3 and 5 wt.% were used. The CoMo catalysts modified with B, Na and K were named here CMAB(*x*), CMANa(*x*) and CMAK(*x*) respectively, where *x* represent the B_2O_3, Na or K contents respectively.

2.2. Catalysts characterization

2.2.1. X-ray diffraction (XRD)

XRD was performed on a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The 2θ range was scanned between 2° and 70° at a rate of 0.02 s^{-1}. Identification of the phases was achieved by using the ICDD-JCPDS database [13].

2.2.2. X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed on samples of the catalysts in the oxidized states with a Kratos Axis Ultra spectrometer. Details about the procedure and quantification were already given by Baldovino-Medrano et al. [14]. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Al 2p, Mo 3d, Co 2p, dopant (B 1s, K 2p or Na 1s according to the support) and C 1s again to check the stability of charge compensation in function of time and the absence of degradation of the sample during the analyses. For the Mo 3d peak, the energy separation for the doublet was fixed at 3.15 eV.

2.2.3. Confocal laser Raman microscopy (Raman)

Raman was performed with a Labram spectrometer (Dilor) interfaced with an Olympus optical microscope. The excitation radiation was a He–Ne laser (780 nm) operated at a power of 10 mW. The 100× objective of the microscope was used, so that a spot of about 1 μm at the surface of the sample was measured at once. Spectra were obtained by averaging 25 scans of the Raman shift range between 1400 and 100 cm^{-1} recorded in 25 s with a spectral resolution of 1 cm^{-1}. The identity of the spectra obtained at different positions of each sample was systematically verified.

2.2.4. Acid–base properties

The acidic properties of catalysts in the oxide state were determined by NH_3 temperature programmed desorption (TPD) and Fourier transformed infrared (FT-IR) spectroscopy using pyridine as a probe molecule. On the other hand, the base properties of the alkaline metal modified catalysts were determined by FT-IR spectroscopy using CO_2 as probe molecule.

For NH_3 TPD experiments, the samples (100 mg) were placed in a quartz reactor and, then, covered by quartz beads. Outlet gases were analyzed with a mass spectrometer equipped with a quadruple mass filter (Balzers QMC 200). Samples were first dehydrated under pure He at 773 K until obtaining a flat water signal (m/z 17 and 18). Then, samples were cooled down under He flow to room temperature (RT) NH_3 adsorption was then performed by passing across the samples a flow of 5% NH_3 in He. Excess NH_3 was evacuated at RT by passing a flow of pure He until obtaining a flat NH_3 signal (m/z 15, 16 and 17). Desorption of the adsorbed NH_3 was performed by increasing temperature until 873 K at 10 K min^{-1}. The signal corresponding to m/z of 16, assigned to NH_3, was used for the analysis of the NH_3 TPD curves.

FTIR spectra of pre-adsorbed pyridine or CO_2 were recorded with an IFS55 equinox spectrometer (Brücker) equipped with a DTGS detector using 100 scans and a resolution of 4 cm^{-1}. Catalyst and support powders were pressed (3 tons) into self-supported wafers (15 mg, 13 mm diameter) and placed in a homemade IR cell. Samples were first dehydrated under vacuum ($<10^{-5}$ mbar) at 773 K for 2 h. After cooling down to RT, a first spectrum was taken as reference. Samples were then exposed to 10 mbar of pyridine for 30 min. FTIR spectra were recorded after outgassed the samples ($<10^{-5}$ mbar) in four steps of 1 h: RT, 373, 473 and 573 K.

2.3. Catalytic evaluation

Catalytic tests were made in a continuous-flow stainless-steel fixed-bed reactor. The composition of the model charge was 2 wt.% 2-methylthiophene (2-MT) and 20 wt.% olefins dissolved in n-heptane. Dodecane (2 wt.%) was used as an internal standard for the chromatographic analysis. Two kinds of essays were performed. In the essays type A, a commercial mixture of 2,4,4-trimethyl-1-pentene (TM1P) and 2,4,4-trimethyl-2-pentene (TM2P) (3:1 approximately) was used. These are representative of terminal and internal branched olefins in FCC naphtha respectively. On the other hand, in the essays type B, 1-octene was used as a representative of linear olefins.

Before reaction, 0.35 g of catalyst (0.18–0.6 mm particle size) was dried in situ under N_2 flow (100 ml min^{-1}) at 393 K for 1 h, and subsequently, activated with a H_2S/H_2 mixture (15/85, v/v) at 673 K (10 K min^{-1}) for 3 h. Then, the following reaction conditions were fixed: 17 MPa, 523 K, liquid-flow rate of 20 ml h^{-1} and H_2/liquid feed ratio of 500. Under these conditions, the absence of any diffusion limitations was previously verified by using the experiments proposed by Le Page et al. [15]. Catalytic tests were conducted until reaching the steady state. Condensable products were analyzed offline in a HP 6890 gas chromatograph equipped with a HP-1 column (100 m × 0.25 mm × 0.5 μm) and a FID detector. Product identification was performed by GC–MS analyses and by comparing the retention times of some reagent-grade pure compounds in the FID and FPD detectors in the same column.