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Thiotolerant $Ir/SiO_2–Al_2O_3$ bifunctional catalysts: Effect of metal–acid site balance on tetralin hydroconversion

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ABSTRACT

The hydroconversion of tetralin over iridium nanoparticles supported on amorphous silica–alumina (ASA) has been investigated in a continuous high-pressure gas-phase micro-reactor in the presence of H_2S. In order to tune the Ir particle size, the bifunctional Ir/ASA catalysts have been submitted to sintering treatments. The samples have been characterized by HRTEM and XPS. From careful analysis of tetralin conversion products by comprehensive two-dimensional gas chromatography (GC×GC–MS) and NMR, compound families have been unambiguously distinguished. Hydrogenation, dehydrogenation, (saturated and aromatic) ring-contraction products, and (saturated and aromatic) one-ring-opening products are formed, without significant cracking. The catalysts exhibit stable activity in the presence of sulfur. As the mean particle size increases from 1.5 to 8 nm, the ring-opening/contraction selectivity increases dramatically. This effect is related to an increase of the acid/metal site ratio.

1. Introduction

The reduction in pollution and energy consumption by vehicles requires new technologies for the production of high-quality fuels. In the case of diesel regulations, cetane number (CN), which measures the fuel combustion efficiency, will have to increase in the next years (CN must be at least 51 since 2000 in Europe). Aromatics in diesel fuels produce particulates in the exhaust gases and, in addition, have poor ignition properties. Thus, their amount has to be reduced. The unprecedented demand of high-quality diesel, especially in Europe, gave birth to commercial upgrading technologies such as aromatics saturation (ASAT) [1] combined with, or following, deep hydrodesulfurization. However, the improvement of CN by ASAT is limited by the feedstock composition and cannot reach high values, since the formed naphthenic compounds present a modest increase in CN relative to their parent aromatic precursors. CNs of petroleum cuts increase with their paraffinic character as well as with their molecular weight. Thus, an additional route, complementary to ASAT, has been proposed, the so-called selective ring opening (SRO) route (see Fig. 1) [2,3].

Since compounds containing two fused six-membered rings constitute most of the aromatic/naphthenic feed, tetralin, naphthalene, and decalins (*cis* and *trans*) are often considered as model molecules representative of diesel fuels in SRO studies. In theory, the SRO reaction may lead to very high CNs but in practice, it is often limited to the opening of one ring, which in some cases may cause a dismal loss of CN [4]. The chemistry of SRO refers to several combined catalytic routes and requires in fact balanced metallic and acidic functions to achieve optimal performances, *i.e.*, reduce the number of rings while retaining the number of carbon atoms of the reactant molecule [5].

Concerning metal-catalyzed hydrogenolysis, an abundant literature demonstrates that three- to five-membered ring opening can be accomplished on group VIII metals and alloys [6–8]. The ring-opening ability depends on a number of factors, such as particle size, nature of the support, and nature of the cyclic compound (ring opening is much more difficult for six-membered rings than for five-membered rings). However, McVicker et al. have evidenced the unique properties of Ir for SRO, showing the propensity of this metal to cleave the C—C bond *via* the dicarbene mechanism [3]. Compared to single rings, opening of multiple-ring molecules has been far less studied due to the lower rate of this type of reactions and its increased complexity [5], but Ir has also been found efficient for hydrogenolysis of bicyclic naphthenes [3].

Carbocation cleavage on acidic catalysts is another way of achieving ring opening, mostly by β-scission. However, together with hydrogen transfer, transalkylation or disproportionation, it may produce more than 200 compounds and fast catalyst deactivation [9]. It has been shown that addition of a noble metal like Pt to

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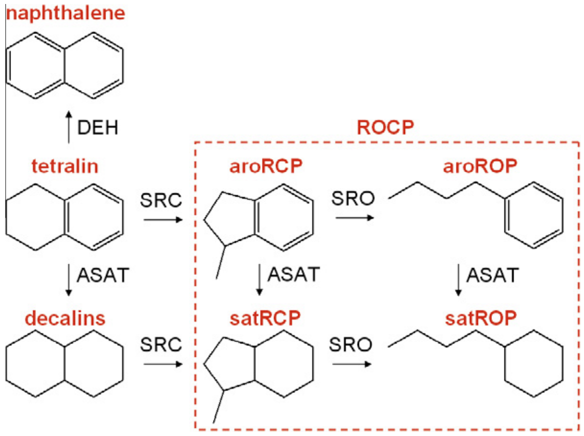

Fig. 1. Simplified reaction scheme showing the various product families for tetralin hydroconversion on Ir/ASA (only one representative product is displayed per family). DEH, ASAT, SRC, and SRO denote dehydrogenation, aromatics saturation, selective ring contraction, and selective ring opening, respectively. This scheme is not mechanistic (*e.g.*, SRO may occur without intermediate SRC).

acidic materials reduces the strength of Brönsted acid sites and significantly enhances isomerization and ring opening of decalin [10]. Unfortunately, the use of zeolites [9–16] can lead to undesirable non-selective cracking, side reactions and pore restriction issues. Thus, recent research has also focused on noble-metal catalysts supported on mesoporous silica-based materials [17–23]. In such bifunctional catalysts, although mild, the acidic function enables ring contraction, which can facilitate further hydrogenolysis of the C—C bond on metallic sites.

An additional important parameter is thiotolerance, *i.e.*, catalyst resistance to the presence of sulfur in the feed. In dual-stage processes, noble metals can be used since H_2S pressure has been drastically decreased between the two reactors. Thus, the design of an optimal catalyst should consider the sulfur resistance toward residual H_2S (from 10 to 250 ppm, depending on the running parameters of the two-stage process and the performances achieved in the first hydrodesulfurization reactor). Interaction between metals and acidic supports favors thiotolerance, the electron transfer from the metal to the support weakening the metal—sulfur bond [5]. Unfortunately, most studies on model molecules do not consider the poisoning effect of H_2S, which notably affects the hydrogenation reaction [24] and possibly the hydrogenolysis reaction.

In order to take advantage of the unique selective hydrogenolysis properties of Ir combined with the ring-contraction ability of acidic catalysts and their benefic effect on metal thiotolerance, several works on SRO have used Ir-based catalysts containing modified supports [20,25,26] or promoters [22,27,28]. Again, multiring compounds have been studied to smaller extent, and only Infantes-Molina et al. have considered the tetralin/Ir system for SRO, using Zr–MSU as a support [20].

In the course of an extensive SRO study of Ir supported on amorphous silica–alumina, we have previously investigated in details the preparation of Ir/ASA catalysts [29] and the effect of support acidity (by tuning the Si:Al ratio in ASA) on tetralin hydroconversion properties [30]. In this article, we report on the structural properties of Ir/ASA and, using an advanced chromatographic technique, on the effect of Ir particle size on the catalyst performances.

2. Experimental

2.1. Materials preparation

Amorphous silica–alumina (ASA, commercial name SIRAL-40) was supplied by Sasol (formerly Condea). The as-received powder in hydrated form was activated by heating at 550 °C in air for 3 h. It resulted in dehydration of the powder and transformation of the AlO(OH) (boehmite) alumina part to γ-Al_2O_3. The silica part is in the form of amorphous islands dispersed on alumina. The average particle size, BET surface area, pore volume, and pore diameter are 50 μm, 500 $m^2\,g^{-1}$, 0.90 $mL\,g^{-1}$, and 6.4 nm, respectively. The silica concentration measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Activa – Horiba Jobin Yvon) after dehydration was 36 wt.% silica (*i.e.*, Si:Al atomic ratio 0.48). Characterizations of the SIRAL product range can be found elsewhere [30,36].

The catalysts were prepared by incipient wetness impregnation of ASA with iridium trisacetylacetonate ($Ir(C_5H_7O_2)_3$, Sigma–Aldrich, purity 97%) dissolved in toluene using the concentration needed to obtain an Ir loading of 1.0 wt.%. After impregnation, the samples were dried at 120 °C overnight and in some cases calcined at 350 °C in air flow (60 $mL\,min^{-1}$) for 3 h (heating rate from room temperature: 2 °C min^{-1}). In all cases, they were reduced in H_2 flow (60 $mL\,min^{-1}$) at a temperature comprised between 350 and 550 °C for 6 h. The sample characteristics are reported in Table 1.

Once the preparation was optimized [29], leading to well-dispersed nanoparticles (mean diameter 1.5 ± 0.2 nm), a sintering procedure was applied to obtain larger particles. To this aim, the sample was heated to 500–700 °C for 4–6 h in 2 vol.% H_2O balanced in N_2 (by flowing 60 $mL\,min^{-1}$ of N_2 at atmospheric pressure through a saturator containing liquid water at RT), similar to the treatment applied by Balcon et al. [31]. Samples sintered at 500 °C and 700 °C are denoted S500 and S700, respectively (Table 1).

2.2. Materials characterization

2.2.1. Transmission electron microscopy

The size distribution of Ir nanoparticles was determined by high-resolution transmission electron microscopy (HRTEM, Jeol JEM-2010 and JEM-2010F).

Carbon replicas were prepared by the following method. A dispersion of the catalyst crushed in ethanol was deposited over a cleaved mica plate, which was then covered with a carbon film

Table 1
Characteristics of the catalysts.

Catalyst pretreatment[a]	Ir loading[b] (wt.%)	Ir particle size[c] (nm) surface-weighted size (nm) volume-weighted size (nm)
C350R350	0.80	$d = 7.8 \pm 4.3;\ 1.4 \pm 0.2$ $d_{surf} = 11.0 \pm 3.5$ $d_{vol} = 12.1 \pm 3.5$
R350	0.96	$d = 1.4 \pm 0.2$ $d_{surf} = 1.5 \pm 0.2$ $d_{vol} = 1.5 \pm 0.2$
R350 + C350 + R350	0.96	Idem
R450	0.90	$d = 1.5 \pm 0.4$ $d_{surf} = 1.7 \pm 0.4$ $d_{vol} = 1.8 \pm 0.3$
R550	0.90	$d = 1.4 \pm 0.3$ $d_{surf} = 1.5 \pm 0.2$ $d_{vol} = 1.6 \pm 0.3$
R350 + S500 + R350 (=S500)	0.81	$d = 4.9 \pm 1.2;\ 1.4 \pm 0.3$ $d_{surf} = 5.4 \pm 1.2$ $d_{vol} = 5.7 \pm 1.2$
R350 + S700 + R 350 (=S700)	0.90	$d = 6.7 \pm 1.9;\ 1.3 \pm 0.2$ $d_{surf} = 7.8 \pm 2.0$ $d_{vol} = 8.4 \pm 2.2$

[a] Cx denotes calcination in air flow for 3 h at *x* °C, Ry means subsequent reduction in H_2 flow for 6 h at *y* °C, Sz means sintering at *z* °C in 2 vol.% H_2O in N_2.
[b] Determined by ICP-OES.
[c] Mean particle size and standard deviation determined from TEM images (see Section 2.2.1 for details).