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Iridium addition enhances hydrodesulfurization selectivity in 4,6-dimethyldibenzothiophene conversion on palladium

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ABSTRACT

38% to 93% selectivity enhancement toward sulfur-free products was observed upon iridium addition to a palladium-only catalyst in the hydrodesulfurization of a refractory sulfur compound 4,6-dimethyldibenzothiophene (4,6-DMDBT) at the same 40% conversion from a 300 ppm, S-containing feed at 5 MPa and 300 °C. Pd promoted hydrogenation to sulfurous intermediates, while Ir catalyzed C—S hydrogenolysis and also improved Pd resistance to sintering. The selectivity in the direct desulfurization path for the Ir-containing catalysts increased up to 26% versus 5% for the Pd-only catalyst. The bimetallic catalyst allowed for a decrease in S from 300 ppm to 11 ppm. It can be used at reduced pressure (3 MPa) with only a 15% decrease in hydrodesulfurization conversion as compared to the operation at 5 MPa.

1. Introduction

Strict environmental regulations on the sulfur content in fuels along with the poorer quality of the upgraded feedstock have reinvigorated considerable interest in deep hydrodesulfurization (HDS) technologies. As an example, Environment Canada—Air limits the maximum level of sulfur to 30 ppm in gasoline and 15 ppm in diesel fuel [1,2], which are now referred to as low-sulfur and ultra-low sulfur fuels. Sulfur reduction to such levels has to do primarily with the elimination of refractory sulfurous compounds such as dialkyl-dibenzothiophenes with alkyl groups adjacent to the sulfur atom, which makes the HDS process quite challenging [3]. 4,6-Dimethyldibenzothiophene (4,6-DMDBT) is a typical molecule in this category and is usually selected as a model compound for deep HDS studies [4].

Numerous works have been published on the HDS mechanism of dibenzothiophene (DBT) and its alkyl-substituted derivatives such as 4,6-DMDBT [5–10], which propose two major pathways for their HDS: (i) direct desulfurization (DDS), the path of lower hydrogen consumption achieved by the hydrogenolysis of the C—S bond of the reactant leading to the formation of sulfur-free aromatic products, and (ii) hydrogenation (HYD), the path that strongly relies on the availability of hydrogen initially to hydrogenate an aromatic ring of the sulfurous molecule before the C—S bond breakage, resulting in a mixture of sulfur-free aromatic and/or saturated rings (depending on the extent of hydrogenation). The DDS route requires the perpendicular adsorption of the reactant on the catalyst surface (σ mode), while HYD proceeds via the parallel bonding of the reactant with the surface (π mode) [4,5,11]. DDS is dominant for dibenzothiophene hydrotreating (80–90%) [12], but the HDS of 4,6-DMDBT mainly takes place through the HYD path, as the presence of methyl groups near the sulfur atom results in steric hindrance and prevents the perpendicular adsorption [3,11–13]. The steric change that occurs in the plane of a hydrogenated ring as compared to the remaining aromatic ring(s) reduces the hindrance imposed by the alkyl substitution [11]. Thus, it is suggested that a good hydrogenation catalyst is required for the deep HDS of 4,6-DMDBT [14].

Transition-metal supported catalysts, primarily based on Co/Mo and Ni/Mo, have been conventionally used for HDS [10,13,15–23], however, they are not active enough for acceptable levels of refractory compound desulfurization. It is suggested either that the catalyst volume must be increased several fold or that higher pressures are required, which is technologically challenging [24,25]. There is also a reported precedent of 85% DDS selectivity over phosphide catalysts of NiFeP/SiO_2 (at 30 atm and 340 °C) [26], but due to the low volumetric activity, reactor volumes must be increased several times to achieve comparable conversions with the existing Ni/Mo catalyst. Improved NiMo and CoMo catalysts have been marketed for ultra-deep desulfurization. As an example, a SMART

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Table 1
Characteristics of the studied catalysts.

Catalyst, support: γ-Al_2O_3	Pd/Ir loadings[a], wt.%	Colloidal particle size, nm	CO uptake, $mol_{CO}/mol_{(Pd+Ir)}$	Pd/Ir molar ratio	Particle size[b], nm
Pd	0.305/0.0	2.5 ± 0.4 [44]	0.04	–	17.2
$Pd_{8.8}Ir$	0.233/0.047	–	0.07	8.8	9.5
$Pd_{7.2}Ir_2$	0.259/0.131	2.9 ± 0.5	0.22	3.6	3.4
$Pd_{3.6}Ir$	0.181/0.090	2.6 ± 0.6	0.12	3.6	6.3
Pd_3Ir_2	0.185/0.225	–	0.16	1.5	5.2
$Pd_{1.4}Ir$	0.080/0.107	2.5 ± 0.6	0.18	1.4	4.6
Ir	0.0/0.231	1.5 ± 0.2 [44]	0.67	0.0	1.9

[a] Determined from NAA.
[b] Based on CO chemisorption and CO/metal surface ratio of 1.

catalyst is able to desulfurize dibenzothiophenes via DDS on its CoMo component and via hydrogenation on its NiMo component followed by hydrogenolysis [12]. Co/Mo catalysts are used at lower pressures than those of conventional HDS because they promote the DDS pathway [12].

An alternative solution is to add a second-stage hydrotreater with more active noble metal catalysts for ultra-deep desulfurization of initially pretreated fuels with 250–300 ppm S [27], which are largely composed of the most refractory molecules such as 4,6-DMDBT. In this scenario, the major emphasis for HDS of refractory sulfur compounds has been placed on promoted noble metal catalysts (Pt group) because of their high hydrogenation activity. The available literature on the use of noble metals for the HDS of 4,6-DMDBT is not very rich, and the existing works are almost exclusively limited to mono- and bimetallic Pd- and Pt-based catalysts [4,14,23,27–32]. In the HDS of DBT on supported Pd catalysts, DDS selectivity values are around 80% on Pd catalysts at conversion levels above 50% [23,33]. This is attributed to the lower activation energy in the DDS path of DBT [23]. However, in the case of 4,6-DMDBT, the steric hindrance of the methyl groups adjacent to the sulfur atom dramatically reduces the contribution of the DDS route on monometallic Pd catalysts, and the catalytic activity dominantly relies on the hydrogenation path. For instance, in a series of 4,6-DMDBT HDS studies performed on supported Pd catalysts [4,14,29], the DDS selectivity values were always found to be around 1% at various conversion levels.

From the capex and opex perspectives, it is desirable to shift the HDS mechanism toward the DDS path that does not require pressures as high as those needed for the hydrogenation path. Since DDS operates through hydrogenolysis, a catalyst with a high hydrogenolysis activity is required to make an impact in the DDS route. As has been shown for thiophene HDS on Pt [34] and Ru clusters [35], when thiophene binds onto sulfur vacancies by σ-bonding through the lone pair in the S-atom (η^1(S)-coordinated thiophene), desulfurization occurs, while its π-bonding through the aromatic ring (η^4-coordinated thiophene) results in hydrogenation. Small Pt clusters exhibit a greater preference for desulfurization due to the prevalence of coordinatively unsaturated edge and corner atoms, which bind with S more strongly and lead to lower metal availability and to a preference for η^1(S)-coordinated thiophene [34]. Thus, a first requirement for an efficient direct desulfurization route is smaller metal nanoparticles. This requirement makes the choice of Pd-only systems rather undesirable because of palladium's low resistance to thermal sintering. Recall that the presence of Pd should be especially desirable for 4,6-DMDBT HDS because its high hydrogenation ability may provide high formation rates of sulfurous hydrogenated intermediates with a weakened steric hindrance of the C—S bond to reach the catalyst surface.

A second metal may improve the sintering resistance of Pd, and, preferably, it should have a high hydrogenolysis activity. A lesson could be adopted from a ring-opening catalysis of naphthenic molecules, which occurs on a metal function either via a dicarbene mechanism, which occurs through the metal-carbon bonding of two carbon atoms standing perpendicular on the metal surface, or via a π-adsorbed olefin mode with flat reactant adsorption [36]. Among different noble metals, iridium reportedly displays the strongest tendency for ring opening via a dicarbene mechanism, and it is known in refineries for its outstanding hydrogenolysis activity [37–40]. Iridium forms a part of reforming Pt-Ir catalysts, which were introduced by Exxon in the 1970s with improved activity as compared to monometallic Pt, which had previously been used in commercial contexts [37].

In terms of HDS, the literature reports the removal of sulfur with Ir catalysts on smaller model molecules [41,42] as well as on real feed [39], but not on 4,6-DMDBT specifically. For instance, an Ir/MgF_2-MgO catalyst presented almost 50 times higher activity than a commercial Co/Mo catalyst in the HDS of thiophene [42]. The high DDS selectivity of Ir (~90%) has been reported in the HDS of DBT over a series of noble metal (Pt, Pd, Ru, and Ir) catalysts supported on zeolite HY [33,43]. However, studies of Ir in the HDS of a mixed feed or of molecules with a non-hindered C—S group do not provide information on how Ir's outstanding hydrogenolysis activity could be useful for the HDS of refractory sulfur compounds. To the best of our knowledge, no information is available for the Ir-catalyzed HDS of 4,6-DMDBT, in neither monometallic nor bimetallic formulations.

The research hypothesis of this work is that the iridium addition to palladium catalysts for 4,6-DMDBT HDS may improve the contribution of the C—S hydrogenolysis in both the parent DMDBT and the partly hydrogenated sulfurous intermediates formed in the hydrogenation route catalyzed by Pd. Iridium may bring about the advantages of an outstanding ring-opening catalyst for C—S bond cleavage. It may also improve the thermal resistance of sintering-prone palladium, thus decreasing the metal cluster size and contributing to a larger proportion of η^1(S)-coordinated intermediates. This is a first report on a noble metal catalyst development that takes advantage of metals with two different functionalities in order to promote both the HYD and DDS routes in 4,6-DMDBT HDS.

2. Experimental

2.1. Materials

$H_2IrCl_6 \cdot xH_2O$ and H_2PdCl_4 were used as metallic precursors. Poly-vinylpyrrolidone (PVP, average MW: 40,000) was used as a stabilizing agent and γ-Al_2O_3 powder (150 mesh) with an average pore size of 58 Å and an SSA of 155 m^2/g (provided by the manufacturer) was used as a support material; these materials were obtained from Sigma-Aldrich. Ethanol and acetone were used as received from Fisher Scientific. Milli-Q water was used as a solvent and for washing the synthesis flasks. All of the gases were ultra-high purity (i.e. 99.999%) and purchased from Praxair. For catalytic reactions, *n*-decane (99.4%) from Fisher Scientific as well as *n*-dodecane (≥99%), indane (95%), and 4,6-dimethyldibenzothiophene (97%) from Sigma-Aldrich were used as received.