INFLUENCE OF THE Ir CONTENT AND THE SUPPORT ON THE THIOTOLERANCE OF THE Ir/SiO_2-Al_2O_3 CATALYSTS FOR SELECTIVE RING OPENING OF DECALIN

Silvana A. D'Ippolito[1], Adriana D. Ballarini[1], Santiago M. Rosas[1], Laurence Pirault Roy[2], Catherine Especel[2], Florence Epron[2], Carlos L. Pieck[1]

[1] Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) (UNL, CONICET), Colectora Ruta Nac. Nº 168 - Paraje El Pozo - CP 3000, Santa Fe, Argentina.

[2] Institut de chimie des milieux et matériaux de Poitiers (IC2MP), Université de Poitiers, UMR 7285 CNRS, 4, rue Michel-Brunet, 86073 Poitiers cedex 9, France.

*Author to whom correspondence should be addressed: pieck@fiq.unl.edu.ar

ABSTRACT

The influence of Ir content on sulphur tolerance for the selective ring opening of decalin was investigated. Ir/SiO_2-Al_2O_3 catalysts (70 and 80 wt% SiO_2) were used. In the absence of sulphur, slight differences wereobserved on the yields according to the metallic content regardless of the support used. Although the results of cyclopentane hydrogenolysis showed that the metallic function acquires importance as the metal content increases, for these metal percentages the acid function limits the rate of decalin opening reaction. Productsdistribution are strongly modified using decalin with S content compared to pure decalin. The formation of dehydrogenated products is virtually null due to S adsorbed on the metal sites. The support has lowinfluence on the thiotolerance. The results related to the amount of S per Ir surface atom, showed that for a moderate S content (S/Ir_{surf} ~ 0.30) 1.5 Ir/Sy appears to be less poisoned than 1Ir/Sy and 2Ir/Sy.

KEYWORDS: selective ring opening, decalin, Ir/SiO_2-Al_2O_3, thiotolerance

1 Introduction

Selective ring opening (SRO) is a particular case of hydrocracking of cyclic hydrocarbons where the endocyclic C-C bonds should be broken without modifying the molecular weight of the molecules. SRO can be used to enhance the light cycle oil (LCO) fraction and thus contribute to meet the growing demand for diesel fuel. LCO products consists mainly of aromatic compounds of two rings, which can be hydrogenated and then opened by SRO to obtain linear or mono-branched paraffins leading to an improved cetane indexfor Diesel fuel application.[1,2] Moreover, the sulphur content of the LCO fractions is about 0.2 to 2 wt% and the industrial fractions must be hydrotreated in a first stage to decrease the S content between 6 to 16 ppm.[3-5]

Ring opening reactions involving C6 cycles are favored using bifunctional catalysts.[6-8] Among metals, such as Rh, Ir, Ru, and Ni, with moderate to high hydrogenolytic activity, Ir is the most selective to ring opening products.

[9] Kubička et al. proved that Brønsted acid sites of the support play an important role due to the need of skeletal isomerization before ring opening.[10] The incorporation of Pt or Ir on acidic materials decreases the strength of Brønsted acid sites of the support, enhances isomerization, and ring opening ofdecalin.[7,11,12] On the other hand, the acid function can lead to excessive cracking lowering the yield to ring opening products. For this reason, it was proposed the use of noble metal catalysts supported on mesoporous silica-alumina whose acid function is lower compared to zeolites, but still enough to allow the ring contraction reaction which facilitates the hydrogenolysis of the C-C bond on the metal sites.[13-18]

As reported above, the oil fractions to be processed in SRO contain sulphur compounds that are known to cause deactivation of noble metal catalysts.[19-22]An improvement of the tolerance to sulphur is observed when noble metals are deposited on acid supports, related to the modifications of the electronic properties of the metals due to their interaction with the Brønsted acid sites of the support (electron acceptor), with an electron transfer from the metal to the support.[21,22] This weakens the metal-sulphur bond and disfavors strong chemisorption of sulphur compounds.[23,24] Non-zeolitic acid supports such as SiO_2-Al_2O_3 could generate moderate or strong resistance to sulphur.[2,25-28] For example, Nassreddine *et al*. stated that iridium catalysts supported on SiO_2-Al_2O_3 present high stability in the presence of 200 ppm of H_2S during SRO oftetralin.[24]

The objective of the present work is to study the influence of the content of iridium and of the nature of the support (SiO_2-Al_2O_3 of various proportions) in selective ring opening of decalin, in the absence and presence of sulphur compounds, in order to determine the formulation with the best balance between the acid and metal functions.

2 Experimental

2.1 Supports

SIRAL 70 and 80 (amorphous silica alumina, SiO_2-Al_2O_3) provided by SASOL were used as supports. SIRAL 70 and SIRAL 80 contain 71.5 and 79.0 wt% of SiO_2, respectively.[12] In the following, they will be named S70 and S80, respectively. The specific surface areas were 377 $m^2\ g^{-1}$ and 337 $m^2\ g^{-1}$ for S70 and S80, respectively. In order to eliminate any organic impurities that it could have due to the adsorption of impurities from the environment and manipulation the supports were calcined during 4 h at 450 °C (10 °C min^{-1}, air, 60 $cm^3\ min^{-1}$). Moreover, this treatment standardizes the moisture content of the support. The procedure involves calcination of the support and its subsequent storage in closed bottles inside a desiccator with silicagel.

2.2 Catalysts preparation

The support was impregnated with HCl (0.2 mol L^{-1}, 1.5 $cm^3\ g^{-1}$) and left 1 h at rest. H_2IrCl_6 was then incorporated to obtain 1, 1.5, and 2 wt% of iridium. The impregnated samples were shaken gently for 1 h, then dried at 70 °C in a thermostatic bath until dry powder was obtained and left 12 h in an oven at 120 °C. Lastly, the catalysts were calcined (air, 60 $cm^3\ min^{-1}$, 300 °C, 4 h) and reduced (H_2, 60 $cm^3\ min^{-1}$, 500 °C, 4 h). The catalysts were called xIr/Sy, where “x” stand for the nominal Ir content (1, 1.5, or 2 wt%) and “Sy” for S70 and S80 supports.

2.3 Determination of metallic and chlorine contents

An X-ray Model EDX-720 (Shimadzu) fluorescence spectrometer was used to determine the composition of the catalysts.

2.4 Temperature-programmed desorption (TPD) of pyridine

Samples were impregnated with pyridine, and the excess removed in a hood. Before, the experiments, theywere treated in nitrogen flow (40 cm^3 min^{-1}) for 1 h at 110 °C to eliminate physisorbed pyridine. The temperature was increased at 10 °C min^{-1} to a final value of 750 °C. The reactor exhaust was connected to a flame ionization detector (FID) to measure the amount of desorbed pyridine.

2.5 Isomerization of 3,3-dimethyl-1-butene (33DMB1)

The reaction was performed in a microreactor using 100 mg of catalyst. At first, the catalyst was reduced *in situ* (H_2, 60 cm^3 min^{-1}, 450 °C, 1 h). After the sample was cooled in N_2 (30 cm^3 min^{-1}) to the reaction temperature (100 or 125 °C), the reaction was started baddition of 33DMB1, with a partial pressure of 20.9 kPa in N_2 and a flow rate of 15.27 mmol h^{-1}. Products were analyzed on-line by gas chromatography.

2.6 Temperature-programmed reduction (TPR)

TPR experiments were carried out at atmospheric pressure using a reductive mixture of H_2-N_2 (5% H_2 v/v, 10 cm^3 min^{-1}). Samples (200 mg) were heated at 10 °C min^{-1} from 25 °C up to 700 °C. The reactor outlet was connected to a TCD to obtain the TPR profile. Before the TPR measurements the samples were calcined *in situ* at 400 °C with flowing air 60 cm^3 min^{-1} g^{-1} for 1 h.

2.7 X-ray Photoelectron Spectroscopy

XPS analysis were carried out on samples reduced *ex situ* at 500 °C during 2 h under pure H_2 (60 cm^3 min^{-1}) with a Kratos Axis Ultra DLD spectrometer using a monochromatic Al Kα source (1486.6 eV) operating at 180W (12mA, 15kV). Operating pressure of the spectrometer was 9 x 10^{-8} Pascal. The charge neutraliser system was operated for all analyses.

High-resolution spectra were recorded using an analysis area of 300µm x 700 µm and 40 eV pass energy. This pass energy corresponds to Ag $3d_{5/2}$ FWHM of 0.55 eV. Data were acquired with 0.1 eV steps. The binding energy was calibrated using Si2p binding energy fixed at 103.9 eV as an internal reference. The following binding energies regions were recorded: C1s, O1s, Al2p, Si2p, Ir4f. Atomic concentration ratios were calculated using sensitivity factors provided by the manufacturer. Peak fitting was achieved with Casa XPS software (version 2.3.17) and Gaussian-Lorentzian profiles (Lorentzian 30%) where used with adding asymmetry peak-shape for Ir4f metallic.

2.8 Determination of the metal dispersion by dynamic chemisorption of CO

Metal dispersion of the Ir particles was determined by CO chemisorption where calibrated pulses of CO were injected in a stream of nitrogen that flowed over the sample until saturation. For that purpose, the sample was reduced (H_2, 500 °C, 10 °C min^{-1}) for 1 h. subsequently nitrogen was flowed over the sample for 1 h at 500 °C to remove adsorbed hydrogen. Finally, the sample was cooled to room temperature in nitrogen and pulses of 0.6 µmoles of CO were sent to the reactor. The CO that was not chemisorbed was quantitatively converted into CH_4 over a kieselguhr-supported Ni catalyst and detected in a flame ionization detector. It was assumed stoichiometry of one CO per surface Ir.[29,30]

2.9 Cyclopentane (CP) hydrogenolysis

The reaction was performed at atmospheric pressure in a conventional fixed bed glass microreactor. The reaction temperature was controlled by using a Novus N1100 controller. Samples were reduced with H_2 at 500 °C for 1 h before reaction. The conditions used were: reaction temperature = 225 °C, CP flow rate = 0.36 cm^3 h^{-1}, catalyst mass= 80 mg, H_2 flow rate = 36 cm^3 min^{-1}, reaction time = 2 h. The products were analyzed on a Thermo Scientific Trace 1300 gas chromatograph equipped with a capillary column Phenomenex ZB-1 connected online. The activity in CP hydrogenolysis was determined from the conversion extrapolate at zero reaction time.

2.10 Ring opening of decalin

The stainless-steel autoclave reactor and the reaction conditions were described previously.[31] Pure decalin (37.5% cis isomer and a cis/trans ratio of 0.60) and mixtures of decalin doped with thiophene (S= 10, 15,and 20 ppm) were used. The reaction conditions were: volume of decalin = 25 cm^3, temperature = 300 and 350 °C, hydrogen pressure = 3 MPa, catalyst loading = 1 g, and stirring rate = 1360 rpm. It was checked thatdiffusional limitations due to mass transfer were negligible in these reaction conditions. The samples were analyzed at the end of the reaction (6 h) by a Thermo Scientific Trace 1300 gas chromatography apparatus using with a Phenomenex ZB-5 capillary column. The identification of the reaction products was carried out on GC-MS Saturno 2000 spectrometer coupled to a GC Varian 3800 using the same chromatographic column. The experimental reproducibility (catalytic test and analysis) was checked by (i) undertaken the same experiment twice and (ii) for each experiment by injecting three times the same collected sample. The yields and conversion were calculated by averaging the three values. Thus, it was estimated that the conversion and yield values were obtained with a precision of ± 1.5%.[32]

3 Results and discussion

3.1 Characterization of the catalysts

Table 1 shows the percentages of chlorine and iridium determined by fluorescence together with the values of total acidity and distribution of acid sites (weak, moderate, and strong) obtained from the TPD traces of pyridine.

It can be seen in Table 1 that the iridium content deviates by 2.5 to 15 % from the nominal value, the 1.5Ir catalyst presenting the highest difference. One can also note that the chlorine content increases with the metal content whatever the support. Moreover, for the same metal content, the chlorine contents are higher on the S70 support than on the S80 one.

Table 1. Chorine and iridium content (wt%), total acidity and distribution of acid sites.

Catalyst	Cl (wt%)	Ir (wt%)	Total Acidity (μmol Py g^{-1})	Acid Amount (μmol Py g^{-1})		
				Weak	Moderate	Strong
S70[a]	-	-	1119	128	493	498
1Ir/S70	0.76	0.93	1763	95	565	1103
1.5Ir/S70	1.07	1.30	1899	25	493	1381
2Ir/S70	1.10	1.95	2189	84	696	1409
S80[a]	-	-	1104	303	384	417
1Ir/S80	0.61	0.96	1820	85	626	1109
1.5Ir/S80	0.71	1.28	1780	88	608	1084
2Ir/S80	0.96	1.80	2084	110	761	1213

[a] Values reported previously[12], Weak: T<300 °C; Moderate: 300<T<500 °C; Strong: T>500 °C.

The TPD profiles of pyridine are shown in Figure 1, while the TPD of pyridine of the supports were previously reported.[12] Contrary to the support alone, both series of Ir catalysts present mostly strong acid sites (desorption temperature above 500 °C). It can be observed in Table 1 that for the same metallic content, both series have similar total acidity (difference < 7%). In both series, the increase in the iridium content correlated to an increase in chlorine content produces a displacement of the peaks at lower desorption temperatures but increases the total acidity. Ozimek et al. proved that the incorporation of chlorine ions on alumina produce an increase of the acidity.[33,34] It was also demonstrated that the increase in the total acidity is due to the deposition of both chlorine and iridium species.[12] It is noteworthy that, whatever the Ir content and the support (S70 or S80), catalysts present a huge majority of strong acid sites (Table 1) contrary to the supports alone.

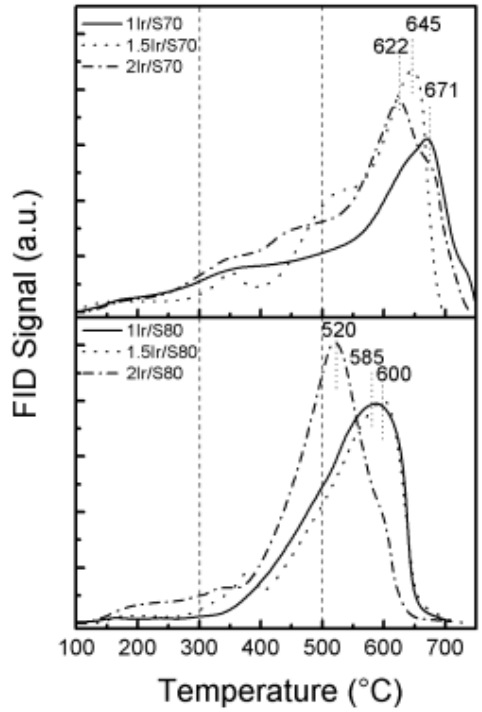

Figure 1. TPD of pyridine traces of both catalyst series.

The support acidity was previously studied by FTIR spectroscopy of pyridine (Py-FTIR) in order to discriminate Lewis from Brønsted acid sites.[32] At 150 °C, the amounts of Brønsted acid sites were of 81 and 72 µmol of Py g_{Cat}^{-1} on S70 and S80, respectively, much lower than the number of Lewis acid sites (148 and 144 µmol of Py g_{Cat}^{-1}, respectively), with a Brønsted/Lewis ratio of *ca.* 0.5. The total numbers of acid sites (Lewis + Brønsted) determined at 150 °C were of 229 and 216 µmol of Py g_{Cat}^{-1} for S70 and S80, respectively, which gives a ratio between S70 and S80 of 1.06, similar to the ratio determined in the present study from the TPD of pyridine (1.01).

The isomerization reaction of 33DMB1 occurring by protonic mechanism is also useful to evaluate the Brønsted acid sites.[35] At reaction temperatures lower than 300 °C only two isomers are formed (2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene) resulting from the reaction on Brønsted acid sites, Lewis acid sites being not involved in their formation.[36-38] In the present study, as the reaction was carried out at 100 and 125 °C, the selectivity to 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene was 100 %, confirming that the reaction only is catalyzed by Brønsted acid sites.

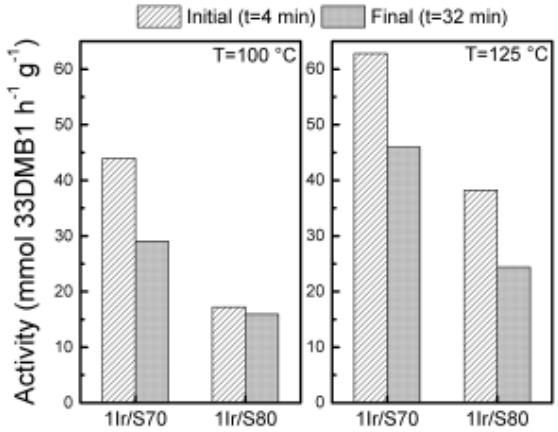

Figure 2. Initial and final activity on the isomerization of 33DMB1 reaction at reaction temperature 100 and 125 °C.

Figure 2 displays the activity of 1Ir/S70 and 1Ir/S80 for the 33DMB1 conversion at initial and final reaction time for both reaction temperatures. 1Ir/S70 catalyst is more active than 1Ir/S80 at both reaction temperatures. It was demonstrated that the conversion of 33DMB1 depends mainly on the support, and is less affected by the metal deposition, the metal being inactive in the reaction.[39] That means that probably the same trends would be observed for 1.5Ir and 2Ir. The much higher activity of the Ir/S70 catalyst compared with Ir/S80 in the 33DMB1 isomerization would suggest a higher ability of this catalyst to protonate olefins, i.e. more Brønsted acid sites, which seems contradictory with the results arising from pyridine adsorption/desorption followed by TPD or FTIR. However, one has to keep in mind that pyridine needs stronger Brønsted acid sites than olefinsto be protonated.[40] For example, pyridine adsorption onto alumina support only gives rise to bands characteristic of pyridine species coordinated on Al^{3+} Lewis acid sites, whereas the same alumina support, pretreated in the same conditions, present a non-negligible activity in 33DMB1 isomerization.[41] Consequently, it can be inferred from the results of 33DMB1 isomerization, that Ir/S70 is more active than Ir/S80 for olefin isomerization, with probably more Brønsted acid sites of moderate or even weak strength. This can be due to the highest chlorine contents of the It/S70 catalysts compared to the Ir/S80 ones.

Figure 3 reports TPR profiles of the both series of catalysts. Considering the hydrogen consumption, in all the catalysts the iridium is reduced to the zerovalent state. It should be recalled that after the pretreatment at 400 °C Ir is present in the form of IrO_2 species. 1Ir/Sy catalysts present two reduction peaks overlapped. The peak at lower reduction temperature is attenuated by increasing the metal content to 1.5 wt% and appears as a shoulder; while, on 2wt% Ir catalysts, only one well defined peak is observed. The presence of these two reduction peaks can be attributed to a heterogeneous deposition of the iridium species.[42,43]Furthermore, in Figure 3 the maximum reduction peak of the 1.5/Sy and 2Ir/Sy catalysts appears at higher temperatures than the corresponding 1Ir/Sy. This trend, already observed for Ir/Al_2O_3 catalysts can be associated with a stronger metal-support interaction.[44]

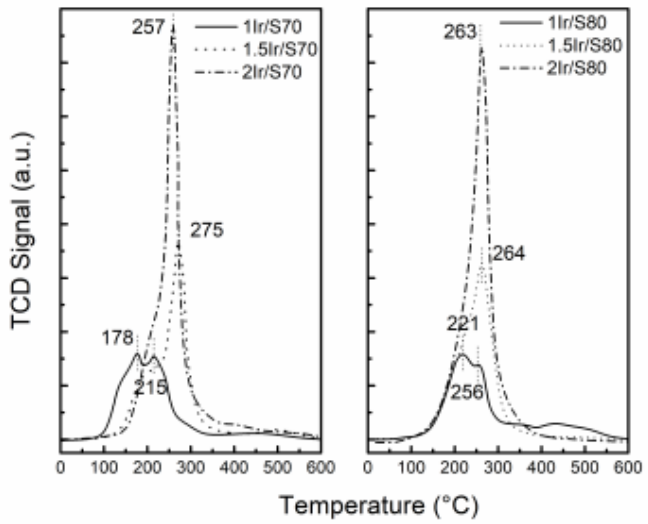

Figure 3. TPR traces of both catalyst series.

Additional XPS analysis was performed in order to corroborate the strong metal interaction observed by TPR experiments. Figure 4 shows that the peak due to metallic Ir ($4f_{7/2}$) appears at 61.85 and 61.06 eV for the 1 and 1.5 catalysts, respectively supported on S80. According to the literature, the Ir $4f_{7/2}$ (metallic) peak should appear at 61 +/- 0.2 eV. The observed displacement was attributed to a strong metal support interaction.[45,46]

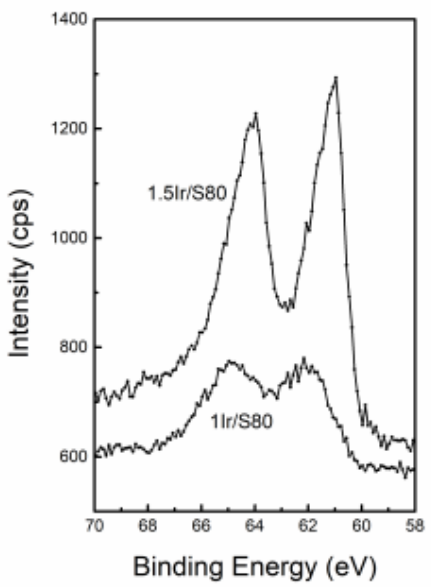

Figure 4. X-ray photoelectron spectra (Ir 4f core levels) for 1Ir/S80 and 1.5Ir/S80 samples reduced ex situ at 500 °C under H_2.

Table 2. Values of the metal dispersion determined from CO chemisorption, Ir particle diameter, the activity in cyclopentane conversion, and the corresponding TOF (reaction temperature = 225 °C, CP flow rate = 0.36 cm^3 h^{-1}, catalyst mass= 80 mg, H_2 flow rate = 36 cm^3 min^{-1}, reaction time = 2 h).

Catalyst	Metal dispersion (%)	Ir particle diameter (nm)[a]	TOF CP (s^{-1})	Activity (μmol CP g^{-1} s^{-1})
1Ir/S70	45	2.5	0.38	8.4
1.5Ir/S70	34	3.2	0.37	8.6
2Ir/S70	32	3.4	0.35	11.4
1Ir/S80	41	2.7	0.39	8.0
1.5Ir/S80	39	2.8	0.34	8.7
2Ir/S80	40	2.8	0.32	11.8

[a] Determined from metal dispersion supposing spherical particles.[48]

Cyclopentane hydrogenolysis is used to evaluate the metallic function of the catalysts for hydrogenolysis activity. It is known that this reaction needs large ensembles of metal atoms to be produced.[47] It can be seen in Table 2 that the activity increases with the Ir content in both series, while the turn over frequency (TOF), molecules of CP converted per Ir surface atom per second, does practically not change because of the small differences in the mean size of the metallic particles as calculated from the metal dispersion.[48]

3.2 Decalin reaction without sulphur

Decalin reaction was carried out at 325 and 350 °C. The reaction products were lumps as cracking (C_1-C_9), ring opening (RO, C_{10}), ring contraction (RC), and dehydrogenated products (DH) naphthalene and other heavy dehydrogenated products.[49] Figure 5 shows the conversion values and yields to different reaction products obtained

during decalin reaction at 325 and 350 °C. It can be seen that the decalin conversion logically increases with the reaction temperature. The increase of the Ir content from 1 to 2 wt% leads to a small increase of the conversion whatever the support. For a given Ir content, the conversion values are practically the same for S70 and S80. This similarity between both series has been observed for CP conversion, pyridine thermodesorption, and amount of Brønsted acid sites as it was determined by Py-FTIR, and then attributed to strong Brønsted acid sites, the only difference being the amount of moderate and weak Brønsted acid sites determined by isomerization of 33DMB1. Then, it can be inferred that these moderate and weak Brønsted acid sites do not play a determining role in the reaction.

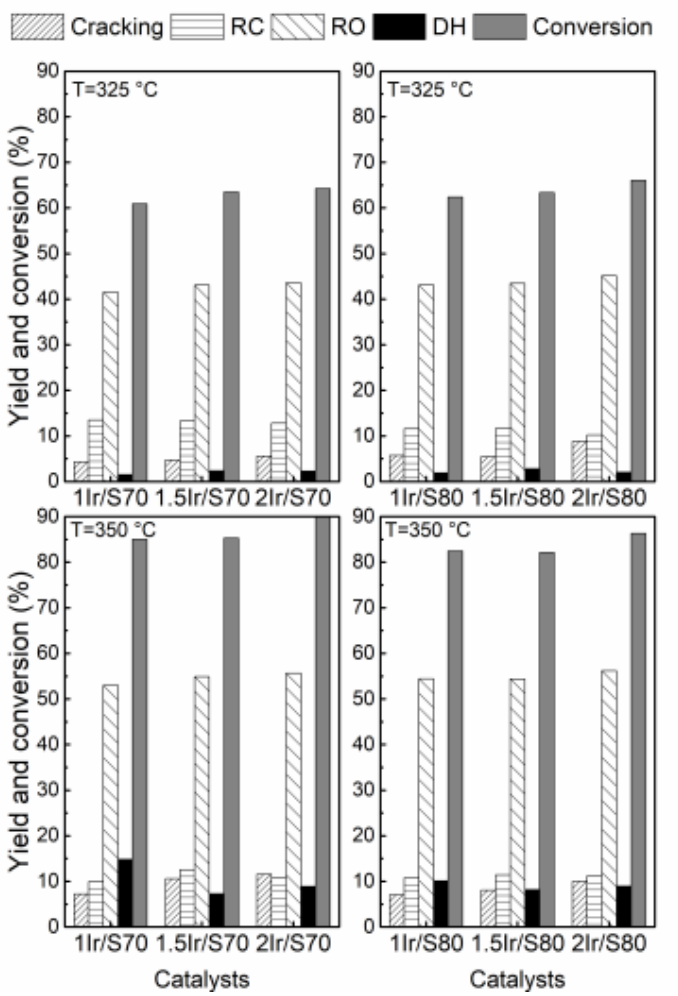

Figure 5. Decalin conversion and yield to cracking (CR), ring contraction (RC), ring opening (RO), and dehydrogenated products (DH) obtained on the decalin reaction (6 h).

The small increase of the conversion with the Ir content is an unexpected result. Catalysts with higher Ir contents have higher hydrogenolytic activity (Table 2) and higher acidity (Table 1). There is no thermodynamic limitation because decalin reaction is irreversible. Therefore, if the reaction time or the amount of catalyst is very high, 100 % of decalin conversion could be achieved. We did not obtain 100 % of conversion. Nonetheless, in order to eliminate the possibility that all the catalysts have the same conversion due to an excess of catalyst into the reactor, additional experiments using 0.5 g of catalysts were performed.

Table 3 shows the conversion of decalin and the yield to different reaction products obtained using 0.5 g of catalyst at 350 °C. It must be noted that the three catalysts have practically the same conversion and distribution of products, as observed for 1 g of catalyst. Consequently, it could be concluded that the increase of metal content from 1 to 2 wt% has little influence on decalin conversion as it was previously reported for RuS_2/HY zeolite and Pt/Beta zeolite.[50,51]

Table 3. Conversion of decalin and yield to different reaction products obtained using 0.5 g of catalyst at 350 °C and 6 h reaction time.

Catalyst	Conversion (%)	Yield (%)			
		CR	RC	RO	DH
2Ir/S70	63.0	9.4	10.3	40.2	3.1
2Ir/S80	62.5	7.8	11.0	40.2	3.5
1Ir/S80	58.6	5.6	8.6	38.2	6.2

It can be observed in Figure 5 that, for all the catalysts, the increase in the reaction temperature leads to an increase in the yield to ring opening, cracking, and dehydrogenated products; and to a decrease in the formation of ring contraction products; this behaviour is more noticeable on the catalysts supported on SIRAL 70. These results are consistent with many publications that postulate that the SRO mechanism of molecules with C6 rings proceeds via consecutive reactions: initially formation of ring contraction products, followed by ring opening and finally cracking.[7,9,10,18,24,52-56] The yield to cracking products increases a little with the iridium content, but as the increase in Ir content induces an increase in both hydrogenolytic activity on the metallic sites and acidity, it is not possible to infer which type of site, metallic or acidic, is responsible of the formation of cracking products. The increase of the Ir content has practically no influence on the yield to ring opening products. Monteiro et al. found that for metal contents greater than 1 wt%, the acid function of the catalyst becomes the limiting step of the reaction rate.[51]

3.3 Decalin reaction with sulphur

The oil fraction to be treated for the selective ring opening process could contain sulphur compounds, mainly thiophenes which are strong deactivating compound of the catalysts.[57-60] Sulphur is considered as a poison of the metallic function because it adsorbs on the metal sites but, it could be also adsorbed on theacid sites of the support.[19-22,61,62]

Figure 6 shows the conversion values obtained using decalin contaminated with different amounts of thiophene at 350 °C. At first, the effect of sulphur on the decalin conversion was studied on the support alone, i.e. without iridium. Values of conversion and yield using decalin without sulphur of the supports were previously reported.[12] The addition of 10 ppm of S decreases the conversion of about 20 % on both supports. This could be associated to thiophene adsorption on acid sites.[62]

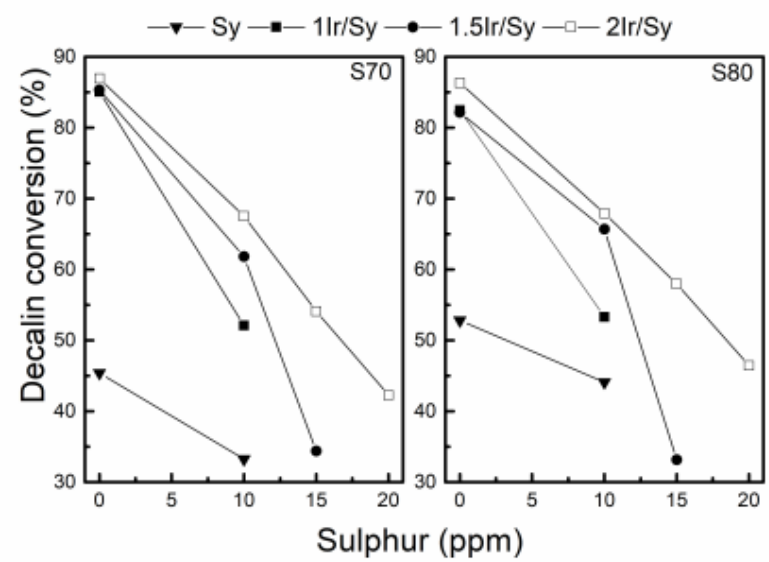

Figure 6. Conversion as a function of the sulphur content (ppm) obtained on decalin reaction at 350 °C.

Before analyzing the S influence on activity and selectivity of the Ir catalysts, it is important to determinate the S/Ir_{surf} atomic ratio used in each decalin reaction. Table 4 gives the S/Ir_{surf} ratios calculated taking into account that the total amount of S incorporated with the decalin is adsorbed on superficial Ir atoms of each catalyst. These values vary between 0.19 to 0.46.

The activity in decalin conversion for both Ir catalysts series decreases more drastically than that of the supports alone, as the sulphur content increases due to the loss of metal activity and some loss of acid function. However, it is observed that the catalysts with the highest Ir content are less deactivated. It can be seen that with 2 wt% Ir, the one supported on S80 is a little more active than the one on S70 for S of 15 and 20 ppm. This behaviour could be due to the higher metal dispersion of the 2Ir/S80 catalyst compared to 2Ir/S70 catalyst (Table 2).

Table 4. S/Ir_{surf} atomic ratio used on decalin reaction doped with 10, 15 and 20 ppm of thiophene.

Catalyst	S/Ir_{surf} atomic ratio		
	10 ppm	15 ppm	20 ppm
1Ir/S70	0.32	-	-
1.5Ir/S70	0.30	0.46	-
2Ir/S70	0.22	0.32	0.43
1Ir/S80	0.34	-	-
1.5Ir/S80	0.27	0.40	-
2Ir/S80	0.19	0.28	0.37

It is interesting to analyze the decline of conversion relative to conversion obtained using pure decalin defined as $\Delta conversion = (X_{pure\ decalin} - X_{decalin\ with\ S})/X_{pure\ decalin}$ (where X is conversion) as a function of the S/Ir_{surf} atomic ratio. It can be seen in Figure 7 a direct relation between the fall of the conversion and theincrease of the S/Ir_{surf} ratio. Sulphur strongly decreases the metallic activity because it can block neighboring metal atoms simply due to its size of the same order of the one of the metals.[63] Similar conclusions were reported by Fischer et al. who suggested that sulphur adatom has an effective blocking radius extending over a number of nearest and next-nearest neighboring metal atoms.[64] The toxicity of sulphur on metal depends on the amount of sulphur, for example when S/Pt = 0.5 the metal is chemically inert.[65] This value corresponds to the total coverage of Pt by sulphur.[66] It was reported a higher adsorption of sulphur on iridium than on Pt which was attributed to its electronic properties, that is, lower electronic affinity (2.12 eV for Pt and 1.6 eV for Ir).[65] According to the values of S/Ir_{surf} ratio reported in Table 4 and considering the aforementioned works related to sulphur influence on the metallic activity, it could be expected that metallic function is partially and totally deactivated by S. It was found that the catalysts evaluated in the decalin conversion in the presence of different amounts of sulphur practically do not present coke deposit, as evaluated by temperature programmed oxidation (results not shown), contrary to the catalysts evaluated in the absence of sulphur. Consequently, it can be inferred that the deactivation observed is due to sulphurpoisoning. Finally, for a similar S/Ir_{surf} ratio = 0.30 ± 0.04, 1.5Ir/Sy presents the highest decalin

conversion compared to 1Ir/Sy and 2Ir/Sy. In other words, it seems more resistant to moderate sulphur loading (10 ppm of S). For highest S/Ir_{surf} ratio (S/Ir_{surf} ratio ≥ 0.4), 1.5Ir/Sy is more strongly deactivated than 2Ir/Sy.

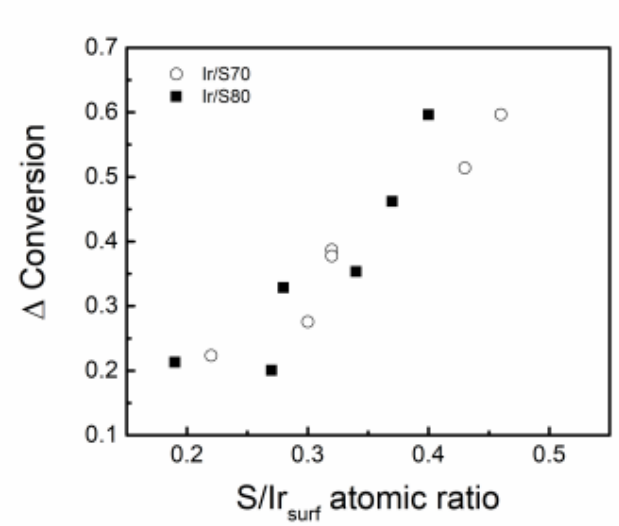

Figure 7. Relative conversion loss due to sulphur as a function of S/Ir_{surf} for both catalysts series. (Δconversion = $(X_{pure\ decalin} - X_{decalin\ with\ S})/X_{pure\ decalin}$).

Table 5. Conversion of trans and cis decalin (considering the initial amount of cis and trans decalin) obtained at 6 h reaction (T = 350 °C) with 0, 10, 15, and 20 ppm of sulphur on the feed.

S content (ppm)	Trans-decalin conversion (%)				Cis-decalin conversion (%)			
	0	10	15	20	0	10	15	20
S70	22.7	31.5	-	-	83.2	36.1	-	-
1Ir/S70	77.8	42.2	-	-	97.1	68.6	-	-
1.5Ir/S70	78.1	59.3	27.5	-	97.3	65.9	45.8	-
2Ir/S70	80.5	66.2	50.3	38.9	97.7	69.6	60.5	47.9
S80	26.8	36.2	-	-	96.3	57.3	-	-
1Ir/S80	74.1	42.1	-	-	96.3	72	-	-
1.5Ir/S80	73.7	63.9	32.6	-	96.3	68.7	34.1	-
2Ir/S80	79.8	72.3	62.1	45.3	97.1	60.5	51.1	48.4

Table 5 shows the conversion values of cis and trans decalin using feed doped with 0, 10, 15, and 20 ppm of sulphur. As expected, in the case of the metal catalysts, the conversion of cis and trans decalin decreases as the increases of the amount of sulphur on the decalin due to the sulphur adsorption on Ir particles. Curiously, for the supports alone, the conversion of trans-decalin increases by using decalin with 10 ppm of sulphur, while the conversion of cis-decalin is strongly decreased. Considering the different molecular configurations of these isomers, it can be inferred that the presence of thiophene prevents (or affects) cis to trans-decalin stereoisomerization.[67] As a result, the formation of trans-decalin is decreased.

The evolution of the various types of products is presented in Figure 8. The yield to cracking products increases with the addition of 10 ppm and 15 ppm of S on both catalysts series while the yield to RC decreases. Sulphur addition strongly decreases the formation of dehydrogenated products (Figure 8). Considering that dehydrogenation reactions are catalyzed by the metal function, the results are consistent with the poisoning of the metallic function. Recently, Catherin et al. found similar results in SRO of decalin, the addition of S to Ru catalysts supported on zeolite HY, decreased coke formation and dehydrogenated products.[50] Therefore, some

increase of the cracking reaction in the presence of sulphur could be due to the lower deposition of coke, as compared with the experiments in the absence of sulphur. Monteiro et al. postulated that the main effect of the S is to modify the balance between the acid and metal activity, which alters the reactivity of the intermediate products and favors the cracking reactions.[50] However, the strong decrease of metal function at the highest S concentration (20 ppm) leads to a lower yield to dehydrogenated products and consequently less cracking products since dehydrogenated products are more easily cracked than saturated compounds.[68]

Additionally, Figure 8 shows that in the presence of 10 ppm of S, the cracking products reach a maximum with 1.5Ir/Sy catalysts and this maximum corresponds to a minimum in the ring contraction products. When increasing the concentration of S to 15 ppm, this maximum was found with 2Ir/Sy catalysts which have the minimum yield to RC products. This shift of the maximum and the minimum to higher metal contents as the sulphur concentration increases shows that isomerization is preponderant when the metal function is deactivated by sulphur. Blanco et al. emphasize that the addition of S on supported noble metals causes changes in the mechanism of reaction because of the poisoning of the metal function.[69]

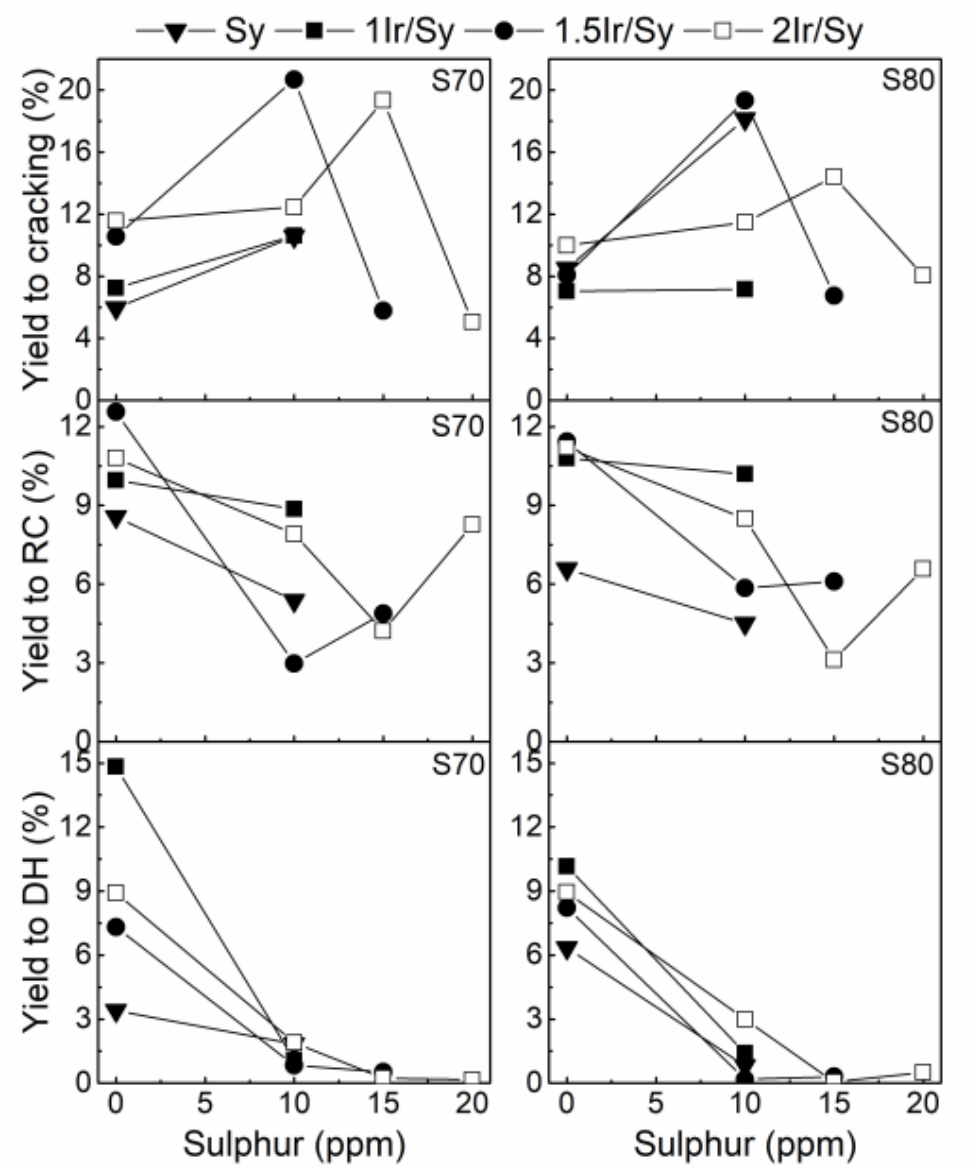

Figure 8. Yield to cracking, ring contraction (RC), and dehydrogenated (PD) products as a function of the ppm of sulphur on decalin obtained at 6 h reaction (T = 350 ° C).

Figure 9 shows the yield to RO products as a function of the sulphur content on decalin. The yield to ring opening products decreases with the amount of sulphur on decalin reaction medium. As expected, higher iridium content, lower decrease in the yield to RO products. On S70, for the same S/Ir_{Surf} ratio (~0.31) the highest yield in RO products (38%) is obtained with 1.5Ir. However, for higher S/Ir_{Surf} value, (≥0.4), and whatever the support, 2Ir/Sy is the less deactivated with a yield ≥ 30%. This behaviour is consistent with a bifunctional mechanism proposed to ring opening reaction of decalin. Sulphur blocks the active metallic sites decreasing the high hydrogenolytic activity of iridium.[61,70] Probably, sulphur causes a decrease in the size of metallic ensembles that inhibits formation of the αβ-adsorption complexes which are esencial for hydrogenolysis reaction catalyzed by metals.[71,72] However, some influence of the sulphur on the acid function cannot be discarded because the decalin conversion on the supports alone was also influenced by the presence of sulphur.

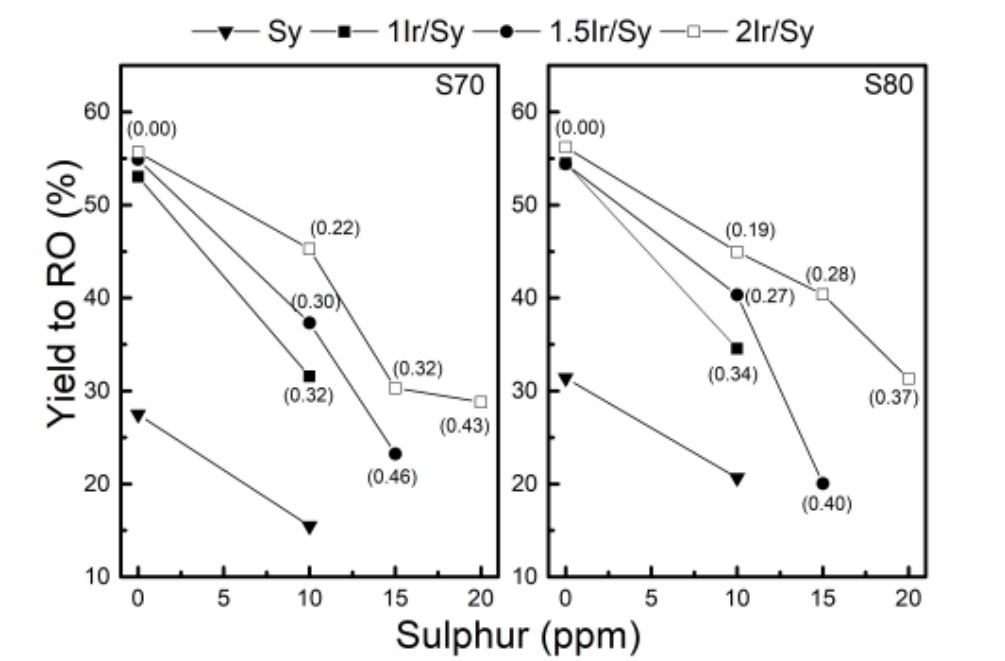

Figure 9. Yield to ring opening products as a function of the S content on decalin reaction obtained at 6 h reaction (T = 350 ° C). Values between brackets correspond to the S/Ir_{surf} ratio.

It can be inferred that higher metallic content favors tolerance to sulphur. Also, the higher thiotolerance exhibited by the catalysts 2Ir/S70 and 2Ir/S80, can be attributed to the strong metal-support interaction, evidenced by TPR, leading to the formation of electrodeficient metallic particles, which in interaction with the Brønsted acid sites of the support decreases the strength of the S-Metal bond.[27] This could be also due to more accessible metal atoms (because of the higher metal content and a similar metal dispersion) since the amount of catalyst and the duration of the catalytic test are the same. Finally, for these two catalysts, the test was performed using 0.5 g of catalyst instead of 1 g but maintaining contant the S/Ir_{Surf} ratio. Obviously, the amount of decalin was also reduced to 12.5 cm^3. Results are reported in Table 6. Surprisingly, the conversions obtained with two times less catalyst are superior to those attained with 1g of catalyst and the decline of conversion (Δ Conversion) is around 0.16, much lower than that observed with 1 g of catalyst for the same S/Ir_{Surf} ratio (Δ Conversion > 0.5).

Table 6. Influence of the sulphur on decalin reaction using equal S/Ir_{Surf} ratio.

Catalyst	Weigh (g)	Sulphur (ppm)	S/Ir	Conversion (%)	Yield (%)			
					CR	RC	RO	DH

2Ir/S70	1.0	20	0.43	42.27	5.05	8.27	28.80	0.15
2Ir/S70	0.5	10	0.43	52.60	9.77	8.99	32.09	1.74
2Ir/S80	1.0	20	0.37	46.45	8.05	6.58	31.32	0.50
2Ir/S80	0.5	10	0.37	53.91	6.52	9.86	35.50	2.07

4 Conclusions

In the experimental conditions used, the metal charges of the catalysts have little influence on the activity and yield using pure decalin because the acid function limits the reaction rate.

Whatever the Ir content and the support, the same trends are observed with a decrease in conversion proportional to the amount of S per Ir surface atom. However, for a moderate S loading ($S/Ir_{Surf} \sim 0.30$) 1.5 Ir/Sy appears less poisoned than 1Ir/Sy and 2Ir/Sy, while for higher amounts of S ($S/Ir_{Surf} \geq 0.40$), the 2Ir is more resistant to S poisoning. This could be attributed to the strong metal-support interaction that leads to the formation of electrodeficient particles, which in interaction with the Brønsted acid sites of the support decreases the strength of the S-Metal bond, as well as the largest available amount of iridium surface particles.

In the presence of sulphur, the yield to dehydrogenated products was almost zero due to the deactivation of the Ir activity by sulphur. Unfortunately, the sulphur also leads to an increase of the cracking products because a change of the reaction pathway.

Although the catalyst supported on SIRAL 80 presented a slight advantage over SIRAL 70 in thiotolerance for S = 15 and 20 ppm, the supports have a lower incidence on sulphur tolerance than the metallic content.

Acknowledgment

The authors warmly thank Christine Canaff from IC2MP for the XPS experiments and the results analysis, performed in particular conditions due to the COVID-19 pandemic.

References

[1] R. C. Santana, P. T. Do, M. Santikunaporn, W. E. Alvarez,J. D. Taylor, E. L. Sughrue, D. E. Resasco,*Fuel* **2006**, *85*, 643.
[2] B.H. Cooper, B. B. L. Donnis, *Appl. Catal. A* **1996**, *137*, 203.
[3] A. Martínez, M. A. Arribas, S. B. C. Pergher, *Catal. Sci. Technol.* **2016**, *6,* 2528.
[4] V. Calemma, M. Ferrari, S. Rabl, J. Weitkamp, Fuel **2013**, *111*, 763.
[5] V. Calemma, R. Giardino, M. Ferrari, *Fuel Process. Technol.* **2010**, *91,* 770.
[6] M. Santikunaporn, J. E. Herrera, S. Jongpatiwut, D. E. Resasco, W. E. Alvarez, *J. Catal.* **2004**, *228,*100.
[7] D. Kubička, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, H. Karhu, T. Salmi, D. Y. Murzin, *J. Catal.* **2004**, *227*, 313.
[8] T. Sugii, Y. Kamiya, T. Okuhara, *Appl. Catal. A* **2006**, *312,* 45.
[9] G. B. McVicker, M. Daage, M. S. Touvelle, C. W. Hudson, D. P. Klein, W. C. Jr Baird, B. R. Cook, J. G.Chen, S. Hantzer, D. E. W. Vaughan, E. S. Ellis, O. C. Feeley, *J. Catal.* , *210*, 137-148.
[10] Kubička, D.; Kumar, N.; Mäki-Arvela, P.; Tiitta, M.; Niemi, V.; Salmi, T.; Murzin, D., *J. Catal.* **2004**,*222*, 65.
[11] R. Moraes, K. Thomas, S. Thomas, S. Van Donk, G. Grasso, J. -P. Gilson, M. Houalla, *J. Catal*. **2013**,*299,* 30.
[12] S. A. D'Ippolito, A. D. Ballarini, C. L. Pieck, *Energy Fuels* **2017**, *31,* 5461.

[13] S. Albertazzi, R. Ganzerla, C. Gobbi, M. Lenarda, M. Mandreoli, E. Salatelli, P. Savini, L. Storaro, A.Vaccari, *J. Mol. Catal. A* **2003**, *200,* 261.

[14] E. Rodríguez-Castellón, J. Mérida-Robles, L. Díaz, P. Maireles-Torres, D. J. Jones, J. Rozière, A.Jiménez-López, *Appl. Catal. A.* **2004**, *260,* 9.

[15] D. Eliche-Quesada, J. M. Mérida-Robles, E. Rodríguez-Castellón, A. Jiménez-López, *Appl. Catal., A***2005**, *279,* 209.

[16] A. Infantes-Molina, J. Mérida-Robles, E. Rodríguez-Castellón, J. L. G. Fierro, A. Jiménez-López,*Appl. Catal. B* **2007**, *73,* 180.

[17] M. Taillades-Jacquin, D. J. Jones, J. Rozière, R. Moreno-Tost, A. Jiménez-López, S. Albertazzi, A.Vaccari, L. Storaro, M. Lenarda, J. M. Trejo-Menayo, *Appl. Catal., A* **2008**, *340,* 257.

[18] K. Chandra Mouli, V. Sundaramurthy, A. K. Dalai, Z. Ring, Z. *Appl. Catal. A* **2007**, *321,* 17.

[19] Z. Paál, *Catalytic Naphtha Reforming.* 2nd ed., Marcel Dekker, New York **2004**, p. 35.

[20] T. Fujikawa, K. Idei, T. Ebihara, H. Mizuguchi, K. Usui, *Appl. Catal. A* **2000**, 192, 253.

[21] S. T. Homeyer, W. M. H. Sachtler, *J. Catal.* **1989**, *117,* 91.

[22] W. M. H. Sachtler, A. Y. Stakheev, *Catal. Today* **1992,** *12,* 283.

[23] H. Du, C. Fairbridge, H. Yang, Z. Ring, *Appl. Catal. A* **2005**, *294,* 1.

[24] S. Nassreddine, L. Massin, M. Aouine, C. Geantet, L. Piccolo, *J. Catal.* **2011**, **278***,* 253.

[25] R. M. Navarro, B. Pawelec, J. M. Trejo, R. Mariscal, J. L. G. Fierro, *J. Catal.* **2000**, *189,* 184.

[26] L. J. Hoyos, M. Primet, H. Praliaud, *J. Chem. Soc. Faraday Trans.* **1992**, *88,* 113.

[27] S. D. Lin, M. A. Vannice, ***J. Catal.*** **1993**, *143,* 563.

[28] M. V. Rahaman, M. A. Vannice, *J. Catal.* **1991**, *127,* 251.

[29] M. Haneda, T. Fujitani, H. Hamada, *J. Mol. Catal. A: Chem.* **2006**, *256,* 143.

[30] A. Bourane, M. Nawdali, D. Bianchi, *J. Phys. Chem. B* **2002**, *106,* 2665.

[31] S. A. D'Ippolito, C. Especel, L. Vivier, F. Epron, C. L. Pieck, *Appl. Catal., A* **2014**, *469,* 541.

[32] S. A. D'Ippolito, L. Pirault-Roy, C. Especel, F. Epron, C. L. Pieck, *RSC Adv.* **2017**, *7,* 46803.

[33] B. Ozimek, J. Grzechowiak, B. Radomski, G. Szezyglowska, *React. Kinet. Catal. Lett.* **1981**, *17,* 139.

[34] B. Ozimek, B. Radomski, *React. Kinet. Catal. Lett.* **1981**, *15,* 407.

[35] D. Martin, D. Duprez, *J. Mol. Catal. A* **1997**, *118,* 113.

[36] E. A. Irvine, C. S. John, C. Kemball, A. J. Pearman, M. A. Day, R. J. Sampson, *J. Catal.* **1980**, *61,* 326.

[37] C. Kemball, H. F. Leach, B. Skundric, K. C. Taylor, *J. Catal.* **1972**, *27,* 416.

[38] C. S. John, C. Kemball, R. A. Rajadhayarsha, *J. Catal.* **1979,** *57,* 264.

[39] S. A. D'Ippolito, C. Especel, L. Vivier, F. Epron, C. L. Pieck, *Appl. Catal. A* **2014**, *469,* 532.

[40] E. Finocchio, G. Busca, S. Rossini, U. Cornaro, V. Piccoli, R. Miglio, *Catal. Today* **1997**, *33,* 335.

[41] F. Epron, C. Carnevillier, P. Marécot, *Appl. Catal., A* **2005**, *295,* 157.

[42] L. Tournayan, N. R. Marcilio, R. Frety, *Appl. Catal.* **1991**, *78,* 31.

[43] U. Nylen, B. Pawelec, M. Boutonnet, J. L.G. Fierro, *Appl. Catal. A* **2006**, *299,* 14.

[44] E. Pachatouridou, E. Papista, E. F. Iliopoulou, A. Delimitis, G. Goula, I. V. Yentekakis, G. E.Marnellos, M. Konsolakis, *J. Env. Chem. Eng.* **2015**, *3,* 815.

[45] P. Reyes, M.C. Aguirre, G. Pecchi, J.L.G. Fierro, *J. Mol. Cata. A* **2000**, 164, 245.

[46] S. Bhogeswararao, D. Srinivas, *J. Catal.* **2015**, 327 65.

[47] A. Roberti, V. Ponec, W. M. H. Sachtler, *J. Catal.* **1973**, *28,* 381.

[48] G. Bergeret, P. Gallezot, *Handbook of Heterogeneous Catalysis,* 2nd ed.. Wiley-VCH, Weinheim **2008**;Vol. 2*,* p. 738.

[49] S. A. D'Ippolito, L. B. Gutierrez, C. L. Pieck, *Appl. Catal. A* **2012**, *445-446,* 195.

[50] N. Catherin, E. Blanco, L. Piccolo, D. Laurenti, F. Simonet, C. Lorentz, E. Leclerc, v. Calemma, C.Geantet, *Catal. Today* **2019**, *323,* 105.

[51] C. A. A. Monteiro, D. Costa, J. L. Zotin, D. Cardoso, *Fuel* **2015**, *160,* 71.

[52] M. A. Arribas, A. Corma, M. Díaz-Cabanas, A. Martinez, *Appl. Catal., A* **2004**, *273,* 277.

[53] S. J. Ardakani, X. Liu, K. J. Smith, *Appl. Catal., A* **2007**, *324,* 9.

[54] D. Kubička, M. Kangas, N. Kumar, M. Tiitta, M. Lindblad, D. Y. Murzin, *Top. Catal.* **2010**, *53,* 1438.

[55] K. Chandra Mouli, V. Sundaramurthy, A. K. Dalai, *J. Mol. Catal. A: Chem.* **2009**, *304,* 77.

[56] D. Kubička, T. Salmi, M. Tiitta, D. Y. Murzin, *Fuel* **2009**, *88,* 366.

[57] M. I. Girgis, B. C. Gates, *Ind. Eng. Chem. Res.* **1991**, *30,* 2021.

[58] D. D. Whitehurst, H. Farag, T. Nagamatsu, I. Sakanishi, I. Mochida, *Catal. Today* **1998**, *45,* 299.

[59] H. Liu, X. Meng, D. Zhao, Y. Li, *Chem. Eng. J.* **2008**, *140*, 424.

[60] J. L. Kao, G. B. McVicker, M. M. J. Treacy, S. B. Rice, J. L. Robbins, W. E. Gates, J. J. Ziemiak, V. R.Cross, T. H. Vanderspurt, *Stud. Surf. Sci. Catal.* **1993**, 75, 1019.

[61] O. Saur, T. Chevreau, J. Lamotte, J. Travert, J. -C. Lavalley, *J. Chem. Soc., Faraday Trans. 1* **1981**, *77,*427.

[62] Y. Aponte, D. Djaouadi, H. de Lasa, *Fuel* **2014**, *128,* 71.

[63] V. K. Shum, J. B. Butt, W. M. H. Sachtler, *J. Catal.* **1985**, *96*, 371.

[64] T. E. Fischer, S. R. Kelemen, *Surf. Sci.* **1977**, *69,* 1.

[65] J. Biswas, G. M. Bickle, P. G. Gray, D. D. Do, J. Barbier, *Catal. Rev. Sci. Eng./span>* ***1988****, 30, 161.*

[66] C. H. Bartholomew, P. K. Agrawal, J. R. Katzer, *Adv. Catal.* **1982**, *31,* 135.

[67] Y. Miyake, A. Baylaucq, C. K. Zéberg-Mikkelsen, G. Galliéro, H. Ushiki, C. Boned, *Fluid Phase Equilib.* **2007**, *252,* 79.

[68] J.M. Parera, N.S. Figoli, *Catalytic Naphtha Reforming. Science and Technology*, 1st ed., Marcel Dekker Inc., New York **1995,** p. 45.

[69] E. Blanco, L. Di Felice, N. Catherin, L. Piccolo, D. Laurenti, C. Lorentz, C. Geantet, V. Calemma, *Ind. Eng. Chem. Res.* **2016**, *55, 49,* 12516.

[70] M. J. Dees, V. Ponec, *J. Catal.* **1989**, *115,* 347.

[71] E. H. Van Broekhoven, V. Ponec, *J. Mol. Catal.* **1984**, *25,* 109.

[72] E. H. Van Broekhoven, V. Ponec, *Prog. Surf. Sci.* **1985**, *19,* 351.