Synthesis, characterization and hydrotreating activity of Ir catalysts supported on titania-modified mesoporous material

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Abstract

A titanium modified catalyst based on noble metal has been prepared with the main aim of obtaining Nitrogen-tolerant catalysts to be used in second stage processes of mild-hydrotreating. We study the catalytic properties of 1 wt% Ir-containing SBA-16 materials modified with Ti as heteroatom and impregnated with TiO_2 (anatase phase), in the hydrogenation of tetralin to decalin in the presence of 100 ppm of N as quinoline at 250°C and 15 atm of pressure of hydrogen, using a Parr reactor. The iridium oxidation sate upon Ti-containing SBA-16 was studied by XPS, EDX, TEM and XRD, arriving at the good proportion of Ir^0. The average metal particle size indicate that the Ir particle size is lower when we used Ti-SBA-16 than anatase/SBA-16. The experimental data was quantitatively represented by a modified Langmuir-Hinshelwood type rate equation. The preliminary results show these materials as promising catalysts for HDS/HDN reactions.

Keywords: Iridium containing SBA-16; Titanium modified SBA-16; Hydrogenation; inhibition; quinoline; Reaction Kinetic.

1. Introduction

It has long been recognized that HDN is more difficult and more demanding than HDS, requiring more severe reaction conditions. However, HDN has historically been of little concern to refiners because the quantities of nitrogen compounds in conventional petroleum feedstocks were relatively small. This situation is changing due to the need for processing lower quality crudes (1, 2). Heavier fuels require the removal of more nitrogen in order to reduce NOx emissions, to avoid poisoning of acidic catalysts, and to meet specifications of marketable products. At the industry, HDN is performed using either $Ni-Mo-S/Al_2O_3$ or $Co-Mo-S/Al_2O_3$ as catalysts. The development of new catalysts that are selective to C-N cleavage and understanding of their catalytic behavior is an important goal in the lasts investigations. For example: Rh, Ir, Ru and Pt supported on silica or alumina are known to catalyze effectively the nitrogen removal from methylamine, quinoline or pyridine also in the reduced state (3). In this paper, we describe the preparation of new mesoporous catalytic materials based on Ti-containing SBA-16, with highly and homogeneously dispersed particles of metallic iridium (Ir^0). To study the effect in the dispersion of transition metal, titanium was incorporated by post synthesis as TiO_2, and will be compared to that obtained with Ti-mesoporous, where Ti was incorporated during sol-gel synthesis. We study the performance of the obtained catalysts in the hydrogenation of tetralin in presence of quinoline at mild conditions in a batch reactor. Langmuir-Hinshelwood type rate equations were used to describe the reaction kinetics with physically meaningful and well-identified parameter values.

2. Experimental Section

2.1 Synthesis of: TiO_2-SBA-16:0.5 g of dried sample was dispersed in a solution containing 2 mL of titanium tetrabutylorthotitanate (TTBT) and 5 mL of ethanol. **Ti-SBA-16:** SBA-16 was synthesized according to (4).Tetraethylorthotitanate dissolved in 10 mL of ethanol was added slowly, then the solution reposed for 20 h without stirring. The resulting suspension was

transferred into the PP bottleat 80ºC for 24 h. **Ir/Ti-containing mesoporous support:** Iridium was incorporated by wetness impregnation followed by thermal treatment and reduction under hydrogen. We use Iridium Acetylacetonate (Aldrich 99.9% Ir(Acac)$_3$) as source of Ir, employing ethanol as solvent, due to its very low solubility in water. The iridium load was 1% wt.

2.2 Catalytic activity: The catalytic activity was measured in a 4563Parr reactor, at 250°C, 15 atm of pressure of hydrogen and 360 rpm. The feed consisted in 50 mL of 5% v/v of tetralin (98.5% FLUKA) in Dodecane in presence of 100 ppm of N as quinolone and 0.5 g of catalysts. The results were compared with a typical HDT catalyst as NiMo/Al$_2$O$_3$ Criterion DN200. The products were analysed with a HP 5890 Series II GC and HP-5 column.

3. Results and discussion

The textural and structural properties of Ir catalysts supported on Ti-containing SBA-16 materials are given in Table 1. The lower Ir crystal size was observed in Ti-SBA-16 support, with higher dispersion, showing an agreement between the data obtained by H$_2$chemisorptions and TEM results. XPS Iridium 4f signal of Ir nanoparticles dispersed in Ir/Ti-SBA-16 and Ir/TiO$_2$-SBA-16 are shown in Table 1. A component corresponding to Ir(0) or Ir–Ir bonds (Ir7/2 at 61.2eV and Ir5/2 at 64.5eV) and an Ir–O contribution at 62.5 and 65.5eV; a little shift is observed towards a higher BE for iridium species by their interaction with the support: 62.0 eV for Ir-O and 61.0 eV assigned to Ir0 (curves not shown)(5,6). In the case of Ti-SBA-16 the peak area analysis gives a contribution of 81% Ir0 and 19% Ir–O. It can be observed that the nanoparticles in Ti-SBA-16 present a good contribution from the Ir–Ir component character, in concordance with XRD and TEM results. For TiO$_2$ -SBA-16 sample, the contribution of Ir0 was 79% and Ir–O was 21%, according the data showed in Table 1, very close to the values of Ir sate on Ti-SBA-16 sample. Analysis of Ti species also were performed by XPS, results are shown in Table 1. According the XPS spectra (not showed) Ti appears as Ti^{+4} (-O4-) Ti2p3/2= 459.4 eV (Table 1), due to the isomorphous Si substitution in Ir/Ti-SBA-16. In this way, for Ir/TiO$_2$-SBA-16 sample, the Ti 2p3/2= 458.5 eV is in agreement with

literature data (TiO_2 as anatase, Ti2p3/2= 458.6 eV (7)). XPS data of Ti indicate that it is incorporated in the mesoporous nanostructure of SBA-16, asanatase phase in one case and as Ti+4 isolated ions in tetrahedral (Td) coordination when Ti is added in the sol-gel stage of the catalyst synthesis. Following the atomic ratio of Si/Ir (270) and Si/Ti (454) from the XPS analysis, the Ti and Ir species are well dispersed in the mesopororus of SBA-16 due to the low signal observed in XPS analysis (100 Å of depth). The same occurs with the noble metal employed is this work; the majority of it is within the pore nanostructure. Moreover, Table 1 also show the EDX results for Si/Ti and Si/Ir in the samples, supporting this idea, taking account the very low Si/Ti and Si/Ir ratios, compared with the ratios obtained by XPS. The TEM images of the catalysts and their corresponding PSDs (particle size distribution) are shown in Table 1 and Figure 1, respectively. The particle size distribution ranging from 0.5 to 6 nm indicate that catalyst metal particles were mainly present inside the porous, the mean particle diameter was found to be close to 2 nm in both cases indicating that majority of the particles reside inside of the pore system. The content of iridium in the catalysts was determined by Inductively Coupled Plasma (ICP) - Elemental Analysis.

Table 1. Ir and Ti species obtained by XPS, EDX and TEM

Sample	XPS Ir4f$_{7/2}$Ti 2p$_{3/2}$Atomic Ratio			EDX	Ir clusters (nm)
Ir/Ti-SBA-16	61.2 (81) Ir^0 62.5 (19) Ir-O	Ti2p$_{3/2}$= 459.4	Si/Ir= 270 Si/Ti= 454	Si/Ti=23.7 Si/Ir= 14.2	1.94^c – 2.30^b; 85^b
Ir/TiO$_2$-SBA-16	61.2 (79) Ir^0 62.5 (21) Ir-O	Ti2p$_{3/2}$= 458.5	Si/Ir= 265 Si/Ti= 360	Si/Ti=26.0 Si/Ir= 14.4	2.11^c – 2.50^b; 60^b
Ir/SBA-16	--	--	--	--	2.40^b – 2.60^{c,d}; 48^b
Ir/Al$_2$O$_3$	--	--	--	--	3.90^b – 4.30^d; 33^b

[a]D (%)= percentage metal dispersion obtained from hydrogen chemisorption.[b]H$_2$Chemisorption [c]TEM. [d] XRD.

Calculated Langmuir adsorption constants for all the samples tested are displayed in Figure 2, for those data obtained at 250°C. Among these compounds, the kinetic rate increased in the order NiMo/Al$_2$O$_3$<Ir/Al$_2$O$_3$<Ir/SBA-16<Ir/TiO$_2$-SBA-16 <Ir/Ti-SBA-16.Adsorption strength of the inhibitors increased in as follows: NiMo/Al$_2$O$_3$<Ir/Ti-SBA-16<Ir/Al$_2$O$_3$<Ir/TiO$_2$-SBA-16 <Ir/SBA-16.
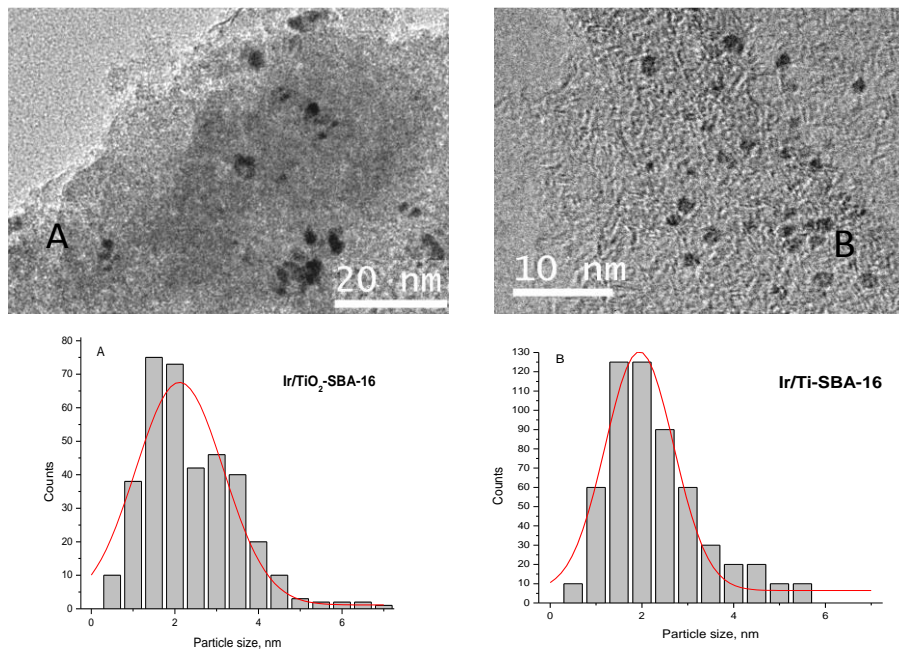
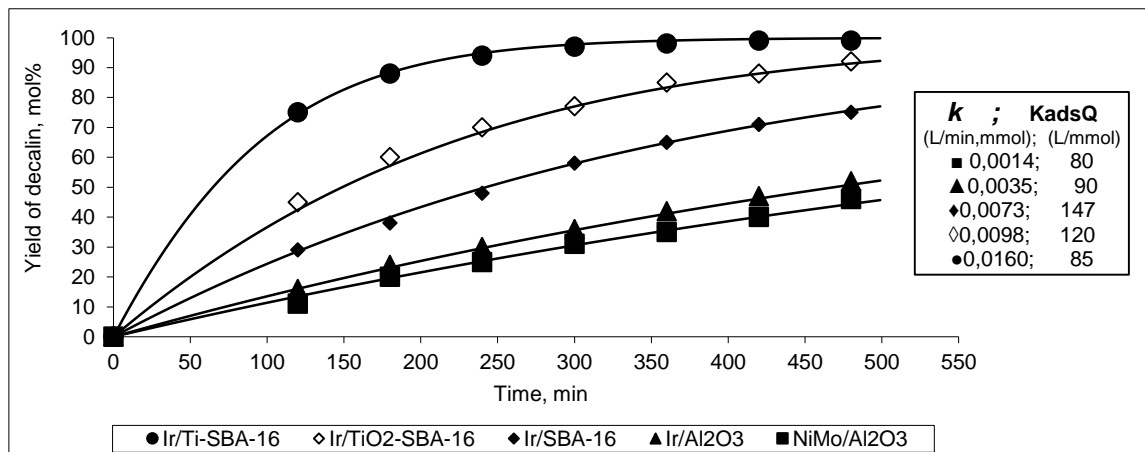**Figure 1.** TEM and Histograms of PSDs of Ir/TiO$_2$-SBA-16 (A) and Ir/Ti-SBA-16 (B)

Figure 2. Kinetic of the hydrogenation of tetralin presence of quinolone at T=250ºC, P=15 atm, 360 rpm. The lines were obtained by fitting the kinetic curves derived from the model to the experimental data.

Even when quinoline adsorption constant for NiMo is lower than for Ir/Ti-SBA-16, the last is far more active for this reaction. The inhibiting effect of nitrogen (according to the adsorption constant values) is strong at concentrations as low as 100 ppm, but still Ir/Ti-SBA-16 was more

active than with commercial NiMo/alumina catalyst (i.e.TL mol% conv. obtained at the same conditions was 75% higher at 4 h of reaction).This maximum in catalytic activity was attributed to the formation of a noble metal active phase with an optimal cluster size and electronic environmental capable to be more nitrogen resistant.

4. Conclusions

The kinetic model was successfully applied to the hydrogenation of tetralin in presence of quinoline. The hydrogenation rates were useful to determine the most active catalyst. The hydrogenation rates of tetralin were lower when quinoline was present in the mixture. The inhibition was described reasonably well by Langmuir-Hinshelwood kinetics model. Our results prove that even at mild conditions (temperatures and pressures much lower than the industrial ones) the catalysts synthesized by us are more active than the commercial ones and could be used in the hydrotreating process with good activity and economic benefits. The nitrogen tolerance of the Ir/Ti-SBA-16 catalyst is sufficiently high to envisage use in the final stages of a refinery process producing diesel fuel of high cetane number by hydrodearomatization.

5. References

1. K. Soni, K. Chandra Mouli, A. K. Dalai, J. Adjaye, *Mic. Mes. Mat.,* **152,** (2012)

2. G. Li, Y. Liu, Z. Tang, C. Liu, *Applied Catalysis A: Gen*., **437**, (2012)

3. A. Infantes-Molinaa, A. Romero-Pérez, E. Finocchio, G. Busca, A. Jiménez-López, E. Rodríguez-Castellón, *J. of Cat.*, **305**, (101-117) (2013).

4. D. Cunha, G. Cruz, *Appl. Catal. A: Gen*., **236** (2002)

5. P. Reyes, M.C. Aguirre, G. Pecchi, J. G. Fierro, *J. Mol. Catal. A*, **164,** (1-2) (2000)

6. H. Tian, T. Zhang, X. Sun, D. Liang, L. Li, *Appl. Catal. A*, **210,** (1-2) (2001)

7. V. Atuchin, V. Kesler, N. Pervukhina, Z. Zhang, *Journal of Electron Spectroscopy and Related Phenomena*, **152,**(12) (2006).