Tetralin hydrogenation and ring opening of decalin over Ir-Pt-SBA-15

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Abstract

A series of Ir and Pt modified SBA-15 were prepared by the consecutive wet impregnation method, with different content of each metal. The final catalysts were characterized by XRD, TEM and H_2 chemisorption to study the effect of content of metal on the dispersion of iridium/platinum. The catalysts synthesized with similar percentage of both metals showed the best activity measured in tetralin hydrogenation and ring opening of decalin at mild conditions.

Keywords: Iridium-platinum containing SBA-15; Hydrogenation; SRO; TEM

1. Introduction

Bimetallic Pt–Pd catalysts have received considerable attention, because they show high activity in a variety of catalytic applications (1,2). From a fundamental point of view, exploring bimetallic catalysts also allows a better understanding of mechanisms and variables involved in the catalytic reactions. The features of the catalysts here studied are going to be correlated with their catalytic

performance in the hydrogenation of tetralin and the consecutive ring opening of decalin. The final goal is to find the optimal proportion of each metal in order to be more active.

2. Experimental Section

2.1 Synthesis: SBA-15 source materials: Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly (ethylene glycol) (MW 5800) (EO20PO70EO20, P123) (Sigma–Aldrich). Tetraethylorthosilicate (TEOS) (Sigma–Aldrich, reagent grade 98%). Hydrochloric acid 1 M (HCl) (Cicarelli). <u>Support and catalyst preparation:</u> 20 g P123 was added to 400 mL 1 M HCl and heated at 40°C. The mixture was stirred to obtain a homogeneous mixture, then 40 g TEOS was dropped under stirring. A white suspension (precipitation) is formed after 1 h. The mixture was kept at 40°C under stirring for an additional 24 h and then transferred into a PP bottle and kept at 100°C for 72 h. The material was filtered and washed with distilled water until pH ~6. The molar composition was 1 Si: 0.018 EO20PO70EO20: 2.08 HCl: 112 H_2O. After that, the material was immersed in ethanol reflux for 6 h in order to extract the surfactant and calcined at 450°C in air for 6 h. Platinum (Pt) and Iridium (Ir) nanoparticles were incorporated into SBA-15 support by the wet impregnation method. The metal precursors ((Iridium acetylacetonate - (Ir(acac)$_2$ and cloroplatinic acid ($H_2PtCl_6xH_2O$)) were dissolved in 50 ml of ethanol at 50°C under reflux to have a nominal content of 0.5-1 wt.% of Ir and/or Pt in the final solid. A finely ground powder fraction of the SBA-15 was dried in static air to 120°C for 12 h, then, it was directly incorporated to the platinum and Iridium solution. The solution was placed in a rotary evaporator to remove excess of ethanol at about 60°C and 60 rpm. Then, the resulting material was dried at 100°C for 24 h and calcined at 450°C. Then, the resulting material was thermally treated in a dynamic inert (N_2) atmosphere with a heating rate of 5°C/ min for 5 h. Finally, the catalyst was reduced by heating at 2°C/ min in a H_2 stream at 450°C for 5 h. Hereinafter this catalyst will be referred as Ir-Pt- SBA-15 (x), with x= 1-3.

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 for tetralin hydrogenation (feed consisted in 50 mL of

5% v/v of tetralin (98.5% FLUKA) in Dodecane) and at 350°C for decalin RO (25mL of 99% Fluka with trans/cis of 1.7). The results were compared with a typical HDT catalyst as $NiMo/Al_2O_3$ Criterion DN200. The products were analysed with a HP 5890 Series II GC and HP-5 column.

2.3 Material characterization

The X-ray diffractions (XRD) patterns were recorded in the 2θ range from 1.6 to 7° (2 θ) and 20 to 80°(2 θ) with a Philips X'Pert PRO PANalytical diffractometer under Cu Kα radiation (λ =0.154 nm). The diffraction data was collected by using a continuous scan mode with a scan speed of 0.02 deg (2 θ)/min. Ir and Pt-particle sizes were evaluated from TEM images recorded in a JEOL 2100F microscope operated with an accelerating voltage of 200 kV and equipped with a field emission electron gun providing a point resolution of 0.19 nm.

3. Results and discussion

Low angle (0.7◦ < 2θ < 5◦) X-ray diffraction patterns for SBA-15 support and Ir-Pt-SBA-15 (x) catalysts are shown in Figure 1. These materials display three well-resolved diffraction peaks; the most intense at 0.92° and two peaks with lower intensity at 1.64° and 1.90° with Miller indexes (100), (110) and (200), respectively. These XRD profiles are characteristic of the two-dimensional p6mm hexagonal mesostructure with d_{100} spacing of 10.16 nm; where the d_{100} spacing upon Ir and Pt incorporation were quite similar to pristine SBA-15. Thus, XRD data pointed out that the inclusion of Pt or Ir do not alter the symmetry of the pore structure of the mesoporous silica, as there are no significant alterations of the diffraction line positions compared with those of the parent SBA-15. However, a decrease of the intensity of (1 0 0) XRD reflection was observed with Pt and Ir incorporation, reflecting a slight decrease on the mesoporous ordering, although unit cell parameter (a_0) and pore wall thickness did not change considerably because of the low concentration and the small sizes of Pt nanoparticles. Accordingly, for low noble metal concentration, the mesoporous structure of SBA-15 accommodates the particles in the inner channels and does not alter the diffraction peaks.

Table 1. Physicochemical and structural properties of the supports and catalysts

Sample	%Ir [a]	%Pt [a]	Area, m^2/g	D(%)	Ir-Pt clusters (nm)[b,c]
Ir-Pt-SBA-15 (1)	1.02	0.55	630	41	6.0-8.0
Ir-Pt-SBA-15 (2)	0.45	0.52	680	60	2.0-4.0
Ir-Pt-SBA-15 (3)	0.50	0.98	645	45	3.5-6.5

[a]Data obtained by ICP; [b]D(%)=percentage metal dispersion obtained from hyd. chemisorption.[b]H$_2$Chemisorption [c]TEM.
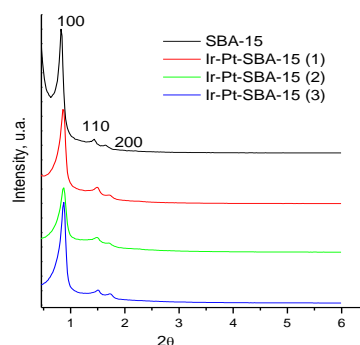

Figure 1. XRD of SBA-15 and Ir-Pt-SBA-15

The TEM images (Figure 2) of the catalysts shows the particle size distribution ranging from 2 to 8 nm indicating that the catalyst metal particles were mainly present inside the porous. The mean particle diameter was found to be close to 3 nm for Ir-Pt/SBA-15(2). It was found to be slightly smaller than that of the catalyst and also gave better dispersion of metal particles (Table 1).
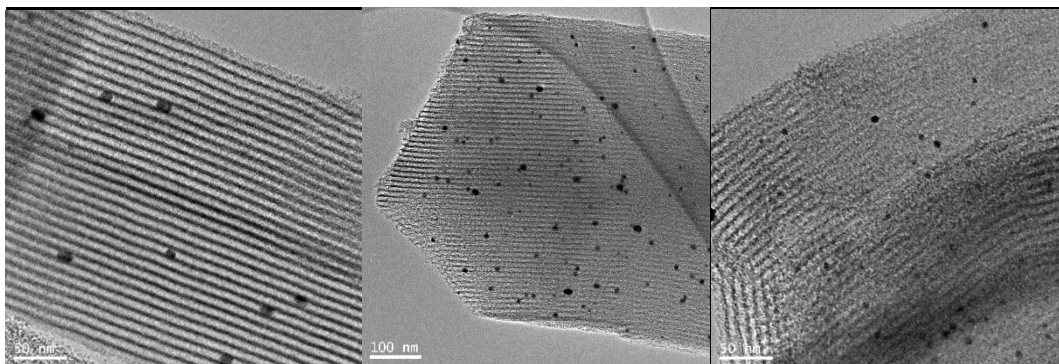

Figure 2. TEM: Image of the Ir-Pt/SBA-15: a (1); b(2); c (3)

In the TPR study (not shown), the appearance of a peak (117°C) not seen in the mono metal systems has been used as a measure of bimetal formation. Another indication of bimetal formation that applies to the platinum-iridium system is the appearance/disappearance of the IrO peak (220°C). It is known that the oxidative agglomeration of iridium to form IrO, is inhibited by platinum iridium bimetal formation (3). Therefore the disappearance of the IrO, peak in the reduction profile can be used to identify bimetal formation. Likewise, the IrO, peak was not observed in the case of the platinum-iridium. The catalytic activity was compared for the three different catalysts (Figure 3). The hydrogenation reactions of tetralin were carried out at 250°C and 15 atm. The major products were trans-decalin and cis-decalin, (trans/cis ratio about 6) naphthalene presence was negligible, due the experiments were performed far below the thermodynamic equilibrium. Sample 2 with 0.5%wt. of Ir and 0.5%wt. of Pt was the most active for the hydrogenation of tetralin, this can be due to its better dispersion and smaller cluster size. All these catalyst were more active than its monometallic counterpart. With the best catalyst we tested its performance in the ring opening of decalin. The products from the decalin ring-opening reaction are classified as follows: (i) Cracking products (CP): Methane, ethane, propane, isobutane, isopentane, methylcyclopentane, methyl cyclohexane, n-octane, 1-octene, n-nonane, 1-nonene, 1,4-dimethylcyclohexane, propylcyclohexane, 1,3,5-trimethylcyclohexane, ethylbenzene, and ethylcyclohexane. (ii) Ring-contraction products (RC): Methylbicyclo[4.3.0]nonane, 3,7,7-trimethylbicylco[4.1.0]heptane, 3,7-dimethylbicyclo-[3.3.0]octane, 1-methylbicyclo[3.3.1]nonane, 1,1-bicyclopentyl, spiro[4.5]decane. (iii) Ring-opening products (RO): Butylbenzene, pentenylcyclopentane, butenylcyclohexane, 4-methyl-1-(1-methylethyl)-cyclohexene, 1-methyl-4-(1-methylethylidene) cyclohexane, 1-decene, pentylcyclopentane, butylcyclohexane, n-decane, 3,4,5-trimethylheptane, 3,5-dimethyloctane, 4-methylnonane, 3-ethyl-2-methyl heptane, and 4-ethyl-3-methyl heptane. (iv) Dehydrogenation products (DH): Benzene, toluene, m-xylene, naphthalene, 1-methylindan, and tetralin.
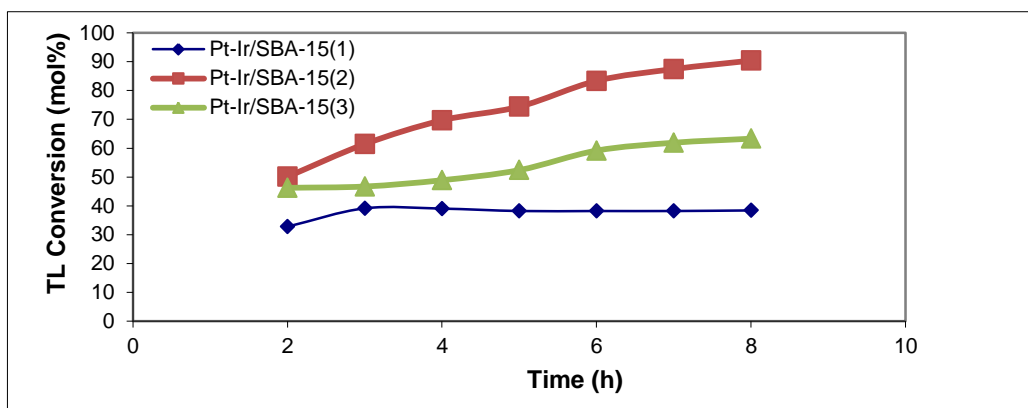
Figure 3. Catalytic activity in the Tetralin hydrogenation: T=250°C, P=15 atm, gTL/gcat= 5

Table 2. Activity in the ring opening of decalin: T=350°C, P=15 atm, gD/gcat= 3, 6h of reaction time

Sample	Conv.%	Yield % (i)	Yield % (ii)	Yield% (iii)	Yield% (iv)
Ir-Pt-SBA-15 (2)	27	5.52	9.21	7.12	5.15

4. Conclusions

The Pt-Ir-SBA-15 catalyst with equal amount of both metals had the highest activity measured in tetralin hydrogenation at mild conditions. The good activity in the Tetralin hydrogenation was correlated with higher Ir/Pt dispersion on SBA-15 mesostructured material used as support, with higher active metal sites exposed to reactant. The preliminary results of ring opening of decalin need a further investigation in order to get better selectivity.

References

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