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Hydrogenation of tetralin over Ir-containing mesoporous catalysts

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Abstract

In this work we study the catalytic properties of 1 wt% Ir-containing mesoporous materials in the hydrogenation of tetralin to decalin in the presence of 100 ppm of dibenzotiophene at 250°C and 15 atm of pressure of hydrogen, using a Parr reactor. We described the preparation of new nanostructured catalytic materials containing highly and homogeneously dispersed particles of Ir^0 after reduction, and investigate their activity for hydrogenation of aromatic compounds, using tetralin as a model substrate. The metal particle size of supported metal catalysts is an important factor affecting the catalytic behavior and the support, in particular, the pore structure, can affect the metal dispersion. The Ir/SBA-3 catalyst synthesized by us had higher activity than Ir/Al-SBA-3 and Ir-MCM-41, measured in tetralin hydrogenation at mild conditions. The experimental data were quantitatively represented by a modified Langmuir-Hinshelwood type rate equation. The catalyst showed a good resistance to sulfur. The preliminary results show this material as a promising catalyst for HDS/HDN reactions.

Introduction

The development of highly active and selective hydrotreating catalysts is one of the most pressing problems facing the petroleum industry. Numerous approaches have been adopted with a view to improving the catalytic performance of the classical formulation ($Co(Ni)Mo(W)/Al_2O_3$). Regarding new support materials, mesoporous molecular sieves such as MCM-41, HMS or SBA-15 [1-4] are promising candidates because of their uniform mesoporous structure, which facilitates the diffusion of the large molecules involved in HDT reactions. Compared with MCM-41 and HMS, the SBA-15 material synthesized under an acidic medium using neutral organic triblock copolymers as structure-directing agents [4,5] seems to be more interesting. Fierro et al. [6] used with success CoMo/Ti-SBA-15 catalysts for dibenzothiophene desulfurization, but the information about SBA-16 support is poor. The SBA-16 silica mesophase with a cubic Im3m structure was prepared first by Zhao et al. [7] from the triblock copolymer surfactant Pluronic F127 (EO106PO70EO106) and TEOS. The synthesis parameters have been systematically investigated by M. Mesa et al [8]. The mesoporosity of this phase consists of two non-interpenetrating three-dimensional channel systems with spherical cavities at the dividing of the channels. It can be expected that this structure offers more interesting opportunities for catalytic applications involving well dispersed metal-supported catalysts and allowing the diffusion of large molecules. Some alumina-supported transition metal catalysts possessed much higher HDN activity and HDN/HDS selectivity than a conventional NiMo system. 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 [9].
In this work we study the catalytic properties of mesoporous Ir catalysts (1 wt% Ir) in the hydrogenation of tetralin to decalin in the presence of Sulfur at 250°C and 200 psi of pressure of hydrogen.

Experimental

Synthesis of Si-SBA-16

Mesoporous silica materials with cubic Im3m structure were synthesized according to the procedure described by [10]. Briefly, poly (alkylene oxide)-type triblock copolymers; F127 (EO106PO70EO106, MW 5 12600) were dissolved in aqueous HCl solution. Tetraethyl orthosilicate is added to the solution at 35°C under continuous stirring during 15 min at that temperature. The molar composition of the mixture was as follows: F127/TEOS/HCl/H_2O = 0.004/1/4/130. This mixture was kept under static conditions in an oven for 6 h at the same temperature. Subsequently, the mixture was placed in an oven at 50°C, over a period of 20 h; afterwards the temperature of furnace is increased to 80°C for aging for 20 h, after that, the solid product was recovered by filtration and dried at 100°C. The Si-SBA-16 sample was immersed in ethanol reflux for 6 h, to extract the surfactant and then was calcined at 550ºC in air for 6 h. The material obtained was identified as SBA-16.

Synthesis of TiO_2-SBA-16

The preparation process of TiO_2/SBA-16 was as follows: the as-synthesized SBA-16 was dried in oven at 80°C for 4 h. Then, 0.5 g of dried sample was dispersed in a solution containing 2 mL of titanium tetrabutylorthotitanate (TTBT) and 5 mL of ethanol. The mixture was stirred at 60°C for 8 h in order to evaporate the solvent, after that, the hybrid products were dried in a rotator evaporator in vacuum at 80°C and calcined in air at 550°C for 4 h, with a heating rate of 5 °C/min. The material obtained was denoted as TiO_2/SBA-16.

Synthesis of Si-SBA-3 and Na-Al-SBA-3

The mesoporous aluminosilicate was synthesized by hydrolysis of tetraethylorthosilicate (TEOS) and sodium-aluminate at room temperature, in aqueous acidic solution, using cetyltrimethylammonium bromide (CTAB) as surfactant. The designed procedure was the following: the surfactant was mixed with water and HCl; then, 3g of TEOS were added, stirring to form a mixture with a molar composition of: TEOS:H_2O:HCl:CTAB = 1:130:9.2:0.12 [11]. After 45 min, a white precipitate was obtained, and then it was filtered, washed and dried at room temperature. The material was immersed in ethanol reflux for 6 h, in order to extract the surfactant. The sample was then calcined at 450°C in air for 6 h. The material obtained was denoted as SBA-3. The alumination procedure of SBA-3 [49, 50], was carried out as follows: Silica SBA-3 (1 g) was stirred in 50 ml of water, containing dissolved sodium-aluminate in different proportions, at room temperature for 20 h. The mixture was filtered, washed, dried at room temperatura overnight and then calcined in air at 450°C for 5 h. Finally, Al-SBA-3 sample with Si/Al= 20 was obtained.

Synthesis of MCM-41

Classical MCM-41 material was synthesized by dissolving 2.4 g of n-cetyltrimethylammonium bromide (CTAB) Aldrich, in 120 g of deionised water and stirred until the solution was homogeneous and clear. After adding 8 mL of ammonium hydroxide (Merck) the mixture was stirred for 5 min, then 10 mL of TEOS (Merck) were added. The molar composition of the gel was 1M TEOS: 1.64 M NH_4OH: 0.15 M CTAB: 126 M H_2O. The reaction mixture was stirred overnight, and then the solution was filtered and washed consecutively with deionised water and ethanol. Calcination was performed at 550°C for 5 h.

Synthesis of Ir/mesoporous

We concentrate here on the direct incorporation of Iridium by wetness impregnation after the calcined form 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 obtained powder was then dried at 80ºC overnight, and then calcined at 500°C for 5 h. After that, the samples were desorbed in inert atmosphere from 25°C to 200°C with a slope of 10ºC/min and kept at this temperature during 5 h, after that the temperature was increased to 470°C with a slope of 10°C/min, kept 5 h at that temperature. Nitrogen flow was always 20 ml/min. Due to iridium is active for the reaction in its metallic state; it was reduced in H_2 flow of 20 ml/min, at 470°C using the same procedure described above. The iridium load was 5% wt. and the materials obtained were identified as Ir/SBA-16, Ir/SBA-3, Ir/Al-SBA-3, Ir/TiO_2-SBA-16 and Ir/MCM-41.

The catalytic activity was measured in a Parr reactor 4563, at 250°C, 200 psi H_2 pressure and 360 rpm, the products were analized with a HP 5890 Series II GC and HP-5 column.

In order to study the behavior of the samples in absence and in presence of S, computation of kinetic parameters can be useful to shed further light on this issue; the data will be used to provide a better value for the constraints used to obtain the rate constants in the model. Generalized Langmuir–Hinshelwood rate equation [12] can represent the behavior of the different catalysts on the tetralin hydrogenation.

Results and discussion

The Ir-SBA-3 catalyst synthesized by us had the highest activity measured in tetralin hydrogenation at mild conditions. The good activity was correlated with higher Ir dispersion on SBA-3 mesostructured material used as support, with higher active metal sites exposed to reactant. The kinetic model was successfully applied to the hydrogenation of tetralin in presence of sulfur. The hydrogenation rates were useful to determine the most active catalyst. The hydrogenation rates of tetralin were lower when sulfur was present in the mixture. The inhibition was described reasonably well by Langmuir-Hinshelwood kinetics. Adsorption strength of the inhibitors increased in as follows: NiMo/Al_2O_3< Ir/SBA-3< Ir/ Al_2O_3 <Ir/Al-SBA-3 <Ir/MCM-41 <Ir/TiO_2-SBA-16 <Ir/SBA-16. Even when DBT adsorption constant for NiMo is lower than for Ir/SBA-3, the last is far more active for this reaction. The sulfur tolerance of the Ir/SBA-3 catalyst is sufficiently high to envisage use in the final stages of a refinery process producing diesel fuel of high cetane number by hydrodearomatization. The catalyst showed a good resistance to sulfur compounds.

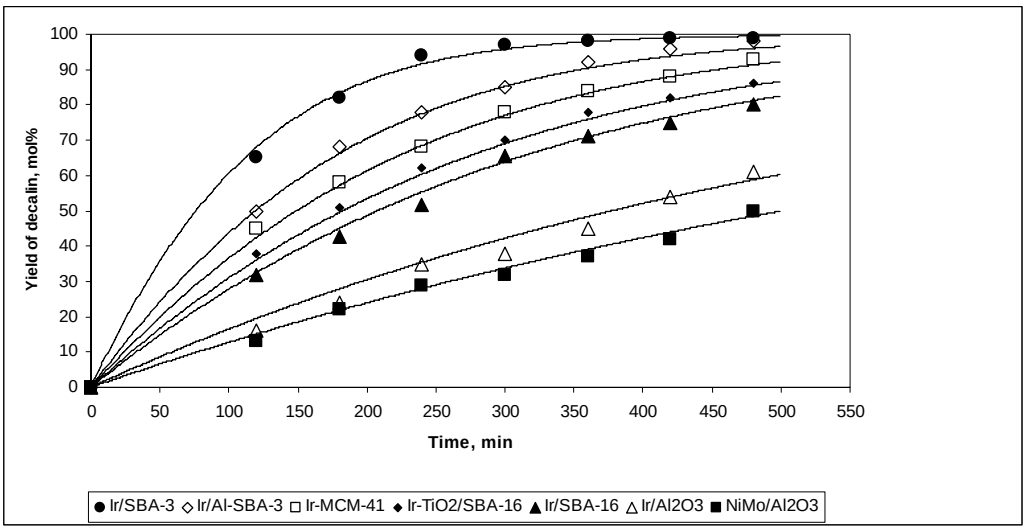

Figure 1: Kinetic of the hydrogenation of tetralin at T=250ºC, P=15 atm, 360 rpm. 100 ppm of sulfur as DBT was added to the feed. The lines were obtained by fitting the kinetic curves derived from the model to the experimental data (F= $1{,}22^{-3}$).

Conclusions

The Ir-SBA-3 catalyst synthesized by us had high activity measured in tetralin hydrogenation at mild conditions. The catalyst showed a good resistance to sulfur and nitrogen compounds. This is a promising catalyts for HDS/HDN reactions.

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