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Study of $Ir/WO_3/ZrO_2–SiO_2$ ring opening catalysts
Part I: Characterization

Sebastien Lecarpentier, Jacob van Gestel, Karine Thomas, Marwan Houalla *

Laboratoire Catalyse et Spectrochimie (UMR CNRS 6506), ENSICAEN-Université de Caen, 6 Bd. Maréchal Juin, 14050 Caen (cedex), France

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Abstract

This paper is the first part of a systematic study of the influence of W and Ir loading on the activity of $Ir/WO_3/ZrO_2–SiO_2$ catalysts for the ring-opening reaction of naphthenic molecules using methylcyclohexane (MCH) as a model compound. A series of Si-stabilized tungstated zirconias, $WO_x/ZrO_2–SiO_2$, containing up to 3.5 at W/nm^2 was prepared. Ir-based catalysts containing up to 1.2 wt% were obtained by impregnation of these solids. The acidity of Si-stabilized tungstated zirconias, ZSiWx, was monitored by low-temperature CO adsorption followed by infrared (IR) spectroscopy. The results indicated the development of strong and relatively strong Brønsted acidity with increasing W surface density above a threshold of 1 atom W/nm^2. The study of the Ir-doped solids showed that the texture, structure, and acidity of the ZSiWx solids were not affected by Ir deposition. The characterization of the metallic function was performed by hydrogenation of toluene and by CO adsorption at ambient temperature, followed by IR spectroscopy. Both methods indicated a low and constant Ir dispersion for the yIr/ZSiW0 ($y = 0.3$, 0.6, 1.2) series. For a given Ir loading (1.2Ir/ZSiWx), a progressive decrease in the dispersion of Ir metal with increasing W surface density was observed.

Keywords: Tungstated zirconia; Iridium; Toluene hydrogenation; Infrared measurements; CO adsorption

1. Introduction

The conversion of light cycle oil feedstock to diesel fuel products requires deep desulfurization and hydrogenation, followed by ring opening of the naphthenic cycles to form alkanes (molecules with higher cetane indices). In general, opening of a C_6 six-membered naphthenic ring is more difficult than opening of a C_5 ring [1–3]. Thus, a suitable catalyst must contain an acid function to allow for ring contraction. The cleavage of a C–C bond is then performed by hydrogenolysis over the metal. To date, no systematic study of the influence of acidity and metal content on C_6 ring-opening activity has been performed. Previous studies have shown that the acidity of zirconia can be modulated with deposition of a controlled amount of W [4]. Thus, a catalytic system consisting of tungstated zirconias and a metal with strong C–C bond cleavage activity, such as Ir, appears promising. This paper is the first part of a systematic study of the influence of W and Ir loading on the catalyst activity for ring-opening of naphthenic molecules using methylcyclohexane (MCH) as a model compound.

The objectives of the present study are to characterize the evolution of the acidity of tungstated zirconia with W surface density and to analyze the dispersion of the Ir phase as a function of W deposition. Evolution of the acidity was monitored by low-temperature CO adsorption followed by infrared (IR) spectroscopy. Dispersion of the Ir phase was examined by IR study of CO adsorption at ambient temperature and catalytic hydrogenation of toluene.

2. Experimental

2.1. Materials

Zirconia doped with 1.2 wt% silica was prepared by dropwise addition of a 10 M aqueous solution of ammonia to a 0.2 M solution of zirconyl chloride octahydrate ($ZrOCl_2$, Fluka) up to a pH of 9.9. Preliminary experiments indicated that sub-

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* Corresponding author. Fax: +33 2 31 45 28 22.
E-mail address: marwan.houalla@ensicaen.fr (M. Houalla).

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stantial stabilisation of the surface of the zirconia support can be achieved with the incorporation of 1.2 wt% Si. Thus subsequent studies of the influence of calcination temperature and W deposition were conducted with this solid. The silicon was introduced before precipitation using the prerequisite amount of liquid $SiCl_4$, (99.8%, Acros Organics). The precipitated material was heated at 363 K for 48 h and then maintained at room temperature for 96 h in the solution. The final product was recovered by vacuum filtration. It was then redispersed in deionised water to remove residual chlorine and filtered. This operation was repeated until no traces of Cl^- could be detected with an $AgNO_3$ solution. The washed product was dried at 393 K for 16 h and calcined in air at 1023 K for 3 h. Completion of the experiments included in the present work required the synthesis of two batches of ZrO_2. The differences in the characteristics of the supports thus obtained were minor and did not significantly affect the results.

The W phase (0–12 wt% W) was deposited by impregnation of the support using ammonium metatungstate solution, followed by calcination at 1023 K for 3 h. The Ir (0–1.2 wt%) was added by incipient wetness impregnation with a basic iridium chloride solution (pH 9), followed by calcination at 723 K with a 20% O_2 + 80% N_2 flow of 25 ml/min. The catalyst was reduced in situ in flowing H_2 at 623 K at atmospheric pressure before use. Tungstated zirconias were designated as ZSiWx, where x is the W surface density expressed as at W/nm^2. The series of Ir deposited on tungstated zirconia was denoted as yIr/ZSiWx, where y is the nominal percentage of Ir in the catalysts.

2.2. BET surface area and pore volume

The specific surface area of the catalyst was determined from physical adsorption of N_2 at 77 K by applying the BET equation on the part of the adsorption isotherm with $0.05 \leqslant p/p_0 \leqslant 0.35$. The adsorption isotherms were measured in a Micromeritics ASAP 2000 apparatus. The samples were first outgassed at 573 K in dynamic vacuum for 1 h. The total pore volume was determined at $p/p_0 = 0.99$.

2.3. X-ray diffraction

Powder X-ray diffraction spectra were recorded with a Philips PW1750 spectrometer using Cu$K\alpha$ radiation. The angle (2θ) was varied from 20° to 70° with steps of 0.02° measured for 10 s. The zirconia phase can be characterized by the specific reflections $(11\bar{1})$ at $2\theta = 28.2°$ and (111) at $2\theta = 31.5°$ for the monoclinic phase and (111) at $2\theta = 30.2°$ for the tetragonal phase. The fraction of the monoclinic phase was estimated using the formula proposed by Toraya et al. [5], and the crystallite size was calculated from the (111) line at $2\theta \sim 30°$ using the Debye–Scherrer formula [6]. The crystalline structure of the present phases was identified through comparison with the database of the Joint Committee on Powder Diffraction Standards (JCPDS).

2.4. IR experiments

The IR spectra were recorded on a Nicolet Nexus FTIR spectrophotometer equipped with a DTGS detector. The powder was pressed into a self-supported wafer (∼20 mg). Activation of the wafer was carried out in situ in an IR cell under flowing dry air at 673 K for 2 h. Then the pellet was treated under dry hydrogen at 623 K for 1 h, cooled to 473 K, evacuated for 2 h, and cooled to room temperature. All spectra were normalized to 20 mg of the solid. Adsorption of CO probe molecule was performed at room temperature to determine the dispersion of supported metal [7,8] and at 100 K to evaluate the acid strengths of catalysts [9,10].

2.5. Toluene hydrogenation

Hydrogenation of toluene (0.026 bar of toluene) was carried out at 323 K in a dynamic Pyrex reactor under atmospheric pressure. The flow of toluene–hydrogen mixture was 90 cm^3/min. Reaction products were analysed using a 50-m Chrompack CP-Sil 5CB column and a flame ionization detector. The mass was adjusted to obtain a conversion <7%, in order to calculate the initial rate. Before catalytic testing, the catalyst was activated in flowing air at 673 K for 2 h and reduced at 623 K in flowing hydrogen for 1 h.

3. Results

3.1. Texture and composition of the ZSiWx solids

Table 1 summarizes the characteristics of various tungstated zirconia catalysts. The specific surface area of the solids was ca. 115 ± 15 m^2/g. The W surface density was calculated assuming that the measured surface area is due to the support.

3.2. Crystalline composition of the support

Fig. 1 shows the XRD patterns for the support (ZSiW0) and tungstated zirconia solids (ZSiWx). The spectra of the ZSiWx solids (x = 0.4, 0.9, 2.5) show only the lines characteristic of the tetragonal form of zirconia ($2\theta = 30.2°$, 35.4°, 50.6°, 60.4°); those of the remaining solids (x = 0, 1.5, 3.4) also show an additional line at $2\theta = 28.2°$, characteristic of the monoclinic form ($(11\bar{1})$ plane). The percentage of the monoclinic phase present was estimated at 9% [5].

Table 1
Composition and texture of various ZSiWx catalysts

Solid	W loading (wt% W)	Surface area (m^2/g$_{cat}$)	V_p (cm^3/g$_{cat}$)	Surface (m^2/g$_{ZrO_2}$)	Density (at W/nm^2)
ZSiW0	0	97	0.29	97	0
ZSiW0.4	1.5	129	0.25	132	0.4
ZSiW0.9	3.7	125	0.25	132	0.9
ZSiW1.5	4.3	91	0.28	96	1.5
ZSiW1.9	7.6	120	0.25	133	1.9
ZSiW2.5	8.4	99	0.23	111	2.5
ZSiW3.4	11.8	98	0.24	115	3.4