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Catalytic ring opening of naphthenic structures
Part II. In-depth characterization of catalysts aimed at upgrading LCO into a high-quality diesel-blending component

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Abstract

The present paper delves into physical and chemical characterization of surface and bulk properties of the twelve 2 wt.% Pt_xIr_y catalysts employed in Part I for ring opening of naphthenic structures. The support materials (ceria, alumina, silica, silica-alumina, zirconia, H-SA and magnesia) were investigated using X-ray diffraction (XRD) for phase identification and adsorption/desorption of nitrogen to obtain the specific surface area and pore size distribution. The catalyst preparation via the incipient wetness technique was closely monitored and the final catalysts were examined by means of X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS) and quantitative TPR followed by dynamic pulse chemisorption of CO, Fourier transform infrared spectroscopy (FT-IR) of adsorbed CO and NH_3-DRIFTS. The XPS analyses are particularly comprehensive and involve all the catalysts in their fresh, reduced and spent states. The combined results from TPR, XPS and FT-IR of adsorbed CO reveal that metallic Pt-Ir alloys are formed directly upon mild reduction.

Keywords: Catalyst characterization; XPS; TPR; CO chemisorption; FT-IR; Pt-Ir; Platinum; Iridium; Ceria

1. Introduction

The availability of fossil fuels is a prerequisite of modern society. Concurrently with a growing population worldwide and the globalization that stimulates the developing countries, more and more people aim for a better standard of living and the fuel demand is skyrocketing. However, fossil fuels are a finite energy resource. According to BP [1], proven reserves of oil, natural gas and coal worldwide will, if taking into account current production rates, last for approximately 41, 67 and 164 years, respectively. When converting these fossil fuels by combustion hazardous emissions are inevitable. It is generally accepted that CO_2 contributes to the greenhouse effect with global warming, coal and oil-derived products give rise to NO_x and SO_x when combusted at high temperatures that lead to, for example, acidification, eutrophication and harmful ground ozone. In the long run, the situation is not sustainable and research must be directed towards finding and producing alternative energy carriers. In this quest, the catalysis community certainly has the potential to epoch-making contributions [2]. For example, many put their hopes to the field of nanotechnology [3]. Yet, if successful, such a fundamental switch-over of society structure will not occur overnight and liquid hydrocarbon mixtures, such as gasoline and diesel will remain the key transportation fuels for many years to come [4,5]. Consequently, maximum utilization of our earths' limited resources is an important issue economically, environmentally and considering future generations' equal rights to prosper. Regarding oil, taking into account the large number of crude barrels that are processed every day, even minor improvements in refining technology may be of considerable value. In Europe, the diesel engine car has during the last decade gained more and more ground compared to its gasoline-fuelled counterpart due to its superior fuel economics and the implementation of new effective exhaust gas filters that drastically reduce the emission of particulate matter. According to the European automobile manufacturers association (ACEA) [6], in 2004 almost every second newly registered passenger car

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(48.9%) in the 15 member states of EU was equipped with a diesel engine, compared to 23.1% in 1994. Consequently, the refining industry needs additional capacity to meet the increasing demand for high-quality diesel fuel, i.e. low in aromatics, sulphur, nitrogen and density but high in cetane number. A desirable contribution to the diesel pool might come from upgrading heavy petroleum fractions, such as light cycle oil (LCO) employing a two-stage catalytic process involving initially hydrodesulphurization, hydrodenitrogenation and hydrodearomatization followed by selective ring opening over a Pt-Ir-based catalyst to improve the cetane number. The technology was presented in detail in Part I with experimental emphasis on the second catalytic step [7].

This communication is entirely devoted to physical and chemical characterization of the catalysts employed in Part I. Combing results from a variety of characterization techniques is a powerful approach to understanding surface phenomena and to correlating support and/or surface properties with catalytic behaviour.

2. Experimental

2.1. Specific surface area (BET) and pore size distribution (PSD) of the support materials

The BET and PSD were calculated based on the measured adsorption–desorption isotherms of nitrogen acquired at its boiling point (−196 °C) employing an ASAP 2010 instrument from Micromeritics. Prior to initiating the measurements, the samples were degassed at 250 °C until no pressure gradients could be detected, usually overnight. The BET area and PSD estimation were calculated from the BET [8] and BJH [9] equations, respectively, all included and automatically performed by the instrument software. The pore volume value is determined at $p/p_0 \sim 0.998$.

2.2. X-ray diffraction (XRD) of the support materials

The phase composition of the support materials was investigated by powder X-ray diffraction employing a Siemens D5000 instrument, operated with the following parameter settings: Ni-filtered Cu Kα radiation powered by 30 mA and 40 kV, 2θ scanning range of 20–80° with a step size of 0.02° and recording data at each step angle for 1 s. The crystal phases were identified by searching and matching the acquired patterns with those contained in the software reference database (JCPDS files).

2.3. Observation of colours during catalyst preparation

The catalyst preparation procedure was described in detail in Part I. Briefly, the catalysts were prepared by traditional incipient wetness co-impregnation using aqueous metal solutions of iridium and platinum salts ($IrCl_3 \cdot 3H_2O$ (dark brown) and $H_2PtCl_6 \cdot 6H_2O$ (yellow)) to yield a nominal metal loading of 2 wt.%. After solvent evaporation in a well-ventilated fume hood the catalysts were dried at 120 °C during 12 h, and then stored in inerted, hermetically sealed scintillation jars. In this state, the catalysts are referred to as ‘‘fresh’’. The catalysts are all enumerated in Table 1 together with remarks on colour during the different steps of preparation. This simple course of action actually helps us to follow and step-wise characterize the oxidation states of the metals.

It must be emphasized that the ceria support employed contains 20 wt.% alumina.

2.4. X-ray fluorescence spectrometry (XRFS)

XRFS measurements were conducted on a Philips PW1480 wavelength-dispersive sequential XRF spectrometer fitted with a side-window dual anode molybdenum-scandium tube operated at 80 kV, 35 mA. The instrument is operable under vacuum-, helium- or air-path conditions. Appropriate diffraction crystals were chosen according to the sample elements under investigation and were utilized in combination with a 35 mm mask and a 0.3 mm fine collimator. The XRF results are considered to be highly reliable as the instrument is calibrated regularly and subjected to careful maintenance.

Table 1
Observation of colours during catalyst preparation

Catalyst	Colour of support material	Colour after incipient wetness, dried up state	Colour after drying at 120 °C for 12 h	Colour after in-situ reduction (H_2, 400 °C)
2 wt.% $Pt_5Ir_{95}/\gamma\text{-}Al_2O_3$	White	White	Green-grey	Brown
2 wt.% $Pt_5Ir_{95}/SiO_2\text{-}Al_2O_3$	White	Pale mixed grey shades	Mixed green-turquoise	Mixed black-yellow-brown
2 wt.% Pt_5Ir_{95}/H-SA	Pale beige	Pale grey-brown	Pale mocha	Pale mocha
2 wt.% Pt_5Ir_{95}/ZrO_2	White	White-grey with a greenish touch	Turquoise	–
2 wt.% Pt_5Ir_{95}/MgO	White	Pale purple	Dark purple	Pale mixed grey shades
2 wt.% Pt_5Ir_{95}/SiO_2	White	Pale golden-brown	Mixed gold-silvery	Mixed black and white
2 wt.% Ir/CeO_2	Pale yellow	Dark brown-grey	Military green	–
2 wt.% Pt_5Ir_{95}/CeO_2	Pale yellow	Brown-grey	Military green-grey	Grey-blue
2 wt.% $Pt_{15}Ir_{85}/CeO_2$	Pale yellow	Brown	Brown	–
2 wt.% $Pt_{25}Ir_{75}/CeO_2$	Pale yellow	Brown-beige	Brown	–
2 wt.% $Pt_{50}Ir_{50}/CeO_2$	Pale yellow	Beige	Brown	–
2 wt.% Pt/CeO_2	Pale yellow	Yellow	Yellow	Black-grey