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Comparative study of the catalytic hydroconversion of cyclopentane over iridium and platinum single-crystal surfaces ☆

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ABSTRACT

In the context of fuel upgrading by selective ring opening of naphthenes, we have investigated the catalytic conversion of cyclopentane in large hydrogen excess over iridium and platinum single-crystal surfaces. Both (111) and (112) orientations have been considered. The catalytic tests have been performed at 1 kPa and 25–600 °C using a recently developed surface reactor equipped with laser heating and online gas chromatography. Only cyclopentene and C_1–C_4 cracking products are formed on iridium, while platinum additionally catalyzes the formation of pentane around 200 °C, which dehydrogenates to pentene at 250 °C. Noticeably, on both metals, the surface steps prevent hydrocarbon cracking (up to 400 °C) at the benefit of dehydrogenation. In all cases, a carbon overlayer is formed on the surfaces in the course of the reaction.

1. Introduction

Depending on the catalytic conditions, a paraffin (open-chain alkane) or a naphthene (cyclo-alkane) interacting with a platinum-group metal can undergo various transformations, including dehydrogenation, isomerization, and hydrogenolysis [1,2]. Hydrogenolysis of a naphthenic ring may lead to ring opening (breaking of one C–C bond) or cracking (breaking of several C–C bonds). The selective ring opening (SRO) process consists ideally of the conversion or aromatic and naphthenic hydrocarbons into linear paraffins with an unchanged number of C atoms [3]. It is currently the subject of intense research due to the envisioned shortening of conventional energy sources. Indeed, in combination with aromatics saturation, this process is expected to improve the cetane number (CN) of highly aromatic and hardly exploited petroleum cuts, such as the light cycle oil. However, catalytic SRO is still far from being efficient due to the difficulty in opening rings selectively, i.e., at substituted carbon positions in order to avoid the formation of branched paraffins, which have lower CNs than the linear ones [4]. Current research in SRO focuses on the use of oxide–metal bifunctional catalysts [5–11], although some attempts with oxide–oxide [12,13], oxide–sulfide [14,15] and oxide–carbide [16,17] combinations have also been reported. The metal nanoparticles, typically platinum or iridium, catalyze the saturation of aromatics and the hydrogenolysis of saturated C–C bonds. The additional use of oxide supports exhibiting Brønsted acidity, like zeolites or mesoporous aluminosilicates seems necessary to both provide sulfur-resistance to the metal nanoparticles and to accelerate C–C bond scission. Nevertheless, it also favors isomerization (especially ring contraction from C_6 to C_5) and cracking to undesired light products [18]. We have recently shown that the hydrogenolytic role of the metal in bifunctional catalysts

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☆ Thematic issue dedicated to François Garin.

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is reduced due to the predominance of competitive acid-catalyzed isomerization [19]. However, metal-catalyzed hydrogenolysis appears as the only way to selectively open C–C bonds. Hence, we believe that non-acidic catalysts containing one or several noble metals must be reevaluated to address the SRO challenge.

While platinum is the reference metal in hydrogenation catalysis, iridium is known for its hydrogenolysis properties [20–24]. The use of well-defined single-crystal surfaces is the best way to compare the intrinsic catalytic properties of different metals, since there is no contribution of side effects, such as particle size, morphology, and support [25]. However, unlike for supported catalysts, to our knowledge and except for highly instable (methyl)cyclopropane [26], there has been no experimental work published on hydrocarbon ring conversion over well-defined Ir surfaces under non-UHV conditions. On Pt single-crystal surfaces, Somorjai et al. have investigated (methyl)cyclohexene hydrogenation and dehydrogenation and benzene hydrogenation [27–30]. Recently, theoretical studies of cyclic hydrocarbon adsorption and ring opening on Pt-group metal surfaces have appeared in the literature [31–33].

In this work, we have compared platinum and iridium model surfaces in the hydroconversion of cyclopentane. This molecule is both one of the simplest naphthenic compounds and an important product subunit in real hydrotreated fuels.

2. Experimental

The experimental setup used for this study has been described in details elsewhere [34]. It is briefly described below and depicted in Fig. 1. A double ultrahigh-vacuum (UHV) chamber (Fig. 1a) allows preparing the samples and analyzing them by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The cleaned samples can be transferred under UHV in two steps from the preparation chamber into an isolatable UHV-compatible reaction cell (Fig. 1c) of small volume (*ca.* 120 cm^3). The combination of a focused infrared laser beam and an infrared pyrometer allows one to accurately control the sample temperature from outside the cell, through portholes, without heating/outgassing the reactor walls. The reactant mixture is prepared in a dedicated chamber (Fig. 1b), and then introduced in the cell. The reactive mixture can be continuously sampled through a leak valve and analyzed by a mass spectrometer located in a separate UHV chamber. However, for this study involving a number of hydrocarbon molecules, a second gas detection system has been recently implemented on the apparatus.

The gas sampling device (Fig. 1d) includes a series of automated valves with pneumatic actuators, and is evacuated by a dry scroll pump. With this device, a fixed amount of gas is periodically sampled from the reactor and injected into the column of a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 6850).

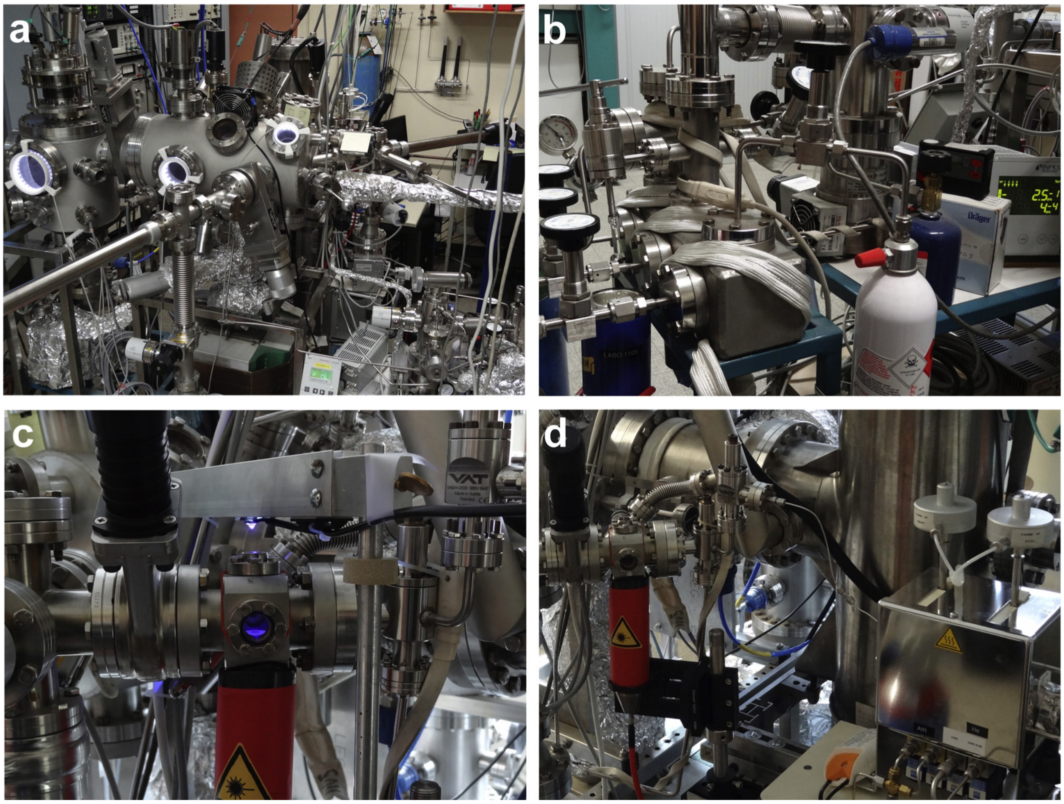

Fig. 1. (Color online.) Pictures of the experimental setup. a: general view of the UHV chambers. The reactor is at the rear, right-hand side; b: gas handling system; c: catalytic cell with IR laser and UV diode. The diode can be replaced with a pyrometer head; d: gas sampling systems for MS and GC analyses.