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Improved oxygen storage capacity on CeO_2/zeolite hybrid catalysts. Application to VOCs catalytic combustion

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ABSTRACT

The aim of this work was to evaluate the possible synergy in hybrid catalysts composed of the two types of solids and to study their performances in the catalytic combustion of isopropanol.

Several catalysts, based on cerium oxide and zeolites, for the catalytic oxidation of volatile organic compounds (VOCs), especially isopropanol, were tested. This study was assessed by determining the catalysts activity, selectivity and deactivation at various temperatures after 5 h of reaction. An important part of the work was the preparation and characterization of the catalysts, in particular the study of oxygen storage and mobility. Hybrid catalysts exhibit a synergy effect in terms of oxygen storage capacity and oxygen isotopic exchange. However, even if a synergy effect is also observed in catalytic oxidation over some samples, the oxygen mobility does not ensure better results in isopropanol combustion.

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1. Introduction

The volatile organic compounds (VOCs) are well known atmospheric pollutants. Governmental regulation qualifies the VOCs as compounds which, except methane (CH_4), carbon oxides and carbonates, contain carbon and hydrogen. Both chemical elements can be replaced by other atoms such as halogen, oxygen, sulfur, nitrogen or phosphorus. These compounds are in gas phase under normal conditions of temperature and pressure. A European guideline project completes this definition by adding that each organic product with vapor pressure superior to 10 Pa under normal conditions of temperature and total pressure is a VOC. In the USA, the limit vapor pressure chosen is equal to 0.13 Pa [1].

VOCs also have a toxic effect on human health, as the main part is carcinogenic, mutagenic and/or harmful for human reproduction and development [1]. Furthermore, their presence in the atmosphere can cause chemical reactions supporting the formation and the accumulation of noxious compounds, or ozone [1].

For several years, this environmental and health problem has been one of the main preoccupations in developed countries. Many conventions have tried to heighten public awareness of it and find appropriate solutions. The Geneva Convention, signed in November 1991, aims at limiting VOC emissions [1]. According to the nature and the concentration of the pollutants, thermal incineration, catalytic oxidation, condensation, absorption, adsorption or recovery by trapping and storage using membranes or biological systems are some of the used techniques, which present advantages and drawbacks [1,2].

Catalytic oxidation is an interesting alternative because of the low energy cost and the relatively low temperatures needed in comparison with thermal combustion, which limit the formation of noxious oxides [2].

In literature several catalysts, like pure metal oxides [3–8], more especially alumina promoted or not with noble metals or oxides, were tested [9–20]. Among potential catalysts, ceria (CeO_2) proved to be effective because of its oxygen storage capabilities [21]. Some mixtures between ceria and oxides and/or noble metals were also studied [22,23]. Several works were performed over zeolites doped or not with metals [24–35]. Basic zeolites and particularly faujasite ones showed also interesting properties for VOCs combustion [36–40].

Moreover, faujasite zeolites are characterized by the presence of one type of large cages (supercages), 13 Å in diameter and ball-shaped, accessible through a 12-ring window with a free aperture of 7.4 Å, which is larger than the size of most of the organic molecules.

In a catalytic combustion point of view, the major issue is the difficulty to anticipate chemical reactions (condensation, polymerization, etc.) during the oxidation. Catalytic tests were performed over isopropanol, which can be partially transformed into acetone and/or propene. Various works were published explaining the mechanism of acetone production, like the one proposed by Chanda and Mukherjee [41] using copper catalysts. They proved that the

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oxidation of isopropanol is complex because of the isopropanol trend to be dehydrated into propene.

The aim of our work is the development of the best catalyst for the total oxidation of VOC (isopropanol) in carbon dioxide (CO_2). The mixture of ceria, which presents interesting performances in VOCs catalytic oxidation, and faujasite (NaX), which exhibits a particular porosity with supercages, would allow the containment of the molecules next to the active sites. Exchange or oxide clusters incorporation are also expected. In addition, the enhancement of oxygen exchange between gas and solid phase (catalyst) and/or oxygen storage capacity would allow better VOCs combustion. Consequently, the main part of this work was the ceria and faujasite mixture preparation to obtain hybrid catalysts with high oxygen storage capacity, especially in dynamic conditions, and with ability for oxygen exchange. Samples were then tested to check this particular preparation profit in catalytic experiments.

2. Experimental

2.1. Catalysts preparation

Cerium dioxide (CeO_2) was prepared by calcining $Ce(NO_3)_3{\cdot}6H_2O$ (Fluka, purity > 99.0%) under air flow (200 mL/min) with a heating rate of 1 °C/min from room temperature to 110 °C with a hold of 1 h. Then the samples were heated up to 550 °C (2 °C/min) overnight.

Faujasite zeolites were supplied by Axens (Si/Al = 1.2).

Several hybrid catalysts were synthesized by mixing ceria and NaX faujasite in various weight proportions (20, 35, 50, 65 and 80 wt% ceria, respectively named HT20, HT35, HT50, HT65 and HT80). The preparation began by a mechanical mixture of the two solids. Thereafter the samples were pelletized under pressure (1.5 t/cm^2) and sieved (between 0.2 and 0.4 mm) to ensure intimate mixture. Finally, the sieved mixtures underwent a high temperature treatment under air flow up to 600 °C. Other samples were prepared to complete the study: C20 (20.7 wt% ceria) which was not pelletized and not sieved before high temperature treatment and M50 which is a simple mechanical mixture between ceria and faujasite (50 wt% ceria) without any high temperature treatment.

2.2. Catalyst characterization

2.2.1. Acidic properties

The catalysts acidity was characterized by pyridine adsorption followed by FTIR spectroscopy. The catalyst was compacted (3 t/cm^2) into a pellet of 16 mm diameter and 2 cm^2 surface. The activation was carried out under air flow equal to 60 mL/min during 12 h at 450 °C (2 °C/min). After cooling until 400 °C, the cell was kept for 1 h under a secondary vacuum (10^{-5} mbar). Pyridine injection was performed for 5 min at 150 °C after pressure stabilization at 2 mbar. The total elimination of physisorbed pyridine was obtained after a treatment at 150 °C for 1 h under secondary vacuum. The thermodesorption of pyridine was then carried out at four temperatures (150, 250, 350 and 450 °C) and the IR spectra were recorded at room temperature. IR spectra were recorded in a Nexus Nicolet spectrometer equipped with DTGS detector (Deuterium TriGlyceride Sulfur) and KBr beam splitter, with a resolution of 2 cm^{-1} and 64 scans. The adsorption of pyridine results in the appearance of two adsorption bands corresponding to pyridium ion, PyH^+ (1545 cm^{-1}), and pyridine bonded to Lewis acid sites, PyL (1450 cm^{-1}). Brønsted and Lewis acid sites were determined and quantified by the subtraction between P_∞ (spectrum of the catalyst before adsorption of pyridine) and P_{150} (spectrum of the catalyst after adsorption and desorption of pyridine at 150 °C). The extinction coefficients of PyH^+ and PyL bands, i.e., respectively 1.13 and 1.28 cm/μmol, were taken from a previous study [42].

2.2.2. Textural properties

Adsorption–desorption isotherms of nitrogen at −196 °C were carried out with a Micromeritics ASAP 2010 apparatus. The sample was kept under vacuum at 90 °C for 1 h and then at 350 °C for 3 h. Micropore volumes were obtained by the *t*-plot method and the Dubinin–Radushkevich equation was used to calculate the mesoporosity.

2.2.3. Structural properties

XRD characterizations ($\lambda_{Cu} = 1.542$ Å, 10° 2θ to 75° 2θ, 0.02° 2θ and 4 s by step) were also performed to check the structures of the several synthesized hybrid catalysts. The space group of ceria is *Fm*3*m* and the one of faujasite is *Fd*-3*m*. These two compounds present a cubic structure, face centered cubic for the ceria. XRD patterns were recorded over a Brüker D5005 diffractometer thanks to Diffrac+ software (XRD Wizard and XRD Commander) and interpreted with Eva and Topas softwares. Scherrer method was used to calculate the particle sizes of ceria and NaX for all the samples. The formula is the following one: $D = (K \times \lambda)/(\mathrm{FWMH} \times \cos\theta)$ in which D is the particle size, K a numerical constant equal to 0.9, λ the wavelength of the incident X-rays, FWMH the width at half weight of the peak and θ the incident or Bragg angle [43].

2.2.4. Oxygen storage capacities (OSCC–OSC)

The oxygen storage capacity was measured following the oxidation of carbon monoxide in transitory regime without oxygen in gas phase by mean of two different techniques (OSC and OSCC). The amount of available oxygen in the catalyst is given by the amount of carbon dioxide formed during the reaction: $CO(g) + 1/2\ O_2(s) \rightarrow CO_2(g) + \square(s)$. The oxygen storage capacities of the samples were measured at 400 °C using a conventional set-up described in a previous report [44]. The sample (30 mg for NaX and 5 mg for the other catalysts) was first brought to 400 °C under flowing He (30 mL/min) before pretreatment under O_2. To calculate the total amount of available oxygen in the sample (OSCC), pulses of CO (0.267 mL) were injected every 2 min up to a maximum sample reduction. Such a treatment gives information about both surface and bulk mobile oxygen species. However, in a catalytic point of view surface species are often more involved under dynamic conditions. Therefore, OSC experiments were also carried out by re-oxidizing the samples with O_2 pulses. Then, alternating pulses of CO and O_2 were injected to probe the amount of O_2 (average of three alternations) immediately available in these materials, which is supposed to be mainly involved in the catalytic process. Results were obtained thanks to a gas phase chromatograph equipped with a TCD and a Porapak Q type column (i.d. = 1/4 in., L = 0.5 m) and oxygen storage capacities (OSCC and OSC) are expressed in $\mu mol_{CO_2}/g$ from the CO_2 formation (after CO pulses), which corresponds to the number of oxygen atoms ($\mu mol_O/g$) removed from the solid.

2.2.5. $^{18}O_2/^{16}O_2$ isotopic exchange experiments

Oxygen isotopic exchange experiments were carried out in a closed-loop reactor system. A recirculating pump was used in order to avoid any diffusion and mass transport effects in the gas phase that affect partial pressures of different isotopomers measured by mass spectrometry (Pfeiffer vacuum). Experimental set-up and data treatment were described in more detail in previous papers [45,46]. Prior the isotopic oxygen exchange experiments, the samples were heated up to 580 °C during 1 h (10 °C/min) under $^{16}O_2$ flow ($D_{O_2} = 50$ mL/min). Thereafter, the sample was evacuated for 15 min and the temperature was brought to the desired temperature for the isotopic exchange study. We carried out temperature-programmed isotopic exchange (TPIE) from 280

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