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Degradation of VOCs and NO_x over Mg(Cu)–AlFe mixed oxides derived from hydrotalcite-like compounds

Dégradation de composés organiques volatils et d'oxydes d'azote sur des oxydes mixtes Mg(Cu)–AlFe issus de la voie hydrotalcites

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ABSTRACT

A series of Mg(Cu)–AlFe mixed oxides derived from hydrotalcite-like compounds has been prepared. These solids were characterized by various physicochemical methods and their catalytic performances were tested towards the catalytic oxidation of propene and the simultaneous elimination of propene and NO_x. X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the formation of the hydrotalcite structure for all the solids, except for Cu_4AlFe HT, for which a mixture of the hydrotalcite and the malachite phases is observed. The XRD study of the calcined samples revealed the existence of metal oxides and spinels of types MgO, CuO, γ-Fe_2O_3 or/and Fe_3O_4, $MgFe_2O_4$ and $CuFe_2O_4$. During propene oxidation, it was shown that the increase in the copper content enhanced the activity of the solids. However, Cu_2Mg_2AlFe 500, with the highest amount of surface copper species, exhibited the best activity towards the simultaneous elimination of propene and NO. Indeed surface Cu species are the active sites, while bulk Cu species could provide the adsorption sites for nitrogen species.

RÉSUMÉ

Mots clés :
Catalyse hétérogène
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Cuivre
COV
NO_x

Une série d'oxydes mixtes Mg(Cu)–AlFe dérivée de composés hydrotalcites a été préparée. Ces solides ont été caractérisés par différentes techniques physicochimiques, puis leur performance catalytique a été testée vis-à-vis de l'oxydation catalytique du propène et de l'élimination simultanée du propène et des NO_x. L'étude par diffraction de rayons X (DRX) et la microscopie électronique à balayage (MEB) ont confirmé l'obtention de la structure hydrotalcite pour tous les solides, à l'exception du solide Cu_4AlFe HT, pour lequel les phases hydrotalcite et malachite sont observées. L'étude par DRX des échantillons calcinés

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a révélé l'existence d'oxydes métalliques et de spinelles des types MgO, CuO, γ-Fe_2O_3 ou/et Fe_3O_4, $MgFe_2O_4$ et $CuFe_2O_4$. Lors de l'oxydation du propène, il est montré que l'augmentation de la quantité de cuivre améliore l'activité des solides. Cependant, le solide Cu_2Mg_2AlFe 500 ayant le plus grand nombre d'espèces de cuivre en surface a présenté la meilleure activité vis-à-vis de l'élimination simultanée du propène et du NO. En effet, les espèces cuivriques présentes en surface sont les sites actifs, alors que les espèces cuivre dans la masse du solide semblent être des sites d'adsorption pour les espèces d'azote.

1. Introduction

Volatile organic compounds (VOCs) and nitrogen oxides (NO_x) arising from industrial gases are dangerous pollutants and have a detrimental effect on the environment and on human health. One of the most prominent results of VOCs and NO_x emission is the formation of ground-level ozone, following the reaction between NO_x and VOCs in the presence of sunlight. Excessive O_3 in the air can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases [1]. To overcome the problem, catalytic devices appear as an efficient technology for complete oxidation of VOCs or/and NO_x reduction. Copper and iron species have been reported to be active in the selective oxidation of propene and/or in the reduction of NO_x [2–4]. Moreover, their excellent low-temperature activity and cost effectiveness makes them a good substitute for noble metal catalysts. However, the most popular copper based catalyst, Cu-ZSM-5, discovered by Iwamoto et al. in 1993 [5], was believed to be the most promising catalyst for NO_x decomposition, thus it did not appear resistant to H_2O and SO_2 present in flue gases from coal combustion [4].

In the past decade, mixed oxides derived from layered double hydroxides (LDHs) known as hydrotalcite-like compounds (HTLCs) have attracted much attention due to their large surface areas, good thermal stability, high dispersion, and basic character [6]. Among many applications, they are known to be powerful for hydrocarbons oxidation [7–9] and/or NO_x reduction with hydrocarbons [2] or ammonia [10].

In this work, a series of $Cu_xMg_{4-x}AlFe$ catalysts derived from hydrotalcite-like compounds was synthesized, then characterized by various techniques. Subsequently, their performance was investigated in propene oxidation and in the simultaneous elimination of propene and NO. Previous studies [2,11] showed that mixed oxides derived from LDHs are potential catalysts for HC-SCR, other ones [3,4] demonstrated that copper and iron are very active species in this process. However, this work is the first to show the roles of copper and iron species coexisting in a single solid via hydrotalcite route in the HC-SCR.

2. Experimental

Mg(Cu)–AlFe hydrotalcite-like samples with a molar ratio equal to 2 were synthetized by a co-precipitation method. An aqueous solution containing appropriate amounts of $Mg(NO_3)_2 \cdot 6\,H_2O$ (FLUKA, 99%), $Cu(NO_3)_2 \cdot 6\,H_2O$ (PANREAC, 98%), $Al(NO_3)_3 \cdot 9\,H_2O$ (ACROS, 99%) and $Fe(NO_3)_3 \cdot 9\,H_2O$ (ACROS, 99%), was added dropwise into a vigorously stirred deionized water solution. During synthesis, temperature and pH were maintained constant at respectively 60 °C and 8 by dropwise addition of a solution of Na_2CO_3 1 M and NaOH 2 M. The obtained solution was stirred at 60 °C for a further hour, and then placed in the oven for 18 h. The precipitate was then filtered, washed several times with hot deionized water (55 °C) and dried at 60 °C for 48 h. The samples were denoted $Cu_xMg_{4-x}AlFeHT$ ($0 < x < 4$). The solids were then calcined at 500 °C under a flow of air ($2\ L \cdot h^{-1}$).

X-ray diffraction experiments were performed at room temperature using a Bruker D8 Advance diffractometer equipped with a copper anode emitting a Kα radiation ($\lambda = 1.5406$ Å) and a LynxEye detector. A step size of 0.02° and a count time of 4 s per step were used for data collection. The crystalline phases were identified by comparing the diffractograms with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) established by the International Center for Diffraction Data (ICDD).

The specific surface area of the dried and the calcined samples was determined by low-temperature nitrogen adsorption (−196 °C) using the Brunauer–Emmett–Teller (BET) method, with a thermo-Electron QSurf M1 sorptometer, while the Barett–Joyner–Halenda (BJH) pore diameters were determined by Sorptomatic 1990 sorption analyzer. Prior to the measurements, each sample was degassed at 400 °C for 3 h.

Scanning electron microscopy analysis was performed on a Mira4 Tescan instrument equipped with an energy dispersive X-ray spectrometer (SEM-EDX). Samples were adhered on aluminum stubs covered with 12-mm carbon adhesive tabs and then coated by a thin film of gold. Typical working parameters were an accelerating voltage of 20 kV, and a beam current of 60 μA.

The reducibility of the calcined samples was studied by H_2 temperature-programmed reduction (TPR). H_2-TPR experiments were carried out in an Altamira AMI 200 apparatus. Prior to the experiments, samples (10 mg) were activated under argon at 150 °C for 1 h. The samples were then heated from ambient temperature to 900 °C under a H_2 flow (5 vol.% in argon-30 mL min^{-1}) at a heating rate of 5 °C min^{-1}.

In each test, a flow of the reaction mixture (6000 ppm propene + air for propene test and 6000 ppm propene + 1000 ppm NO + air for propene–NO test) passes through 100 mg of a catalyst placed in a fixed-bed reactor. The reaction products (NO, CO and CO_2) were analyzed