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Influence of structural, textural and chemical parameters of silver zeolites on the retention of methyl iodide

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ABSTRACT

An experimental screening of silver-exchanged zeolites towards the trapping of methyl iodide was carried out with the general aim of limiting as much as possible the iodine release in case of severe nuclear accident. For the first time, a systematic study was implemented in order to better understand the effects of some important parameters such as the zeolite structural type (FAU-X and Y, MOR, *BEA, MFI and FER) and chemical properties (namely the silver content and its speciation) on the adsorption behaviour. Characterization of 18 zeolitic sorbents, before or after iodine retention tests, was performed using elemental analyses, N_2 porosimetry at $-196\,°C$, XRD, DR-UV-Vis spectroscopy and TEM. The distribution of silver species, namely as isolated Ag^+ cations or charged clusters in the internal porosity, and/or to a lesser extent as metallic nanoparticles, was found to depend mainly on the zeolite structural type and the Si/Al ratio and to a lesser extent on silver content.

CH_3I retention properties were evaluated from dynamic adsorption tests carried out at 100 °C. Quantitative exploitation of breakthrough curves showed that the silver faujasite zeolites of the Y type (Si/Al ratio = 2.5) with more than 15 wt% silver were the most efficient in order to achieve high adsorption capacities both at breakthrough and saturation. More generally, it is found that dispersed silver entities efficiently catalyze the dissociation of CH_3I and the production of AgI precipitates.

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1. Introduction

The capture of radioactive fission products in the context of severe nuclear accident is a major issue for safe nuclear energy. In the course of an accidental sequence, radiotoxic iodine species may be released from the degraded fuel and reach the nuclear containment building via the Reactor Coolant System (RCS). In most of nuclear power plants, a venting system is implemented with the aim of maintaining the integrity of the containment in case or overpressure. These containment venting systems (CVS) could be equipped with a filtration device to limit the external release of radioactive fission products [1]. Among these species, iodine is a significant contributor owing to its ability to exist as volatile species (namely I_2 and CH_3I), radiological consequences linked with its

involvement in human metabolic processes and high mobility in environment [2,3].

After the Fukushima accident, one of the main concerns of the nuclear industry has been to review the mitigation strategies which could be employed to limit the radiological consequences of a severe accident. An efficient solution may consist in combining existing filtration devices (such as metallic filters, aqueous scrubbers or sand bed filters [4]) with an additional filtration stage which can be made of inorganic porous adsorbent. Among the possible adsorbing materials, zeolites are obvious candidates, thanks to their thermal stability and radiation resistance, high specific surface areas, tunable pore size and chemistry [5]. In past works, silver-exchanged faujasite zeolites were identified as the most efficient adsorbents towards both I_2 and CH_3I while zeolitic sorbents containing other cations (lead, copper, manganese, palladium…) were found less promising [6]. This is explained by the very high affinity of silver for iodine to form thermally stable AgI precipitates. By now, most of academic and industrial research works were focused on Ag/zeolites with faujasite X or mordenite structures [7,8].

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Because of their low Si/Al ratio (<2), Ag/X sorbents were claimed to be not acid resistant and not applicable in the presence of high amounts of steam and NO_x [3]. By contrast, Ag/MOR zeolites, which generally possess higher Si/Al ratio, were reported to be more efficient under such conditions [3,8,9]. However, such studies were conducted in a different context, *i.e.* reprocessing of nuclear fuel, and it has also to be acknowledged that the chemical stability of Ag/MOR zeolites comes at the cost of their cation-exchange capacity. Hence, the amount of adsorbed iodine will be limited using these adsorbents.

Overall, scientific gaps persist about the possible implementation of zeolitic materials for severe accident applications. No systematic study was carried out in order to address the effects of important zeolitic parameters on iodine retention. For instance, no attempt were made to examine the respective influences of the silver content and speciation, the Si/Al ratio, the pore size and connectivity on iodine adsorption characteristics and diffusional properties.

In this work, we aimed to bridge this gap by reporting on the chemical and structural parameters influencing the CH_3I sorption performances onto silver zeolites with different structural types (FAU (X and Y), MFI, MOR, FER, *BEA). In the first part of the paper, characterization of the ion-exchanged materials was achieved by different techniques (XRD, N_2-porosimetry, DRS-UV-Vis…) in order to establish afterwards structure-activity relationships with retention properties. In the second part, adsorption capacities at breakthrough and saturation, as determined from the quantitative exploitation of CH_3I breakthrough experiments at 100 °C, are discussed. Since they could affect the storage stability, diffusional constraints will also be considered. After-test characterization was also performed in order to give additional insights onto the trapping mechanism.

2. Experimental part

2.1. Materials

Commercial zeolites of structural types FAU (Y, Si/Al = 2.5, *CBV 300*), MOR (Si/Al = 10, *CBV21A*), FER (Si/Al = 10.5, *CP914C*), *BEA (Beta, Si/Al = 10.1, *CP814E*), MFI (ZSM-5, 11.5, *CBV 2314*) were all provided by Zeolyst in ammonium form. A 13X (NaX) zeolite (Si/Al = 1.2, 60–80 mesh, *20305*) was supplied by Sigma Aldrich.

Various loadings of silver were introduced into the different zeolitic frameworks by means of ion exchange with silver nitrate (Sigma-Aldrich, purity > 99.9%). Exchange reactions were carried out using 200 mL of a 0.01M silver nitrate solution. 2 g of zeolites were added to this solution at 25 °C and stirred for 24 h. Then, the exchanged-zeolites were vacuum-filtered and dried at 80 °C overnight. Whenever necessary, this ion-exchange procedure was repeated up to 2 (MOR) or 3 times (Y, ZSM-5, and 13 X) in order to achieve higher exchange degrees and Ag contents. Prior to adsorption and characterization studies, all the zeolitic materials were calcined under air in a muffle furnace with a heating rate of 5 °C/min from room temperature to 200 °C (plateau of 1 h) and then to 500 °C (plateau of 2 h). In order to avoid any photo-reduction of silver species, all preparation steps and samples storage were done in the dark. Obtained zeolitic samples were denoted as *xAg/Structure (Si/Al)* where x is the mass percentage in silver.

A "benchmark" Ag/13X zeolite (Si/Al = 1.2, *382280*, $Ag_{84}Na_2$ $[(AlO_2)_{86}(SiO_2)_{106}].xH_2O$) with 35 wt% silver was purchased from Sigma-Aldrich for comparison purposes. This zeolite was denoted thereafter $35Ag/13X_{comm}$ (1.2).

2.2. Physicochemical characterizations

Elemental ICP analyses (Ag, Na, Al and Si) were performed at the Service Central d'Analyses of the CNRS and at the Service d'Analyses des Roches et des Minéraux (France). Measurements of the content of each element were performed using two-times ICP analyses. The uncertainty in the determination of each element was certified to be about 2% of its value (in wt%), except for elements whose concentration is close to the detection limit (<0.05%).

ATR infrared spectroscopy was used in order to measure the percentage of exchanged ammonium ions with silver. The different measurements were carried out using *Bruker Alpha* spectrometer equipped with *Alpha P* ATR accessory and diamond crystal. ATR-IR spectra were collected between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. Then, areas related to specific vibration modes of NH_4^+ (around 1450 cm^{-1}) were quantified before and after the different ion-exchanges with silver.

Powder X-ray diffraction (PXRD) measurements before and after test were carried out using a *Rigaku-Miniflex II* (Japan) with the CuKα radiation (λ = 0.15418 nm). PXRD patterns were recorded between 5 and 70° (2θ) using increments of 0.02° and a counting time of 2 s. The mean size of AgI particles detected by XRD after Ag-zeolites exposure to CH_3I was calculated using the Debye and Sherrer Equation [10]:

$$D_{AgI} = \frac{K \times \lambda}{\cos\theta \times \sqrt{L^2 - L_{inst}^2}} \tag{1}$$

Where D_{AgI} is the mean size of AgI crystallites (nm), K is a dimensionless shape factor (equal to 0.9), λ is the X-ray wavelength (0.15418 nm), θ is the Bragg angle (rad), L is the full width at half maximum (FWHM) of the diffraction peak (rad) and L_{inst} the instrumental line broadening (0.07° = 0.0012 rad).

Porosimetric properties were determined from N_2 adsorption isotherms recorded at −196 °C on an automated *Autosorb IQ* sorptiometer supplied by Quantachrome. Prior to each adsorption measurement, samples were outgassed *in situ* in vacuum at 80 °C for 1 h and then at 350 °C for 6 h to remove most of adsorbed impurities. Specific surface areas (S_{BET}) were determined using the BET equation (0.05 < P/P$_0$ < 0.35). Microporous volume (V_{micro}) was calculated according to the *t*-plot method [11]. The total pore volume (V_{pore}) was measured from N_2 adsorption isotherms at P/P$_0$ = 0.97 whereas the mesopore volume (V_{meso}) was deduced by the difference: $V_{meso} = V_{pore} - V_{micro}$.

Transmission electron microscopies studies and EDS analysis were performed on a *FEI Tecnai G220* microscope. Powdered samples were deposited on a copper grid coated with an amorphous carbon film using a "dry method", similar to the one described by Sayah et al. [12]. The grid was contacted with the powder then gently shaken in order to remove excess powder from the carbon film. This deposition method was used instead of the classical one (wet method using ethanol as solvent) in order to avoid any reduction of silver species [12].

DRS UV−Vis spectra were collected on a *Varian Cary 4000 UV−Vis* spectrometer equipped with a double monochromator and *DRA900* integrating sphere. Spectra were registered between 200 and 800 nm, with a resolution of 2 nm and a scan rate of 600 nm/min. Reflectance spectra were plotted in pseudo-absorbance mode, after correction with a Spectralon standard (taken as reference).

2.3. Description of gas-phase dynamic sorption tests

The adsorption behaviour of silver-exchanged zeolites towards CH_3I was studied using dedicated breakthrough experiments.