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A comparative *in situ* TEM and UV–visible spectroscopic study of the thermal evolution of Ag species dispersed on Al_2O_3 and NaX zeolite supports

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ABSTRACT

The oxidation states and dispersion of silver supported on alumina and faujasite were monitored by TEM, TPR and *in situ* UV–visible spectroscopy along the steps of thermal dehydration, then oxidation and finally reduction of the freshly prepared materials. An original transmission electron microscopy approach was conducted, based on the use of a pseudo-environmental TEM holder that provides direct observations, on given zones of the samples, of the formation (in the case of zeolite) or not (in the case of alumina) of reduced silver particles upon dehydration of the material in air. Besides, the question of the high propensity of the silver species supported on alumina to be reduced in hydrogen at temperatures as low as ambient temperature is addressed.

1. Introduction

In the last decades, industrial countries have been facing increasing regulations and restrictions regarding the emission of green house effect gases. Amongst the numerous heterogeneous catalysts that have been developed to answer encountered needs in air treatment, a high number of them involve noble metals (often Pt or Pd) supported on porous oxides. This kind of catalysts, although rewarding in term of activity and selectivity, faces two important drawbacks related to the known toxicity of noble metals, to their necessary recovery and to their cost that significantly impacts the final price of products. To overcome these constraints, many studies have been focused on the replacement of noble metals by cheaper, more widely available and still efficient transition metals.

In this general context, a renewed interest is being dedicated nowadays to the development of porous Ag/oxide catalysts for which promising catalytic activities have been recently reported in reactions such as the oxidative decomposition of VOCs (volatile organic compounds) [1–3] or the SCR (selective catalytic reduction) of NO_x in presence of hydrocarbons [4–12] or alcohols [12–15]. In these catalysts, silver is dispersed and stabilized by taking advantage of the high surface area of the porous oxide support, often an alumina [3–6,11–15] or a zeolite [7–10]. In the case of alumina, the classical method of silver deposition consists in impregnating the support with silver nitrate in wet or in excess water conditions whereas cationic exchange in solution is preferred in the case of zeolites due to the cationic exchange capacity they offer [16]. Then, drying followed by thermal activation treatments in appropriate gas flow is commonly applied to remove the adsorbed impurities (especially water) and transform the sites to their catalytic active form.

Whatever the preparation step, understanding of the silver speciation and of its evolution along the procedure is important for proper control of the final catalyst. However, in the case of silver, no general consensus seems to exist yet on the precise characteristics of the supported phases. Especially, after calcination, many distinct silver species have been reported, depending on the work, that vary from isolated Ag^+ cations or Ag_m^{n+} aggregates [3,6,9], to silver alumina-like phases [4,5,17,18] or nanosized Ag_2O clusters [19,20]. Moreover, although silver halides are known for their high photosensitivity [21], the high sensitivity of the cationic silver species to other factors such as their chemical environment have been much less considered up to now in the domain of heterogeneous catalysts. Nevertheless, recent studies have highlighted the high instability of supported cationic silver in presence of specific gaseous or liquid environments such as alcohol-containing ones. For instance, we

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showed recently by TEM, XAS and UV–visible spectroscopy that the exposure of a freshly calcined silver/alumina catalyst to a flow of air enriched with 5000 ppm of gaseous ethanol (as is applied during SCR of NO_x with EtOH) was sufficient to provoke the reduction, at room temperature, of all silver present in the catalyst [22,23]. Similarly, the high propensity of silver to be reduced was reported during SCR of NO_x promoted by the addition of H_2 in presence of oxygen, the boosting of the catalytic activity at low temperatures being attributed by the authors to the reversible formation of Ag(0) nanospecies in the flow of reactants [24]. It was also noted that the structure and nature of the silver phases of Ag/Al_2O_3 catalysts can markedly change under reaction feed containing only a fraction of reducing agent (*i.e.* 500 ppm of propene) in net oxidizing conditions (2.5% O_2) [18].

The present work was conducted in this context with the aim to analyze in more details, and in a comparative manner, the behaviour, along the steps of silver deposition, drying and then thermal calcination and reduction, of silver ionic species dispersed on two representative porous oxide supports having distinct structural and chemical features, namely Al_2O_3 and zeolite NaX. Alumina was chosen because this oxide has been widely used in the recent years as support of silver to prepare catalysts with very promising activity in the domain of the conversion of NO_x [4–15], whereas the choice for a zeolite support was based on the fact that such microporous solids provide both well-organized structures [25] and a cationic exchange capacity that commonly favours metal dispersion. In addition to macroscopic (sample colours) and conventional microscopic (TEM) observations, temperature-programmed reduction (TPR) was used to identify the reducible species present in the two samples after calcination. Also, the evolution of the silver species was monitored by *in situ* UV–visible spectroscopy while thermally treating the samples in controlled flowing gases. Finally, an innovative pseudo-environmental TEM approach using a special sample holder was applied, which allowed observing the same zone of the material along the treatments.

2. Experimental

2.1. Preparation of samples

The respective parent supports were (i) a zeolite NaX with faujasite (FAU [25]) structure (Union Carbide, Si/Al = 1.4) and (ii) a γ-Al_2O_3 obtained from a parent boehmite AlO(OH) (Dispal® 23N4-80, Sasol North Am. Inc.) that was calcined under flowing air ($10\,mL\,min^{-1}$) for 2 h at 550 °C (heating rate $10\,°C\,min^{-1}$) to give alumina. The same amount of silver (3 wt.% Ag) was added on these two supports using silver nitrate (Aldrich) as silver precursor. For the preparation of the Ag/Al_2O_3 sample, the silver addition was made by excess solvent impregnation of 1 g of alumina with 10 mL of the aqueous solution containing 0.04 g of $AgNO_3$. The suspension was stirred and heated for 2 h in a rotavapor under mild conditions (60 °C, low vacuum) in order to evaporate the excess water. In the case of the zeolite, the silver addition was made by conventional cationic exchange consisting in stirring 1 g of the parent NaX for 2 h in 100 mL of an aqueous solution containing 0.04 g of $AgNO_3$, then recovering the solid by centrifugation and washing it 3 times in water. After the last centrifugation, the Ag/NaX material was recovered and placed 24 h in room atmosphere in order to achieve drying in ambient conditions. Part of each sample was kept as such, the other part being dried at 80 °C in an oven overnight.

2.2. Physicochemical characterizations

Chemical compositions (contents of Ag, Na, Al and Si) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in the Central Analysis Service of the CNRS (France).

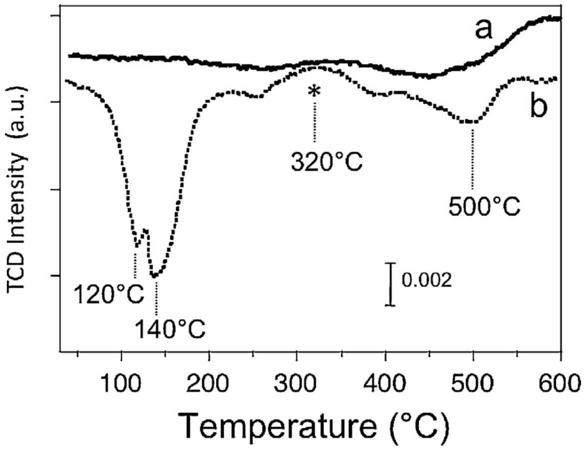

Fig. 1. TPR profiles in the 30–600 °C temperature range for samples (a) Ag/Al_2O_3 and (b) Ag/NaX.

Pore volumes and surface area were characterized by N_2 physisorption on a Micromeritics ASAP 2010 instrument. The adsorption–desorption isotherms were registered at −196 °C after preliminary evacuation of the samples at 300 °C under vacuum. The microporous volumes and external surface area, expressed per gram of support, were determined by the t-plot and BET methods, respectively.

The hydration water contents (weight per weight of dry solid, in %) were measured by TG analysis performed on a SDT Q600 (TA Instruments) in flowing air and with a temperature ramp of $7\,°C\,min^{-1}$. The nature of desorbed products (water and nitrate) was checked by on line mass spectrometry analysis (Pfeiffer Thermostar mass spectrometer) made at the exit of the TG cell.

Temperature programmed reduction (TPR) profiles were obtained on an Autochem Micromeritics apparatus equipped with a differential thermal conductivity (TCD) detector. The sample (about 100 mg) was first treated in flowing air ($25\,mL\,min^{-1}$) for 50 min at 500 °C (heating rate $5\,°C\,min^{-1}$) in order to dehydrate the sample and to remove the nitrate molecules retained after impregnation (case of Ag/Al_2O_3). After cooling, the lines were purged in Ar for few minutes, then the flow was switched to a flow ($25\,mL\,min^{-1}$) of gas containing 5%H_2 in Ar. After TCD stabilization (10 min), the hydrogen consumption was monitored by TCD while heating the sample from room temperature up to 600 °C with a rate of $7\,°C\,min^{-1}$. Note that no cold trap was placed between the sample and the TCD detector, the water possibly formed in the case of the reduction of oxide specie being therefore also detected. It can be also added that, in the recording conditions applied for the experiments, a negative peaks stands for the measure of the difference in thermal conductivity between the H_2/Ar gas (reference) and the same gas deprived from the consumed hydrogen as the reduction occurs.

Transmission electron micrographs were registered on a JEOL JEM 2011 UHR (LaB6) microscope operating at 200 kV and equipped with an ORIUS Gatan Camera. For the observations, the sample powders were deposited on 3 mm copper grids coated with an amorphous carbon film. Deposition was performed by a dry method [22] in which the powder was first contacted with the grid and then gently shaken in order to remove the excess of powder from the carbon film. For “in situ” observations, a special Gatan HHST4004 “Heating Environmental Cell Holder” was used in order to allow the observation of the same zone before and after thermal treatment in controlled atmospheric conditions.