AgNaMordenite catalysts for hydrocarbon adsorption and deNO$_x$ processes

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ABSTRACT

Silver catalysts were prepared by ion exchange of NaMordenite with 5, 10 and 15 wt% Ag. Various characterization techniques such as TPR, UV–vis and XPS indicated the presence of small particles of highly dispersed Ag$_2$O together with isolated Ag$^+$ cations located in α, β and γ exchange sites of NaMOR. The formation of clusters of cationic silver (Ag$_n^{m+}$) was also considered.

The prepared samples were active in the Selective Catalytic Reduction of NO$_x$ in the presence of toluene or butane as reducing agents, excess oxygen and 2% H$_2$O. The solid with 15 wt% Ag was the most active one in the presence of water, reaching a maximum conversion of NO$_x$ to N$_2$ of 47.5% or 51.2% when butane or toluene were respectively used. Under dry conditions, the maximum conversion of NO had an optimum between 5 and 10 wt% Ag for both hydrocarbons.

The NaMOR support showed a higher adsorption capacity than the exchanged samples with both hydrocarbons. For the silver loaded solids, the toluene adsorption capacity at 100 °C increased with the increase of the metal content. In contrast, the amount of butane adsorbed was similar for the different contents of Ag. Consequently, silver has two opposite effects: one is the partial obstruction of the mordenite channels, as seen by the loss of crystallinity and the decrease of surface area and pore volume; and the other effect is the chemical interaction that depends on the nature of the adsorbed hydrocarbon. The interaction between toluene and Ag$^+$ ions is stronger with the π-electrons of the aromatic ring of the toluene molecule than with the σ-electrons of the linear chain of butane. For this reason, toluene is retained at higher temperatures than butane. In addition, between 300 and 500 °C, the appearance of signals corresponding to H$_2$, CO$_2$ and H$_2$O is observed during the TPD of toluene. This indicates that the toluene decomposition occurs, producing coke and hydrogen. Most probably, the generation of CO$_2$ and H$_2$O is a consequence of the reduction of Ag$_2$O particles with toluene.

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1. Introduction

Air pollution is mainly due to the emission of nitrogen oxides (NO, NO$_2$), carbon oxides (CO, CO$_2$), unburnt hydrocarbons (HCs), particulate matter (PM) and volatile organic compounds (VOCs) from power plants, chemical and petrochemical plants, and vehicles. The Selective Catalytic Reduction (SCR) using HCs as reducing agent is one interesting way which allows NO$_x$ abatement under oxidizing conditions [1–3]. An important issue for automobile catalyst manufacturers is the study of contaminant abatement under conditions close to real behavior. In this sense, it is important to take into account a possible effect of the presence of other compounds such as H$_2$O and unburnt hydrocarbons. In fact, during the engine cold-start, 80% of the unburned hydrocarbons are emitted to the atmosphere through the converter without reacting. In addition, the three-way catalysts (TWC) are weak or inactive at low temperatures and require temperatures above 300 °C to have an optimal

performance. For these reasons, it is necessary to implement new systems aimed at reducing these emissions [4–6].

An interesting alternative consists in the combination of the excellent adsorption properties of zeolite materials with the high catalytic activity of exchange cations such as Co, Fe, In, Ag and Cs, in the Selective Catalytic Reduction of NO$_x$ using adsorbed HC as a reducing agent [7–9]. Thus, this is a promising system able to adsorb HCs at low temperature and to reduce NO$_x$ at the normal operating temperature of the converter. Given this situation, it is clear that the study of a combined adsorption of hydrocarbon with nitrogen oxides reduction is a major issue.

In this vein, some HCs adsorption and desorption experiments have been reported on various zeolites such as BEA [10], Ferrierite [11] and H-ZSM5 [12]. The adsorption capacity of zeolite materials depends on several factors, namely, the quantity, accessibility and distribution of active sites, as well as the topology of the zeolite. Specifically, in the Na-mordenite zeolites the substitution of a Si^{4+} ion by an Al^{3+} ion with a lower valence produces a negative charge on the structure that is neutralized by the Na$^+$ cation forming a conjugate acid–base pair. The Na$^+$ cation acts as a Lewis acid site, while the oxygen of the zeolite structure with partial negative charge acts

as a Lewis base. Thus, the cations in Na-mordenite are adsorption sites for molecules with π electrons and many compounds of this type have been studied, particularly benzene. The two main modes of benzene adsorption involve two interactions, one between its π electron cloud with the counter-ions and another between the CH group with framework oxygen bearing the negative charge of the lattice [13].

This is supplemented by several investigations which have studied the catalytic properties of silver catalysts for the SCR-NO$_x$ with different hydrocarbons [14,15]. Silver-alumina (Ag/Al$_2$O$_3$) catalysts have been widely explored due to their ability to reduce NO$_x$ with HCs and H$_2$ [16–18]. Farrauto et al. [19] found that Ag-ZSM-5 was a good candidate of HC trapping materials under cold-start conditions and other authors tested thiophene on NaY zeolite exchanged with Ni^{2+}, Ag$^+$ and Zn^{2+} [20]. In the same way, Kaliaguine et al. [21] reported that the Ag-ZSM-12 catalyst was a promising adsorbent due to its low sensitivity to H$_2$O and CO$_2$ which are essentially present in the exhaust stream of vehicles. Elangovan et al. [22] used MCM-68 and SSZ-33 exchanged with Ag$^+$, Co^{2+} and Mg^{2+} as hydrocarbon trap. Therefore, the presence of Ag seems to be important for the combination of adsorption/desorption and SCR-NO$_x$ processes.

The purpose of this work was to study the behavior of Ag-NaMordenite catalysts in the Selective Catalytic Reduction of NO$_x$ with hydrocarbons. Basic studies were performed on the adsorptive and catalytic properties of these materials. Two different HC specifications were considered: butane as a saturated short HC and toluene, representative of the aromatic family.

The catalysts were prepared with different loadings of silver and they were thoroughly characterized by temperature-programmed reduction (TPR), X-ray diffraction (XRD), UV–vis diffusive-reflectance (UV–vis DRS) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

The ion-exchange method generally results in a strong metal-support interaction and a better dispersion of metal in the zeolite. Hence, this method was applied to incorporate silver into a commercial sodium-type mordenite zeolite sample (NaMOR, SiO$_2$/Al$_2$O$_3$ = 13) provided by Zeolyst International. In this procedure, 4 g of the zeolite powder were added to 150 ml of AgNO$_3$ solution with concentrations from 0.04 to 0.10 M. The mixture was then stirred at 25 °C for 24 h. All the above procedures were performed in the dark due to the sensitivity of silver to the light. The suspension was then filtered and dried at 80 °C, followed by treatment in O$_2$ flow at 500 °C. The calcined samples were denoted as Ag(x)M, where 'x' was the percent by weight of silver. The silver loadings were 5, 10 and 15 wt% determined by atomic absorption spectrometry flame (AASF), which corresponded to ion-exchange degrees of 17.8, 35.5 and 53.1%, respectively. It was assumed that each monovalent Na$^+$ ion was exchanged with one monovalent Ag$^+$ ion.

A mechanical mixture was prepared between Ag$_2$O and NaMOR, known as Ag$_2$O/M and used as reference sample in some of the characterization techniques (XPS, TPR and UV–vis).

2.2. Catalyst characterization

2.2.1. Determination of pore volume and surface area

Nitrogen adsorption–desorption isotherms were obtained at −196 °C on a Quantachrome Autosorb instrument. Previously, the samples were outgassed at 300 °C for 6 h (10^{-4} Torr). The Brunauer–Emmett–Teller (BET) equation was used for calculating the specific surface area of the materials from N$_2$ adsorption isotherms. The micropore volume was determined by applying the t-plot method [23].

2.2.2. X-Ray diffraction

This technique was employed for the detection of metallic Ag, Ag$_2$O and to determine the crystallinity of the Ag(x)M catalysts. The X-ray diffraction measurements were taken using an XD-D1 model Shimadzu diffractometer operated with Cu Kα radiation at 30 kV and 40 mA, using a scanning rate of 1° min^{-1}. The database employed was the one provided by the manufacturer. The crystallinity was estimated from the ratio of the sum of the intensity of the prominent peaks corresponding to planes (1 1 1), (3 3 0), (1 5 0), (2 0 2) and (3 5 0) of Ag(x)M samples and NaMOR support. The maximum degree of crystallinity was taken equal to 100% and corresponded to calcined NaMOR [24].

2.2.3. Temperature-programmed reduction

The TPR experiments were performed using an Okhura TP-2002-S instrument equipped with a TCD detector. A mixture of 30 ml min^{-1} of 5% H$_2$ in Ar was used. The heating rate was 10 °C min^{-1} up to 900 °C. Fresh samples were pre-treated in O$_2$ flow in situ, heating at 5 °C min^{-1} from room temperature up to 500 °C and kept at that temperature for 2 h. The amount of Ag(x)M samples was 0.10 g. The H$_2$ consumption was referred to the silver content of the prepared samples.

2.2.4. Diffusive-reflectance UV–vis experiments

UV–vis spectra were collected on a Shimadzu UV–vis–NIR model UV-3600 spectrophotometer, with the use of a diffusive-reflectance attachment with an integrating sphere coated with BaSO$_4$. Diffuse reflectance spectra (DRS) were registered for samples storage under ambient conditions. BaSO$_4$ was used as a reference. The absorption intensity was calculated from the Schuster–Kubelka–Munk equation, $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the reflectance.

2.2.5. X-Ray photoelectron spectroscopy

The XPS measurements were performed with the multitechnique system (SPECS) equipped with a dual X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV and Mg Kα radiation ($h\nu$ = 1253.6 eV) operated at 200 W and 12 kV. The working pressure in the analyzing chamber was less than 5.9×10^{-7} Pa. The binding energies (BE) of core-levels Si 2p, Al 2p, Ag 3d, C 1s, O 1s, and the kinetic energy (KE) in the region of the Ag M$_4$VV Auger transitions were measured. The Si 2p peak at 102.4 ± 0.1 eV of binding energy (BE) was taken as internal reference.

The binding energy positions of Ag 3d do not identify the oxidation state of the silver species, because the characteristic states of oxidized (Ag$_2$O) and metallic silver (Ag°) are close together (within 0.5 eV) [25]. Thus, the modified Auger parameter (α') was used to characterize the chemical state of Ag. This parameter is the sum of the kinetic energy of the Auger electron (AgM$_4$VV) and the binding energy of the core-level (Ag 3d$_{5/2}$) peak. This parameter is independent of charging, but still sensitive to chemical shifts.

The data treatment was performed with the Casa XPS program (Casa Software Ltd., UK). The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mixture of Gaussian and Lorentzian functions in a 70/30 ratio. For the quantification of the elements, sensitivity factors provided by the manufacturer were employed.