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Selective catalytic reduction of NO_x using propene and ethanol over catalysts of Ag/Al_2O_3 prepared by microemulsion and promotional effect of hydrogen

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ABSTRACT

The present study explores the possibilities of catalysts of Ag/Al_2O_3, in which silver has been deposited using reverse microemulsions with the aim of getting maximum dispersion and homogeneity in the active superficial species, for the selective catalytic reduction of NO_x in excess of oxygen, using both propene and ethanol as reductants and in the scope of the control of the emissions produced by vehicles that operate in conditions of lean mixture like the diesel engine or those of gasoline direct injection. The promotional effect of the hydrogen presence in the reactive mixture has also been analyzed. For both reductants, when in presence of hydrogen, an important enhancement in NO_x conversion is produced, in particular for a catalyst with 3 wt.% silver. The production of acetaldehyde during the reaction employing ethanol is also analyzed and its role on the NO_x reduction process has been examined. The interpretation of catalytic properties has been complemented by means of in-situ DRIFTS.

1. Introduction

One of the main challenges, at the environmental level, faced by the catalytic community since the end of last century is related to the control of toxic emissions produced by vehicles that operate in conditions of lean mixture (with excess of oxygen), such as diesel vehicles or direct injection engines. These engines are efficient in terms of decreasing fuel consumption but they present the limitation that conventional three-way catalysts are only efficient for the conversion of NO_x when the engine operates in the stoichiometric region. For this reason, it is vital to develop catalysts that are also selective for the reduction of NO_x emitted under lean conditions by diesel engines or direct injection gasoline engines which could have appreciable hydrogen contributions in exhausting gases [1,2].

Thus, whereas oxidation catalysts based on noble metals are able to almost completely eliminate unburn hydrocarbons and the CO and/or particulate matter produced during the combustions or partial oxidation of fuel in the cylinders [3], they are not able to reduce NO_x emissions. Within the different physico-chemical methods investigated to control lean-burn emissions, it stands out the possibility of selective catalytic reduction (SCR) of NO_x, which makes use of unburn hydrocarbons or other reductants produced in the combustion such as CO, H_2, etc., or, alternatively externally added fuel or other reductants in a post-combustion treatments process.

The NO_x-SCR process requires the use of highly selective catalysts, since combustion processes of the reducing gases are generally favored using oxygen, in excess from the reactive mixture, rather than NO_x. In this sense, the systems that have shown activity for the process can be classified basically in two groups, the catalysts based on metals of the platinum group and the catalysts based on highly dispersed base metals or gold, the latter generally appearing in oxidic form [3]. The first ones (mainly the systems based on Pt/Al_2O_3) have shown significant activity, presenting a window of NO_x conversion at relatively low temperatures. They have, however, the disadvantage of the production of relatively high amounts of N_2O at low temperature during the reduction of NO_x and an enhanced activity of hydrocarbon combustion which make them little selective at relatively high temperatures. On the other hand, systems based on base metal oxides have the drawback of presenting their NO_x conversion window at relatively high temperatures, although they have high selectivity. One of the systems that have presented outstanding catalytic properties within this last group is that related with highly dispersed silver on γ-Al_2O_3 [3–8]. Nevertheless the NO_x conversion window in this type of systems appears at relatively high temperatures, particularly when more refractory hydrocarbons are used as reductants for the SCR process, usually

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over temperatures expected for the emissions produced during normal fuel lean-burn combustion.

Within the investigations directed to the decrease of the operation temperature of this type of system, two types of approaches can be emphasized. On the one hand, there is the use as hydrocarbon reductants much easier to activate as the oxygenated ones [9]. On the other hand, it could be possible to modify the engine in order to produce exhaust gaseous mixtures able to promote the SCR process. In this sense, Satokawa found an important promotional effect of the hydrogen gas when C_3H_8 is used as a reductant [10]. In this context, the present paper analyzes the properties of Ag/Al_2O_3 catalysts for the SCR of NO_x using both propene or ethanol (also considering its appeal at a production level in the Latin American scene) as NO_x, reductants, as well as the promotional effect of the introduction of a small amount of hydrogen in the reactant mixture. To this end, two catalysts with low silver loadings (1.5% and 3% in weight) have been synthesized by means of a microemulsion method aiming to obtain high levels of dispersion in conditions of maximum homogeneity for the active superficial species [7]; their catalytic performance has been compared with that of the support employed, high surface γ-Al_2O_3, used as reference. The systems have also been analyzed by means of DRIFTS in-situ in order to explore most relevant aspects of the activation of reaction molecules and have been characterized by means of XRD and DRS-UV–vis spectroscopy.

2. Experimental

The Ag/Al_2O_3 catalysts (with 1.5% and 3% in weight of silver; denoted as 1.5Ag and 3Ag, respectively) were prepared by precipitation of silver on high surface area alumina (200 $m^2\,g^{-1}$; Condea) within reverse microemulsions in which the minority water phase was constituted by aqueous silver nitrate solution. The details of the method employed have been reported in a previous study [7]. The alumina (from Condea) used, in the form of spheres of ≈2 mm, was crushed in agate mortar and pre-sieved to the sizes adapted for the catalytic study (0.125–0.250 mm). In any case, the systems were calcined under air to 773 K as a final treatment and were pretreated in-situ under oxygen flow diluted in inert gas to 773 K before catalytic testing.

Catalytic activity tests were carried out using mixtures of propene or ethanol (0.1%), NO (0.1%), NO_2 (120 ppm), N_2O (10 ppm) and O_2 (5%) diluted in inert gas, in the absence or presence of H_2 (0.1%). They were done in a pyrex tubular reactor at a fixed space velocity of 30,000 h^{-1}. The analysis of reactants and products was carried out by means of FTIR (PerkinElmer equipment 1725X) using a gas cell of multiple reflection. Typical tests were performed in the light-off mode by increasing the temperature at 5 K min^{-1} from 298 to 823 K.

The analyses by means of DRIFTS in-situ were carried out under similar reaction conditions using a DRIFTS cell of Harrick and a Bruker FTIR spectrometer (Equinox 55 model with MCT detector). XRD analysis (performed on a Siemens D-500 diffractometer) and DRS-UV–vis (Varian 2300 spectrophotometer) showed exclusively the presence of γ-Al_2O_3 in all the cases, demonstrating the high degree of dispersion of silver in any of the catalysts.

3. Results and discussion

The results of catalytic activity for SCR of NO_x using propene as a reductant on the three investigated systems are displayed in Fig. 1. They show that the silver presence decreases the temperature of conversion of propene and improves the selective reduction of NO_x although some differences as a function of the silver content are observed. Thus, in general terms, the system with less silver (1.5Ag) shows a behavior close to that of the Al_2O_3 support, reaching in both cases a greater degree of conversion of NO_x although a small part of hydrocarbon could be partially oxidized on the basis of observation of a small amount of CO in those cases, as well as residual amounts of other by-products of partial oxidation processes like HCN. In contrast, the 3Ag system shows greater activity for the nonselective combustion of propene, although the selective reduction of NO_x begins at a slightly lower temperature. On the other hand, generation of N_2O is not practically observed during the reduction of NO_x for none of the catalysts.

In addition to this, differences between the two silver systems are observed concerning their activity for the oxidation from NO to NO_2 since such process is apparently favored for the 1.5Ag system, similarly to what is observed for the Al_2O_3 sample. It may be noted in this sense that NO_2 was considered a NO_x-SCR promoter in catalysts of Au/Al_2O_3 combined with Mn_2O_3 [11], as well as over

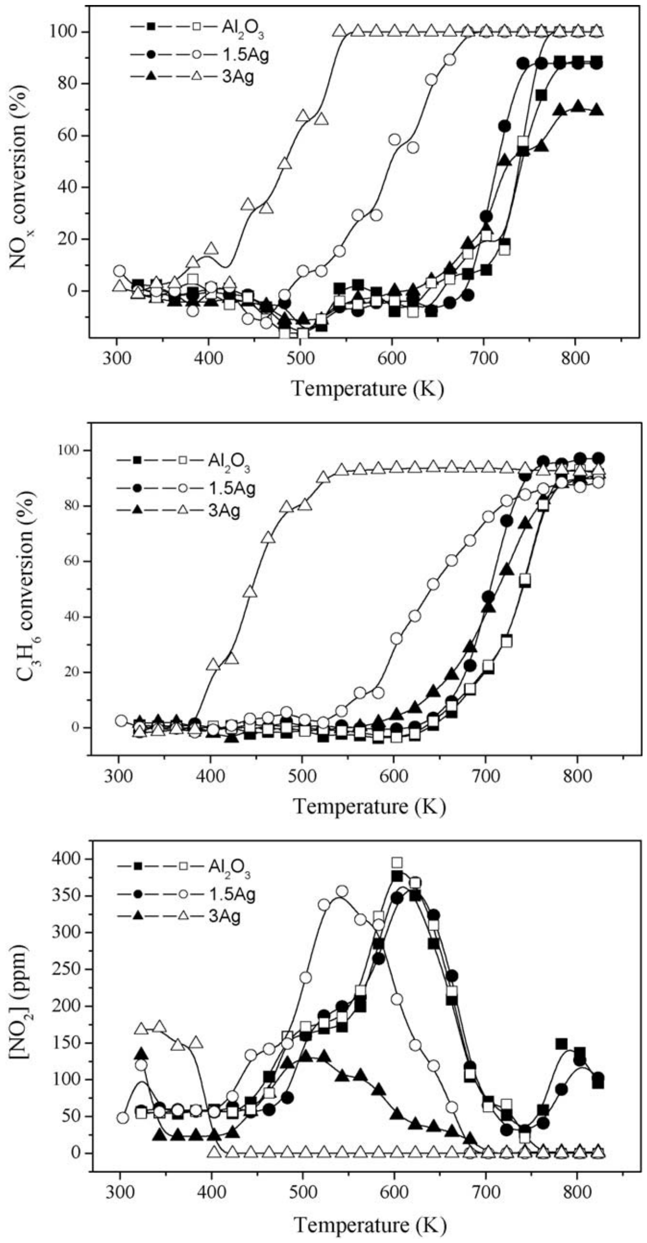

Fig. 1. Main results of catalytic activity for the reaction of SCR of NO_x with propene in the absence (full symbols) and presence (empty symbols) of H_2 over the indicated catalysts.