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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

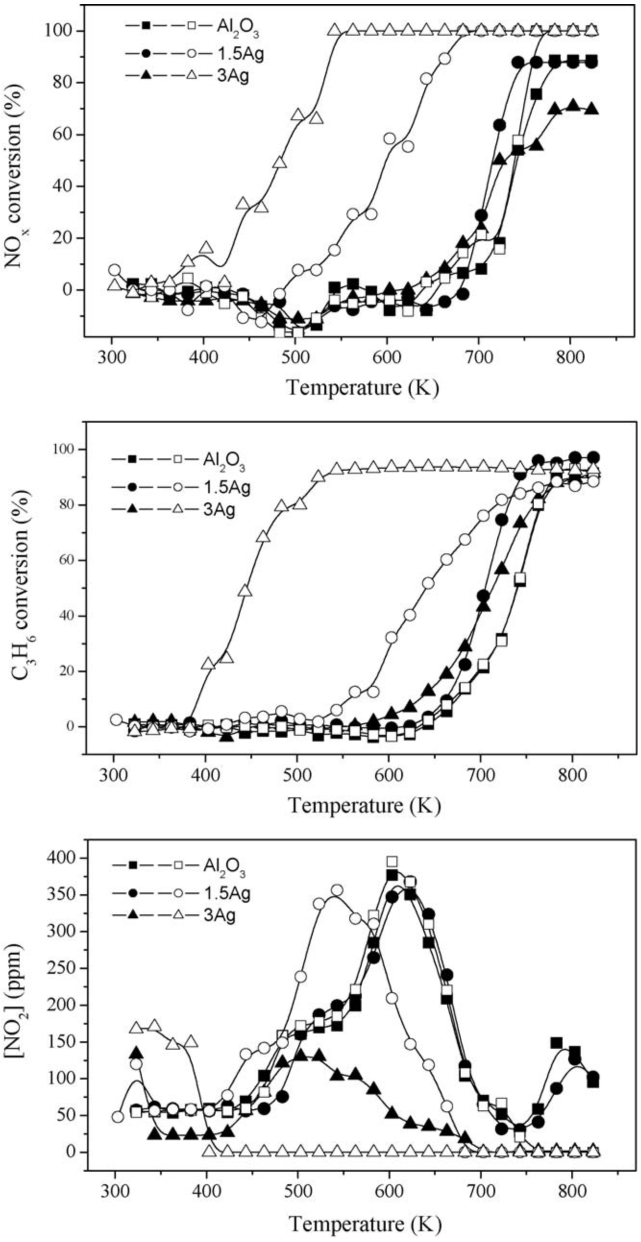

Fig. 1. Main results of catalytic activity for the reaction of SCR of NO_x with propene in the absence (full symbols) and presence (empty symbols) of H_2 over the indicated catalysts.

Ag/Al_2O_3 systems during independent tests in which NO_2 was provided directly as a reactant [6]. Comparative results suggests instead a limited role for this compound in our case, at least for the sample with greater content of silver (3Ag), in agreement with previous investigation [12]; however, it is not possible to discard that it can be involved in NO_x-SCR processes taking place over the other two systems investigated (1.5Ag and Al_2O_3).

The analysis of in-situ DRIFTS shows that the role of the silver could be related to the promotion of the reactant activation processes not only for propene but also for NO. Thus, the analysis of Fig. 2 shows that NO_x activates through the formation of monodentate or bidentate nitrate species (bands at 1710, 1550 and 1252 cm^{-1}) [7]. However, propene appears fundamentally activated through the formation of acrylate species (bands or shoulders to 2909, 1636, 1562, 1457, 1381 and 1294 cm^{-1} [13]); this attribution is also based on the observation of the same type of bands in absence of NO [7]. This mode of propene activation differs from some proposals in the available scientific literature in which its activation through the formation of acetate species has been indicated [12], although it agrees with proposals made for dispersed tin oxide catalysts or for catalysts of Ag/Al_2O_3 prepared by impregnation with AEDT complexes and investigated under similar conditions [3,14]. In addition to this, the spectrum shows the generation of species attributable to adsorbed cyanide (band to 2147 cm^{-1}) which would constitute an intermediate of reaction in the final steps of the mechanism, as proposed by other authors [3,12]. On the other hand, the activity of alumina must be related to the presence of certain active hydroxyl groups on its surface (fundamentally those of greater acidity), as they show changes in this zone of the spectrum upon interaction with the different reactants (Fig. 2), and that justifies that the support itself must play a relevant role in the reaction mechanism.

The hydrogen introduction in the reactant mixture produces significant promotional effects on the conversions of NO_x and propene, whose magnitude depends to a great extent on the silver loading of the catalyst (Fig. 1). The system showing a greater promotional effect is that with higher silver content (3Ag) whereas the Al_2O_3 support does not practically present changes as a result of the hydrogen presence in the reactant mixture. Other appreciable differences among the systems in the presence of hydrogen are related to the production of a significant amount of N_2O during the selective reduction of NO_x at low temperature only over the most active catalyst (3Ag), whereas for the other two systems (1.5Ag and Al_2O_3) this compound appears practically absent.

Different hypotheses have been put forward to explain the promotional effect of hydrogen on the SCR of NO_x [12,15]. It has been proposed that hydrogen could be directly involved in the reaction mechanism and in the promotion of one or several steps of such mechanism. In this sense, it has been observed that the hydrogen presence could promote the generation of oxygenated intermediates of hydrocarbons like acetate species [16], known also to be more active for the NO_x-SCR when employed themselves directly as reagents [9], while it could also promote the formation of nitrate species or their reactivity as well as the transformation of cyanide species to isocyanate species, which constitute one of the key processes in one of the last steps of the mechanism [12]. On the other hand, it has been pointed out that the role of hydrogen could include its indirect action on structural changes in the silver species under the reactive atmosphere, which could lead to the generation of $Ag_n^{\delta+}$ clusters or very small particles of metallic silver, which would constitute sites of high activity for the SCR process [15–18]. In this sense, the significant production of N_2O in the 3Ag system suggests that hydrogen presence in the reactant mixture could indeed promote the generation of small metallic clusters in this system, which would favor, in contrast to expectation for active sites of oxidic character, processes of dissociation of NO typically involved in the generation of this product. DRIFTS studies (Fig. 3) have shown, considering the comparison with results obtained in the absence of hydrogen, that there is also a promotional effect on the generation of isocyanate species (band at 2235 cm^{-1}), as well as the possible generation of intermediate NH_x (bands to 2908 and 3001 cm^{-1}), processes which could also be favored in the presence of active sites of a metallic character [7,14,17,19]. On the other hand, experimental results related to production of NO_2 (Fig. 1), suggests, as it occurred in the absence of hydrogen, that such intermediate could be involved in some of the elementary steps of SCR process for 1.5Ag or Al_2O_3 also in the presence of hydrogen, being more doubtful its participation in the case of the 3Ag sample.

As for the SCR of NO_x, using ethanol as a reductant, the data displayed in Fig. 4 reveal, in accordance with results by other authors [3,9], the high efficiency of the process for the three tested catalysts. The silver presence improves to a certain extent the conversion of NO_x at low temperature although it presents a certain lower activity for the nonselective combustion in a small

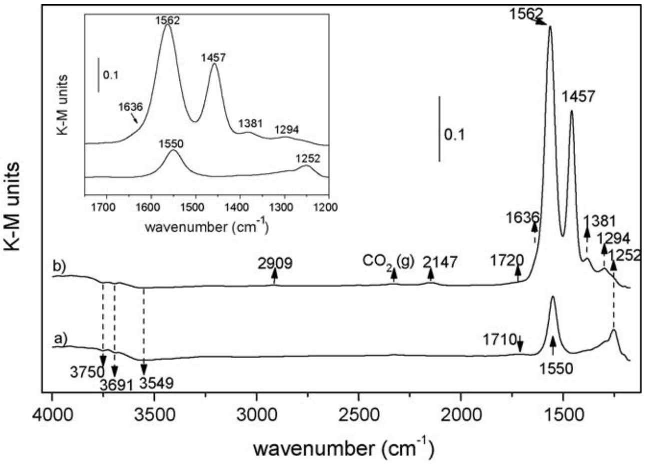

Fig. 2. DRIFTS difference spectra of 1.5Ag under the following reactant atmospheres: (a) NO + O_2; (b) NO + O_2 + C_3H_6. The inset expands the zone in which most intense bands related to species resulting from NO_x or C_3H_6 activation appear (see text).

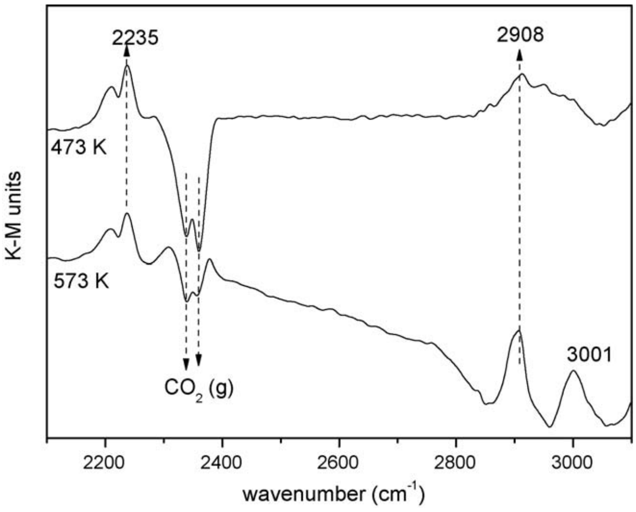

Fig. 3. DRIFTS difference spectra of 3Ag under NO–O_2–C_3H_6–H_2 reactant mixture at the temperatures indicated.

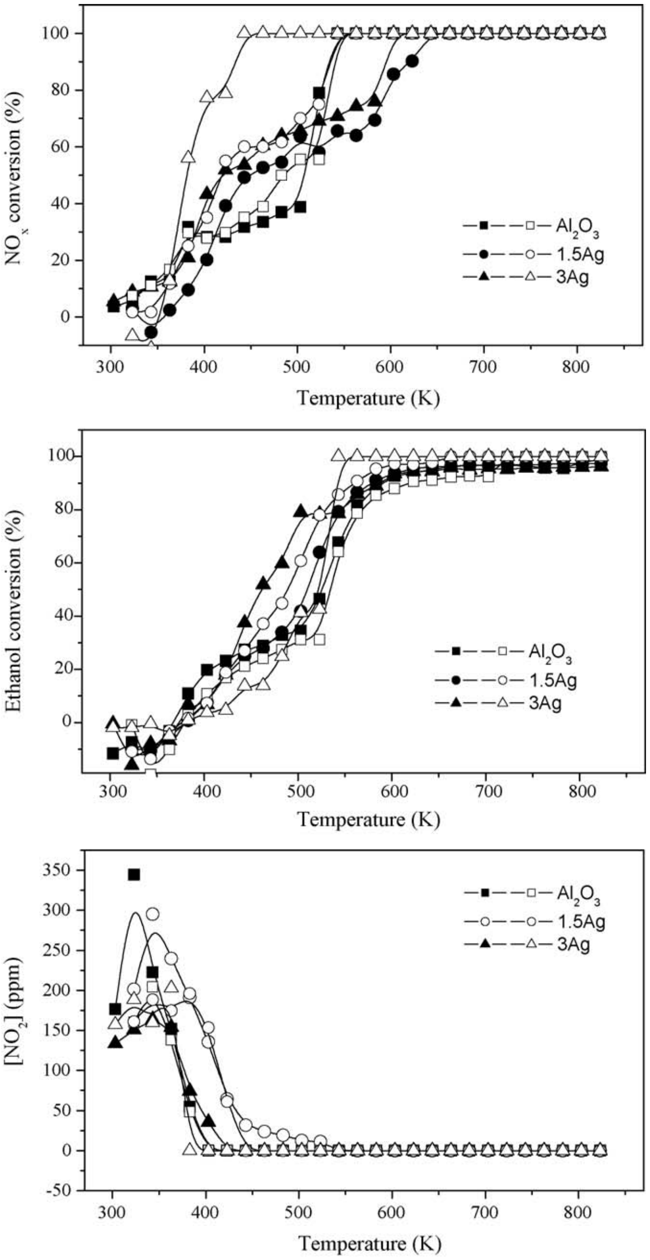

Fig. 4. Main results of catalytic activity for the reaction of SCR of NO_x with ethanol in the absence (full symbols) and presence (empty symbols) of H_2 over the indicated catalysts.

temperature range. In any of the cases, the irregularity detected in the conversion profiles suggests that different processes can be taking place during the course of the run. Indeed, FTIR analysis of the gases evolving from the reactor shows that a process of partial reduction of the ethanol takes place initially which gives rise to acetaldehyde formation, as displayed in Fig. 5. The formation of acetaldehyde for the Ag-containing catalysts starts at 355 K reaching the highest production at ca. 423 K and then decreases becoming practically absent at temperatures over ca. 583 K; in the case of the Al_2O_3 support, the onset of its formation occurs at higher temperatures. It must be noted that generally speaking, acetaldehyde can present greater activity for the SCR of NO_x than the ethanol itself, although during certain range of intermediate temperatures, an important competition between both reductants could be produced (also considering the relative differences between their respective partial pressures during the course of the reaction), which could give rise to the irregularities observed on the conversion profiles. Nevertheless, it may be noted that direct correlation between partial oxidation activity towards acetaldehyde and NO_x-SCR activity is not easily established on the basis of the obtained results. On the other hand, a certain promotional effect of hydrogen presence is also observed in the reactive mixture when the ethanol is used as reductant (Fig. 4). On the basis of the analysis of reaction products, one of the main effects of hydrogen, at least in the case of 3Ag which exhibits the greater promoting effect, can be related to a small promotion of the partial oxidation of the ethanol to acetaldehyde, also according to recent data from other authors [20,21]. In this sense, studies conducted by Zhang et al. have shown that the hydrogen presence promotes the formation of oxygen containing molecules (such as CH_3CHO) as well as molecules containing nitrogen (such as CH_3NO_2) during the SCR of NO_x by ethanol at low temperatures [21]. Although the present study has not analyzed the superficial enolic species (RCH = CH–O), it is important to point out that there are references for the formation of such species during the reaction with ethanol in the presence of hydrogen [22,23]. The formation of superficial enolic species can be attributed to the isomerisation equilibration of the acetaldehyde between the gaseous phase and the surface of the catalyst and are proposed to be highly effective for the ethanol reduction of NO_x with Ag/Al_2O_3 catalysts. On the other hand, the effect of the addition of hydrogen in enhancing the activity for the SCR of NO_x can also be attributed to the formation of metallic silver nano-agglomerates as a consequence of the reduction of Ag^+ ions dispersed on the surface of the γ-Al_2O_3 [15], as proposed for the reaction with propene. Such nano-agglomerates can promote the selective catalytic reduction of NO_x through the activation of reductor hydrocarbons for further reaction over active oxidized sites nearby [24]. According to Fig. 4 the conversion of NO_x is observed only at temperatures close to the starting temperature of acetaldehyde formation. According to the available literature [22,23,25] the high reactivity upon interaction of enolic species with NO_3^- species is cited as the most efficient path for the reduction of NO_x when ethanol is used as reductant. The production of NO_2 is lower at low temperatures likely because hydrogen inhibits the formation of nitrates on the surface of the Al_2O_3 and NO_2 could immediately be converted by the acetaldehyde. The 3Ag catalyst likely reaches optimum coverage of the γ-Al_2O_3 surface among

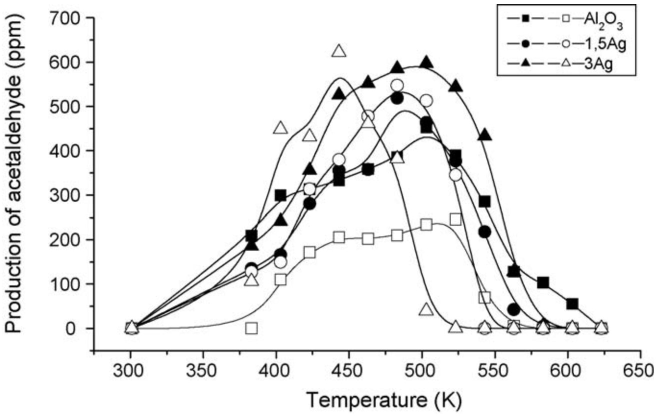

Fig. 5. Production of acetaldehyde during the reaction of SCR of NO_x with ethanol in the absence (full symbols) and presence (empty symbols) of H_2 over the indicated catalysts.

the examined series, which prevents nitrates adsorption and eventual formation of NO_2. It is verified that when reaching the maximum conversion for the NO_x-SCR with the 3Ag catalyst, a certain amount of reductant was still present, guaranteeing in such a way the presence of reducing species in the reactant atmosphere.

4. Conclusions

The catalysts of Ag/Al_2O_3 prepared by microemulsion method present a considerable activity for SCR of NO_x using hydrocarbons. The conversion window of NO_x can be extended considerably with a decrease of the conversion temperatures through the use of ethanol as a reductant as well as through the introduction of a relatively small amount of hydrogen in the reactant mixture. According to the results obtained by activity measurements along with in-situ DRIFTS examination, it is proposed that the main promotional effects of hydrogen could be related to the generation of small metallic clusters when propene is used as a reductant and with the promotion of the partial oxidation to acetaldehyde when using ethanol as a reductant in the presence of hydrogen.

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