On the effect of poor metals (Al, Ga, In) for NO_x conversion by SCR ethanol

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Introduction

SCR with ammonia injection by reducing NO_x emitted by thermal Diesel engines is one of the systems that will available to reach the future EUROVI standards in term of NO_x emissions. However, the presence of urea precursor in the exhaust line can lead to serious problems such as crystallisation, polymerisation. One possible alternative solution will be to substitute ammonia by ethanol in the selective catalytic reduction.
Catalysts containing "poor" metals (group III elements) such as B, Al, Ga and In have received much attention in recent years. Besides their use as supports for active metal centers, particulary in Al_2O_3 based materials, these elements play an important role in novel catalytic materials such as promoters, supported metal oxides and mixed oxides, supported bimetallic catalysts and modified zeolithes [1]. It has been recently demonstrated that Ga_2O_3 and In_2O_3, supported on acidic supports, such γ-Al_2O_3, TiO_2 and SiO_2-Al_2O_3 present a remarkable deNO_x catalytic activity [2].

The aim of this work is to provide a detailed study of In_2O_3 systems supported on Al_2O_3. Different indium loadings (0.5<wt%<5) were investigated. The properties and catalytic activity of the selective reduction of NO_x with ethanol in Lean burn conditions were investigated. Other catalysts based on gallium (0.35<wt%<1) have been also synthesized and compared with those containing indium.

Materials and Methods

The γ-Al_2O_3 support was obtained by calcination of a boehmite AlO(OH) at 500°C under air flow during 2 hours. The catalysts were prepared by excess solvent impregnation of the γ-Al_2O_3 with $In(NO_3)_3$ or $Ga(NO_3)_3$ aqueous solution. Before the catalytic runs, the samples were calcined in situ under air flow at 500°C. The catalysts were characterized by elementary analysis (ICPAES), X-ray diffraction (XRD), Transmission Electronic Microscopy (TEM), Diffuse reflectance UV-Vis, X-ray photoelectron spectroscopy (XPS) and Temperature Programmed Reaction (TPR). Temperature-programmed surface reaction (TPSR) and steady state experiments were carried out, in a U-type glass reactor, using a gas mixture containing 500ppm NO + 2500ppm C_2H_5OH + 10% O_2 in Ar (GHSV = 160 000 h^{-1}). As water and hydrogen are present in real experimental conditions, the effects of such compounds addition were also investigated.

Results and Discussion

The XRD spectra for the materials In(x)/Al_2O_3 shows that the crystalline indium oxide phase was weakly observed for the sample at 5% of In. For the least-loaded samples (In(0.5), In(1.0) and In(2.5)/ Al_2O_3), no signal was observed due to the small crystal size or the presence of amorphous indium oxide. TEM images of In(2.5)/Al_2O_3 reveal the presence of In_2O_3 particles scattered on the surface. Thus, the crystalline structure of the In_2O_3 phase was observed for high-In-loading.
The effect of indium loading was also investigated on the DeNOx activity. Screening tests were carried out using the following feed: 500ppm NO + 2500ppm C_2H_5OH + 10% O_2 in Ar. The curves of NO_x conversion vs. temperature are presented in Fig. 1. The total NOx reduction activity increases with the loading of indium up to a maximum of 2.5 wt % of indium, then a decrease is observed.

The maximum of conversion was found with In(2.5) catalysts. The NO_x reduction curves pass through a maximum depending on the competition between total oxidation of ethanol by O_2 and its oxidation by NO. For a sake of comparison, gallium based catalysts were tested in NO_x reduction (SCR) by ethanol (Fig. 2) in the same operating conditions. The catalytic activity is lower at low temperatures but is comparable to In_2O_3 based catalysts at high temperatures.

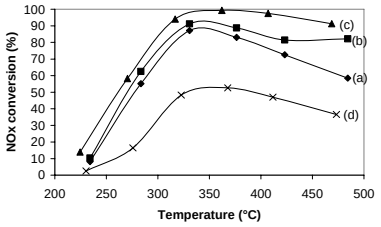

Fig. 1: Effect of indium loading over γ-Al_2O_3 for C_2H_5OH-SCR of NO_x: (a) In(0.5), (b) In(1.0), (c) In(2.5) and (d) In(5.0).

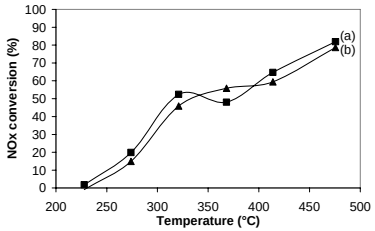

Fig. 2: Effect of gallium loading over γ-Al_2O_3 for C_2H_5OH-SCR of NO_x: (a) Ga(0.35) and (b) Ga(1.0).

Significance

In a sustainable process, ethanol could replace ammonia as reducing agent in vehicles for NOx abatement. In_2O_3/Al_2O_3 catalysts demonstrate higher NO_x reduction performance for SCR ethanol than typical phases such as Ag/Al_2O_3 Thus, such catalysts will be washcoated on small carrots (extracted from monolith) to be evaluated in a synthetic gas bench close to real Diesel exhaust gases conditions.

References

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