Fourier transform IR study of $NO + CH_4 + O_2$ coadsorption on In-ZSM-5 $DeNO_x$ catalyst

Andrea R. Beltramone, Liliana B. Pierella, Felix G. Requejo, and Oscar A. Anunziata*

Grupo Fisicoquímica de Nuevos Materiales /Centro de Investigación y Tecnología Química (CITeQ), Universidad Tecnológica Nacional, Facultad Regional Córdoba, Maestro Lopez esq. Cruz Roja, s/n, 5016, Córdoba, Argentina

Received 9 June 2003; accepted 7 August 2003

Reactivity of the NO and NO_2 adspecies in the coadsorption of NO with CH_4 and O_2, and the effect of Si/Al ratio of In-ZSM-5 were studied by FTIR *in situ*. The relation between the adsorbed species and catalytic activity in the SCR of NO_x to N_2 was also investigated. The adsorption of NO over this catalyst was performed at room temperature with pure NO followed by purging with vacuum. When NO was introduced to the samples, three peaks were observed by FTIR: 1622 and 1575 cm^{-1}, which can be assigned to adsorbed (ONO)- over InO^+ site and NO_2 over InO^+ site, respectively, and at 1680 cm^{-1} corresponding to NO_3^--H. Coadsorption of nitrogen monoxide, methane and oxygen at room temperature of the samples with Si/Al ratio of 17(a), 27(b) and 50(c), allowed us to determine that sample (b) has large amount of NO_2–InO^+ adsorbed species, which are the most important intermediates in the SCR of NO_x. The bands at 1575 and 1680 cm^{-1} are more intense in samples (a) and (c). When the coadsorption of the mixture was performed at 400 °C, we can see that the adsorbed species are larger in sample (b). Taking into account the catalytic performance of the catalysts and the PAC results obtained by us earlier, this last indium specie, only present in the sample with Si/Al = 27, should be associated with the catalytic active specie for the SCR of NO_x.

KEY WORDS: NO_x and methane adsorption; FTIR; intermediate species.

1. Introduction

The nitrogen oxides are undesired air pollutants since they are highly toxic and are one of the main reasons for the appearance of smog and acid rain [1]. That is why the NO_x removal from different waste gases is a central problem in modern industry. One of the most widely applied techniques for $deNO_x$-ing is the selective catalytic reduction (SCR) [2–6]. The reducing agent utilized in the actual commercial processes, when the gas source is stationary, is ammonia and the most used catalysts are V_2O_5-WO_3-TiO_2 or V_2O_5-MoO_3-TiO_2 [2–7]. However, the potential use of SCR for the purification of diesel exhaust gases has suggested the search for effective catalysts for the reduction of NO_x by hydrocarbons. Recently, successful SCR $deNO_x$ by different hydrocarbons has been reported on some copper, cobalt, nickel, rhodium, indium and gallium exchanged zeolites [8–10].

The three-way catalyst, which contains supported noble metals, transforms NO_x to N_2 by nonselective reduction with hydrocarbon residues, carbon monoxide and hydrogen. However, for diesel engines or gasoline engines operating under lean burn conditions, such catalysts cannot be applied because of the predominant direct oxidation of the reductants and a fast catalyst deactivation. There has been much effort to develop alternative catalysts for the SCR of NO_x with hydrocarbons in the presence of excess oxygen. In particular, zeolites modified with various redox components (transition and/or precious metals) have been investigated [11]. In the case of exhaust gases from diesel engines on ship and gas or diesel engines used for electricity generation, ammonia is employed for the selective reduction of NO_x on V, WO_x/TiO_2 and copper zeolite catalysts [12]. A substitution of ammonia by methane or light alkanes could become a promising alternative, in particular, with natural gas–fuelled engines. However, an SCR $deNO_x$ with methane requires catalysts activating the relatively inert methane molecule more selective than zeolites promoted with transition metal ions, being suitable for SCR by alkenes or higher alkanes. Gallium or indium supported on zeolites was discovered to be better suitable for CH_4-SCR than copper or iron, which favors the direct oxidation of CH_4 to CO_2 [13–15]. Ogura and colleagues [16] have reported that indium ion exchanged into H-ZSM-5 showed high catalytic activity for the CH_4-SCR, and the reduction of NO with CH_4 on the catalysts seems to proceed in two stages: firstly NO is oxidized to NO_2 and then NO_2 reacts with CH_4 into N_2. It has also been indicated [17] that NO oxidation on the acidic site of the zeolite is strongly retarded by water vapor. On the other hand, InO^+ site, which is ion exchanged in the zeolites [18], moderately catalyzed NO_2-CH_4 reaction even in the wet conditions. However, it has not been clear whether the adsorbed NO_2 on InO^+ sites is

* To whom correspondence should be addressed.
E-mail: oanunziata@scdt.frc.utn.edu.ar

1011-372X/03/1100–0019/0