Selective Catalytic Reduction of NO x by Hydrocarbons/Oxygenates. Application for the Control of NO x from the Regenerator of a Fluid Catalytic Cracking Pilot-Plant Unit

Selective Catalytic Reduction of NO$_x$ by Hydrocarbons/Oxygenates. Application for the Control of NO$_x$ from the Regenerator of a Fluid Catalytic Cracking Pilot-Plant Unit

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Rh supported on γ-alumina and unpromoted γ-alumina were used as catalysts for the selective catalytic reduction of NO by propene and methanol, respectively. Fixed-bed experiments were initially performed to study the catalytic activity using a feed that simulates flue gases. Emphasis was placed on the SO$_2$ effect on the NO reduction activity. A fluidized-bed deNO$_x$ unit was connected to the exit of the regenerator of a pilot-plant-scale fluid catalytic cracking unit aiming at the cleanup of this stream from gaseous pollutants. The deNO$_x$ catalysts and the reductants were the same as those in the fixed-bed experiments. More than 70% of the incoming NO was converted to N$_2$ when the deNO$_x$ unit was operated at the appropriate temperature range. Moreover, up to 90% of the inlet CO was oxidized to CO$_2$ at sufficiently high temperatures. At the same temperatures SO$_2$ was adsorbed by alumina.

Introduction

The fluid catalytic cracking unit (FCCU) is the part of a refinery that offers the greatest potential to increase its profitability. In the FCCU large molecules crack into smaller ones, and thus useful products such as gasoline, LPG, and diesel are produced. Cracking of heavy hydrocarbons takes place in the FCC reactor (riser). In the riser, coke is produced and deposited on the catalyst, typically a modified zeolite Y. The coked (spent) catalyst is regenerated in the FCCU regenerator, and the flue gases are released to the atmosphere. The gas emissions from the regenerator contain SO$_x$, NO, CO, CO$_2$, and O$_2$. Environmental restrictions in the SO$_x$ and CO emissions led to the development of additives and promoters for the FCC catalyst, which minimize the formation of these toxic species. The deSO$_x$ additives consist of metal oxides that adsorb SO$_x$ and form sulfates in the regenerator. The sulfates are reduced in the riser to H$_2$S. The CO emission problem was confronted by the development of CO promoters. Most of the FCCUs currently use platinum-based promoted catalysts. The use of these catalysts leads to the operation of the regenerator in a full combustion mode. Problems associated with the environmental pollution caused by FCCUs were extensively discussed in a review paper.[1]

The deSO$_x$ additives and the CO promoters are essentially oxidation catalysts that inevitably enhance the oxidation of coke nitrogen and, therefore, the NO formation. The oxidation of nitrogen-containing reaction intermediates over the oxidation sites and/or the ceasing of the NO reduction by CO are mentioned as reasons that lead to high NO emissions upon the addition of above additives.[1] The NO$_x$ emissions from the FCCU are typically in the range of 50–500 ppmv. Most of the NO$_x$ at the exit of the regenerator is in the NO form, while NO$_2$ and N$_2$O can also be formed in small quantities. The release of NO$_x$ to the atmosphere mainly derives from the FCC feed ("fuel NO$_x$"), while traces (<10 ppmv) of these oxides can be formed as a result of the N$_2$ oxidation ("thermal NO$_x$") and the reaction between radicals ("prompt NO$_x$") in the regenerator.[1,2] Zhao et al.[3] performed a nitrogen balance around the FCCU, and they postulated that less than 3% of the feed nitrogen formed NO$_x$ as a result of the oxidation of coke nitrogen, while the rest was released as N$_2$. The fraction of feed nitrogen that is converted to NO$_x$ varies from 3 to 25% in commercial regenerators, depending on the design and the operating conditions.

The commercially available, catalytic deNO$_x$ technologies aim at the conversion of NO$_x$ to N$_2$ by a reductant over a catalyst that is activated under the reaction conditions of the process. They can be classified according to the type of catalyst and the reductant as follows: (a) The selective catalytic reduction (SCR) of NO by ammonia is performed over vanadia–titania catalysts when the effluent stream is oxygen-rich.[4-7] This method is mainly applied for the cleanup of flue gases from stationary NO$_x$ sources (e.g., power stations). Problems associated with this technology are the NH$_3$ slip, the formation of solid waste accumulated in the process piping [(NH$_4$)$_2$SO$_4$ and (NH$_4$)HSO$_4$] and the expensive equipment for the storage and handling of NH$_3$. (b) The so-called "three-way catalysts" are currently employed for the simultaneous reduction of NO$_x$ and combustion of CO and unburned hydrocarbons from automotive exhausts. They consist of noble metal-based catalysts operating near the stoichiometric air–fuel combustion ratio, and they are deactivated by the presence of excess oxygen.[8-11] (c) The SCR of NO by hydrocarbons or oxygenates in the presence of excess oxygen offers an attractive way to convert NO to N$_2$, and it overcomes most of the problems associated with the above two processes.[4,12-17] However, comparison between the SCR of NO with hydrocarbons and NH$_3$ showed lower yields to nitrogen and activity rates in the former process than in the latter one for tail-end deNO$_x$ units.

Currently, the FCCU NO$_x$ emissions are not tightly regulated; however, the toxicity of these species and the tendency to zero or lower of any harmful emissions from

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refineries are expected to lead to strict regulations on the NO_x emissions. The increase in the NO_x emissions as a result of oxidation additives used in the FCC inventory and the foreseen restrictions directed Grace Davison to the development of a commercial deNO$_x$ additive[3] and Ashland Petroleum Co. to a novel two-stage regenerator that lowers the NO_x emissions.[18]

In the present work an alternative route for NO_x reduction is investigated. The proposed methodology is based on the SCR of NO_x by a hydrocarbon or an oxygenate using a tail-end deNO$_x$ unit. It must be noted that NO_x are produced in a refinery not only in the FCCU, which contributes to about 20% of the overall refinery NO_x, but also from furnaces, boilers, gas turbines, and flares. Consequently, all NO_x-containing flue gases can be directed to the entrance of a deNO$_x$ unit, where NO_x to N_2 reduction takes place. In the first part of this study, bench-scale experiments were carried out using a feed with composition similar to that of flue gases from a refinery. The fixed-bed experiments constituted the database for the design of the fluidized-bed experiments that simulate better the industrial operation conditions. In the second part of this work, flue gases produced in the regenerator of a pilot-plant FCCU were sent to a fluidized-bed reactor loaded with a deNO$_x$ catalyst to examine the NO_x reduction capacity of catalysts under realistic reaction conditions. Efficient NO_x reduction was measured in both the laboratory- and pilot-plant-scale experiments.

Experimental Section

Catalyst Preparation. Rh/alumina catalyst was prepared using γ-alumina extrudates, supplied by Engelhard (sample code: Al-3992 E $^1/_8$ in.), as the support. The extrudates were crushed and sieved to separate the particles of $180-355$ μm. An aqueous solution of rhodium chloride was prepared from the dilution of pure $RhCl_3 \cdot 3H_2O$ (38% Rh, Merck) for the catalyst formation. This solution was impregnated on the γ-alumina particles by applying the dry impregnation technique. Following the impregnation, the catalyst was dried at 120 °C for 2 h and then calcined at 600 °C for 9 h under air flow. Another γ-alumina sample, denoted as CK300, supplied by Akzo Chemie was also used in our experiments unpromoted. CK300 was calcined using the same conditions as in the Rh/alumina sample. In the beginning of each experiment, the catalyst was calcined at 500 °C under He flow for 1 h to desorb species adsorbed at ambient conditions.

Catalyst Characterization. The inductively coupled plasma and atomic emission spectroscopy (ICP/AES), X-ray photoelectron spectroscopy (XPS), H_2 chemisorption, N_2 adsorption, and mercury porosimetry techniques were used for the characterization of our samples. The ICP/AES analysis was carried out in a Plasma 400 (Perkin-Elmer) spectrometer, equipped with Cetac 6000AT+ ultrasonic nebulizer. The XPS spectrum of fresh and postreaction samples was obtained by a SPECS, system LHS10, spectrometer. Mg Kα radiation (1253.6 eV) was the X-ray source. The N_2 adsorption data measured in an Autosorb-1 (Quantachrome) apparatus were used in the calculation of the BET surface area. The pore structure of the sample was determined in an Autopore II (Micromeritics) porosimeter.

Fixed-Bed Reactor. The fixed-bed reactor, used for the prescreening of catalysts, consists of the feed gas system, a three-zone furnace controlled by proportional–integral–differential (PID) controllers, and the gas analysis system. All experiments took place in a quartz flow reactor of 2 cm o.d. The catalyst was placed in the middle of two quartz zones. Mass flow controllers were used to control the flow rate of gases of standard composition. The flow rate of the inlet gas was 1000 mL/min, and the reactor loading was 2 g ($W/F = 0.12$ g s cm^{-3}). In the experiments where C_3H_6 was employed as the reductant, the following gas mixtures were mixed to prepare the feed for the fixed-bed activity studies: 2% NO/He, 2% C_3H_6/He, 20% O_2/He, 1% SO_2/He, and pure He. In the experiments with methanol in the feed, helium was saturated with methanol at the appropriate temperature, and it was then mixed with the reactive gas mixture. We did not add water in the feed because we have previously shown[21] that it does not inhibit significantly the NO reduction over precious metals supported on alumina.

Samples from the exit gas stream were analyzed to determine the extent of the SCR reaction and to identify the gas products. The nitrogen oxides (NO and NO_2) were measured in a chemiluminescent NO_x analyzer (Thermo Environmental model 42H) and CO and CO_2 by a dual-channel NDIR analyzer (Rosemount model NGA 2000). For the SO_2 concentration measurements, a pulsed fluorescent analyzer (Thermo Electron model 40) was used. Gas samples were automatically injected in a Varian 3600 CX gas chromatograph (GC), equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. A molecular sieve 13X column was used for the separation of the inorganic species and a Haysep N column for the separation of the organic species. Gas mixtures of standard composition were used to calibrate the gas analysis system.

In the presentation of the experimental results, NO_x conversion is defined as the percentage (mole percent) of the inlet NO that is converted to N_2 and N_2O. C_3H_6, CO, and SO_2 conversions are defined as the percentage (mole percent) of the initial C_3H_6, CO, and SO_2 concentrations that is consumed, determined by the GC analysis and CO and SO_2 analyzers, respectively. Methanol was not detected by our GC; therefore, we used the carbon mass balance and the readings of the CO_x analyzers to estimate the methanol conversion in the fixed-bed experiments, where the feed contained no CO_x.

FCC Pilot-Plant Unit. The FCC pilot plant was designed and constructed at Chemical Process Engineering Research Institute (CPERI) based on the results from a cold model unit. The unit consists of a vertical reactor (riser) with 7.08 mm id, a fluidized-bed regenerator, the stripper, and the lift line. The feed is injected in the bottom of the riser, and it comes in contact with the catalyst flowing through a slide valve. The reactions take place in the riser, and the separation (stripping) of gases from the solid catalyst occurs in the stripper vessel. The solids flow through a second slide valve and, through the spent catalyst lift line, return to the reactor bottom following regeneration. The reaction products flowing through a heat exchanger are led to a stabilizer for the separation of liquid and gaseous products. The mixture of gasoline, light cycle oil (LCO), and heavy cycle oil (HCO) is obtained through the bottom of the stabilizer.

The catalyst regeneration takes place in the fluidized-bed regenerator reactor. The fluidization gas is air that is introduced from the base of the regenerator, and a mass flow controller controls its flow rate. The regen-

erator exit stream passes through cyclones that remove any entrained solids. The volumetric flow rates and the compositions of the flue and cracked gases are determined by two wet test meters and two GCs, respectively. An on-line oxygen analyzer always monitors the excess of oxygen to obtain good catalyst regeneration. A more detailed description of the pilot plant is presented elsewhere.[19,20] The pilot plant is fully automated, and the process control system of the unit is based on a special industrial control system. The control system collects the values of the input and drives the output signals.

The feed for the FCC unit was a gas oil supplied by a Greek refinery, while the catalyst was an E-cat from the same refinery. The exit of the regenerator had the following "typical" composition (dry basis): 4% O_2, 7% CO_2, 225 ppm CO, 235 ppm SO_2, 80 ppm NO_x, and N_2 balance.

Fluidized-Bed Reactor. The flue gas from the regenerator was the feed of a tail-end $deNO_x$ unit. The $deNO_x$ unit consisted of a fluidized-bed reactor connected with the same gas analysis system as in the fixed-bed experiments. The feed of the reactor was a mixture of 1000 mL/min derived from the exit of the regenerator and the appropriate flow of a reductant/He mixture so that the concentration of propylene or methanol was 500 and 1500 ppm, respectively. The reactor was loaded with 30 g of catalyst. The experimental results from the $deNO_x$ unit were collected and analyzed in the same way as in the fixed-bed experiments.

Results and Discussion

The compositional analysis of the catalyst using ICP/AES showed that Rh/alumina contained 1.86 ± 0.05 wt % Rh. Characterization of the catalyst using the XPS technique revealed that the fresh catalyst consists of Rh_2O_3, while reacted Rh/alumina consists of a mixture of reduced (ca. 10%) and fully oxidized Rh. We used the nitrogen adsorption technique to measure the surface area of the fresh catalyst. We estimated a surface area of 182 m^2/g by applying the BET method. Mercury porosimetry measurements showed that the overall pore volume of the catalyst was 0.5 cm^3/g and the pore diameters varied in the range of $0.005-0.02$ μm, mainly. The pore structure of the CK300 alumina was similar to that of the above sample. The physical properties of the catalysts were measured before and after the reaction. No significant pore structure changes due to the chemical reaction were noticed.

Catalyst Evaluation in the Fixed Bed. NO_x reduction experiments were carried out in our fixed-bed facility to evaluate the following candidate catalytic systems: Rh/alumina and unpromoted γ-alumina. We chose Rh/alumina as the $deNO_x$ catalyst of this work because it was shown as one of the most promising catalysts for its high $deNO_x$ activity when C_3H_6 is the reductant and its tolerance to the SO_2 presence in the feed.[21] On the other hand, Burch and co-workers[22] showed that γ-alumina is a catalyst of extraordinary $deNO_x$ activity when methanol is the reductant.

In Figure 1 we compare the NO_x conversion over Rh/alumina and alumina using a feed of 1000 ppmv NO, 1000 ppmv C_3H_6, or 1000 ppmv CH_3OH, 5% O_2, and He balance. Both systems exhibited typical conversion vs temperature curves: the NO_x conversion increased with the temperature up to the temperature where the
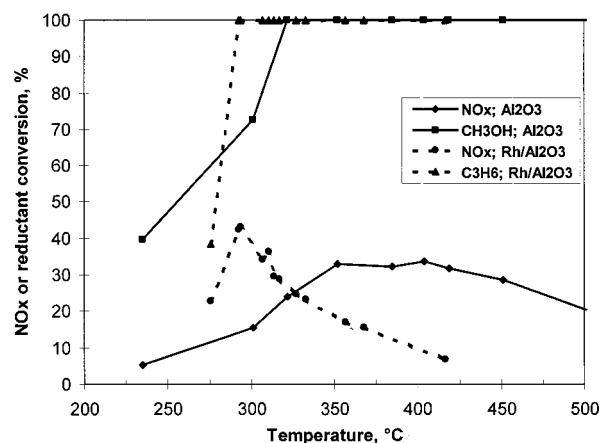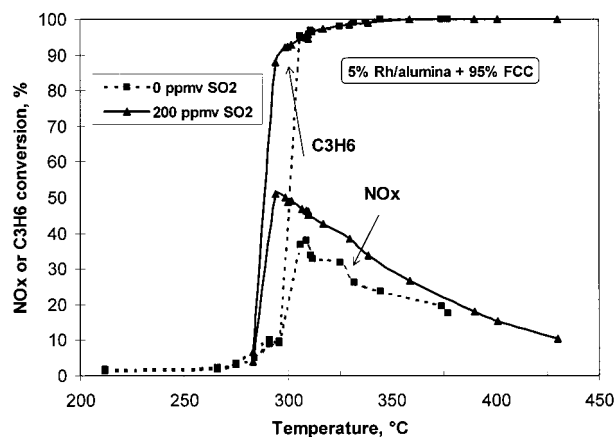

Figure 1. Fixed-bed results for the SCR of NO over Rh/alumina or γ-alumina. Loading: 2 g. Feed: 1000 ppmv NO, 1000 ppmv C_3H_6 or CH_3OH, 5% O_2, He balance.

reductant was completely consumed (T_{peak}). At higher temperatures the reductant was oxidized selectively by O_2 and was not available for the NO_x reduction. The Rh/alumina catalyst was activated at lower temperatures than alumina and exhibited higher reaction rates at this temperature range. Our previous studies[23] showed that unpromoted γ-alumina activates C_3H_6 at high temperatures (ca. 500 °C). Use of oxygenate (methanol in Figure 1) caused a significant decrease in T_{peak}. In Figure 1, we present experimental data for a reductant/nitric oxide mole ratio equal to 1. When the reductant/NO mole ratio was increased, higher NO_x conversions were measured. The methanol conversion vs temperature curve in the above figure is inaccurate because it does not account for the formation of dimethyl ether, a byproduct detected in the work of Burch et al.[22] Significant amounts of dimethyl ether are formed in the temperature range of 100–350 °C, according to the above work.

Besides the NO_x reduction in tail-end units, $deNO_x$ additives mixed with the FCC inventory can be used for the same purpose, i.e., the reduction of the NO_x emissions from the FCCU. Grace Davison developed commercial additives, which mixed with the FCC catalyst reduce by 50% the NO_x emissions from FCCU.[24] Based on this concept, a set of experiments was designed to test this possibility, though this problem is far more complex. Preliminary experimental results showed that the FCC catalyst was inactive for the NO_x reduction. Mechanical mixtures of the FCC catalyst (equilibrium Y-type zeolite) and the $deNO_x$ catalyst (Rh/alumina) were prepared to simulate the conditions in the FCCU. The efficient operation of the FCCU requires that the additive for the NO_x reduction is only a small percentage of the overall inventory. As a result, a mechanical mixture of 5:95 $deNO_x$ catalyst–FCC catalyst was loaded in our fixed-bed reactor, and its activity was measured using our standard reaction conditions. The $deNO_x$ catalyst was the same as that in Figure 1. In Figure 2 we present experimental data using the above loading for a feed of 1000 ppmv NO, 3000 ppmv C_3H_6, 0 or 200 ppmv SO_2, and 5% O_2 in He. The variation of the NO_x and C_3H_6 conversion with the temperature was similar to that of Figure 1, implying the competition of two chemical reactions: the NO_x reduction and the reductant oxidation. The presence of SO_2 in the feed decreased the activation temperature (T_{peak}) of Rh/alumina and caused a moderate increase in the NO_x

Figure 2. Fixed-bed results for the SCR of NO over a Rh/alumina−FCC blend. Loading: 0.1 g of Rh/alumina and 1.9 g of standard FCC catalyst. Feed: 1000 ppmv NO, 3000 ppmv C_3H_6, 0 or 200 ppmv SO_2, 5% O_2, He balance.
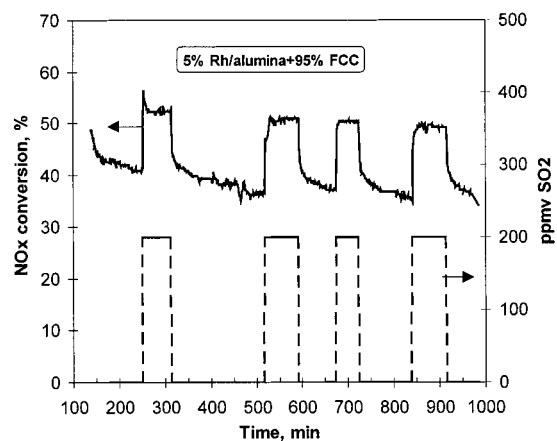

Figure 3. Effect of SO_2 addition in the feed over a Rh/alumina−FCC blend at 308 °C. Loading: 0.1 g of Rh/alumina and 1.9 g of standard FCC catalyst. Feed: 1000 ppmv NO, 3000 ppmv C_3H_6, 0 or 200 ppmv SO_2, 5% O_2, He balance.

conversion for a given temperature. This is in accordance with our previous results over pure Rh/alumina,[25] where two different reaction mechanisms were proposed for the NO_x reduction by C_3H_6 over Rh/alumina in the presence and absence of SO_2 in the feed.

The flue gases in the regenerator contain SO_2, a toxic gas that could deactivate catalysts permanently. Contrary to this, we noticed an activity enhancement over Rh/alumina mixed with the FCC catalyst as a result of the SO_2 presence in the feed (Figure 2). We further examined the effect of the SO_2 presence in the feed in the experiment shown in Figure 3, where fresh catalyst (5:95 Rh/alumina−FCC catalyst) was exposed to SO_2-free and SO_2-containing feeds successively at 308 °C. These results imply that activity changes due to the SO_2 presence are reversible.

The effect of sulfur species on the catalytic surface of γ-alumina was examined by Burch et al.[22] by the sulfation of alumina prior to the NO_x reduction experiment. The NO_x reduction by CH_3OH was slightly decreased as a result of the alumina presulfation. In conclusion, both catalytic systems of this study, Rh/alumina with C_3H_6 and alumina with CH_3OH reduced NO_x to N_2 in the presence of SO_2 traces in the feed.

Pilot-Plant-Scale Experiments. An attractive process for the cleanup of the regenerator flue gases is the SCR of NO_x by a hydrocarbon or an oxygenate. The NO_x
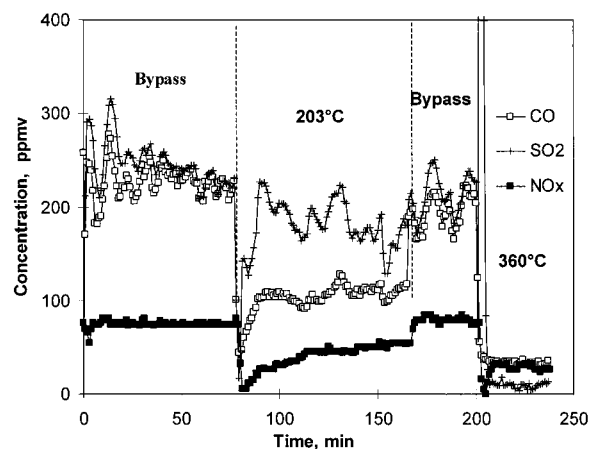
Figure 4. Variation of the NO_x, CO, and SO_2 concentrations with the reaction time at 203 and 360 °C. Loading: 30 g of Rh/alumina. Feed: 80 ppmv NO, 500 ppmv C_3H_6, 225 ppmv CO, 235 ppmv SO_2, 4% O_2, 7% CO_2, N_2 balance.

reduction can take place either in situ or in a tail-end $deNO_x$ unit. In the former case, the $deNO_x$ additive is mixed with the FCC catalyst and the reductant is added to the regenerator. There are, however, two important factors that should be taken into account: the effect of the additive to the yield of the gas-oil cracking and the modification in the configuration of the regenerator so that the stream of the reductant is added to the flue gases. The entrance of the reductant in the regenerator should be appropriately located so that the reductant is not burned before the NO_x reduction takes place. Another important parameter is the concentration of the $deNO_x$ catalyst in the regenerator because the $deNO_x$ additive is a small percentage of the FCC inventory. The above remarks imply delicate modifications of the regenerator that were beyond the scope of this study. Therefore, we performed $deNO_x$ experiments out in a tail-end unit connected with the exit of the regenerator. NO_x reduction in a tail-end unit overcomes the above problems, but it is expected that this solution has a higher NO_x reduction cost than that of the in situ method because it requires the construction of a new catalytic reactor unit.

The following catalysts were loaded in the fluidized-bed reactor connected with the exit of the FCC regenerator: Rh/alumina, a blend of 5% Rh/alumina with FCC catalyst and CK300 γ-alumina. In accordance with the fixed-bed tests, the Rh/alumina−FCC blend was loaded to roughly estimate the effect of a candidate $deNO_x$ additive in the FCC inventory during the in situ NO_x reduction. The reductant for the Rh/alumina catalyst was propene (500 ppmv), and that for the alumina catalyst was methanol (1500 ppmv). In the beginning of the fluidized-bed experiments, the flue gases from the regenerator were sent directly to the gas analysis system (bypass the reactor) to measure the composition of the inlet gas stream. Following that, this stream was sent to the fluidized-bed reactor, and the NO_x reduction experiment was started. We measured the NO_x reduction, CO oxidation, and SO_2 sorption rates at different temperatures over the above three loadings. Typical experimental data are shown in Figure 4 using the Rh/alumina catalyst and for two reaction temperatures. We present the variation of the NO_x, CO, and SO_2 concentrations with the reaction time before (bypass) and after (203 and 360 °C) the entrance of the flue gas in the $deNO_x$ unit. The same procedure was followed in the
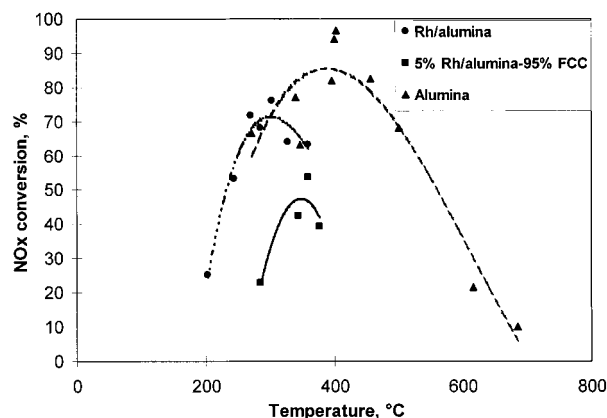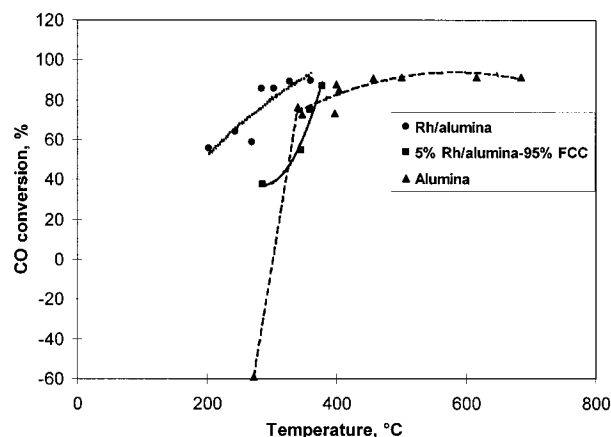
Figure 5. Variation of NO_x conversion with the reaction temperature in the fluidized-bed reactor. Loading: 30 g. Feed: 80 ppmv NO, 500 ppmv C_3H_6 or 1500 ppmv CH_3OH, 225 ppmv CO, 235 ppmv SO_2, 4% O_2, 7% CO_2, N_2 balance.

SCR experiments over the 5:95 Rh/alumina–FCC and the alumina catalysts at different temperatures. Our experimental data exhibited fluctuations in the CO and SO_2 concentrations larger than those of the NO_x concentration. The transient data of Figure 4 show that the NO_x curve was slower at reaching its steady-state value as compared to the CO and SO_2 curves at low temperatures, where adsorption is favored. In the following part of this study, experimental data will be presented for a given temperature at steady state.

In Figure 5 we present the variation of the NO_x conversion with the reaction temperature using the three loadings of this study after steady state was reached. All curves exhibited the same "volcano"-type dependence as that in the fixed-bed experiments (Figures 1 and 2). At low temperatures, the NO_x conversion increased with the temperature, while at higher temperatures, the reductant was not used efficiently for the SCR of the NO_x and it was oxidized to CO_2. High NO_x conversions were measured over both the Rh/alumina and alumina catalysts, while lower conversions were observed over the 5% blend of Rh/alumina with the FCC catalyst. Rh/alumina was active for the NO_x reduction at lower temperatures than the unpromoted alumina because the former catalyst activated C_3H_6 at lower temperatures than the latter one activated methanol. The alumina–methanol system showed higher NO_x conversions and a broader temperature range of significant activity than the Rh/alumina–propene system. Lower NO_x conversions were measured over Rh/alumina diluted in the FCC catalyst than those over the pure Rh/alumina, though a 20-fold decrease in the $deNO_x$ catalyst loading caused a 2-fold loss of activity only. This implies that the utilization of the catalyst in the experiment where pure Rh/alumina was loaded was limited with respect to that over the Rh/alumina–FCC blend.

Oxidation of CO was noticed during the fluidized-bed experiments over all of the catalysts of this study (Figure 6). All curves in this figure exhibit the same trend, i.e., a sharp initial increase of the CO oxidation up to a temperature where about 90% of the incoming CO was converted to CO_2. This temperature was 285, 378, and 400 °C over Rh/alumina, 5:95 Rh/alumina–FCC, and alumina, respectively. Pure Rh/alumina oxidized the CO at significantly lower temperatures than the other two samples. This implies that Rh enhances the CO oxidation by favoring the CO adsorption on the

Figure 6. Variation of CO conversion with the reaction temperature in the fluidized-bed reactor. Loading: 30 g. Feed: 80 ppmv NO, 500 ppmv C_3H_6 or 1500 ppmv CH_3OH, 225 ppmv CO, 235 ppmv SO_2, 4% O_2, 7% CO_2, N_2 balance.
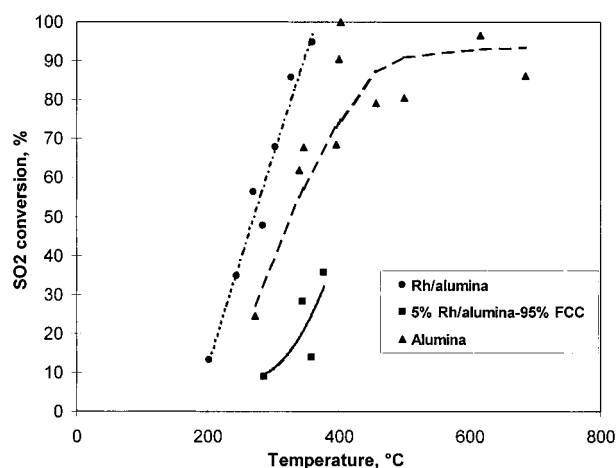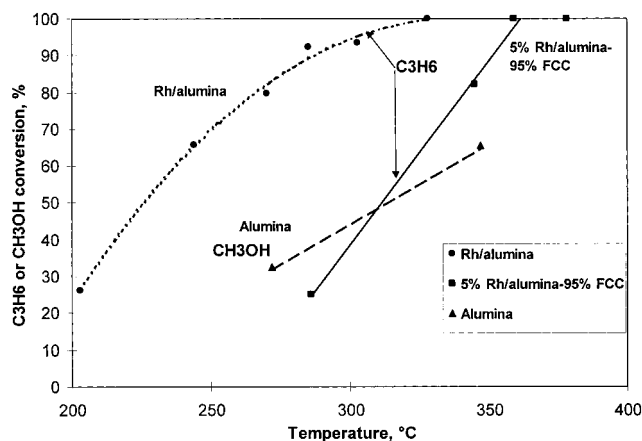

Figure 7. Variation of SO_2 conversion with the reaction temperature in the fluidized-bed reactor. Loading: 30 g. Feed: 80 ppmv NO, 500 ppmv C_3H_6 or 1500 ppmv CH_3OH, 225 ppmv CO, 235 ppmv SO_2, 4% O_2, 7% CO_2, N_2 balance.

metal sites, where oxidation can take place in addition to that occurring on the support. The CO formation over alumina at 272 °C (−58.9% CO conversion in Figure 6) was attributed to the conversion of CH_3OH to CO. Therefore, the alumina–methanol system can be used only at high temperatures, where both NO_x reduction and CO oxidation are favored.

The experimental data of Figure 7 show that SO_2 was removed from the feed over all samples of this study. This was attributed to the sulfation of alumina. Additives, the so-called "SO_2 adsorbers", are typically mixed with the FCC loading for the cleanup of flue gases from the SO_2. The sulfation proceeds faster over Rh/alumina than over alumina at a given temperature. We postulate that Rh/alumina enhances this reaction by the oxidation of SO_2 to SO_3. It is reported in related studies[26] that another precious metal, Pt, promotes the SO_2 oxidation, as well. Subsequently, SO_3 spills over alumina and forms aluminum sulfate. The low SO_2 conversions over the 5:95 Rh/alumina–FCC catalyst were attributed to the low alumina concentration.

Almost complete oxidation of propene was measured at temperatures higher than 280 °C when the reactor was loaded with Rh/alumina (Figure 8). At this temperature only one-fourth of the initial propene was consumed over a blend of 5% Rh/alumina with the FCC

Figure 8. Variation of reductant conversion with the reaction temperature in the fluidized-bed reactor. Loading: 30 g. Feed: 80 ppmv NO, 500 ppmv C_3H_6 or 1500 ppmv CH_3OH, 225 ppmv CO, 235 ppmv SO_2, 4% O_2, 7% CO_2, N_2 balance.

catalyst, while complete consumption of the reductant was noticed at ca. 350 °C. Our gas analysis system did not detect methanol; therefore, we applied a different procedure to calculate the methanol conversion. Gas samples were collected from the exit of the reactor in sampling bags when steady state was reached and then analyzed in a GC/mass spectrometer (MS) system. The gas analysis in the GC/MS revealed the formation of dimethyl ether from methanol over alumina. Dimethyl ether was detected only at low temperatures (<300 °C). The oxidation rates of methanol over alumina were lower than those of propene over Rh/alumina at a given temperature. As a result, the methanol could adequately reduce NO_x over alumina at high temperatures (Figure 5). The incomplete consumption of methanol and the formation of dimethyl ether at low temperatures render the use of the alumina−methanol system less attractive than that of Rh/alumina−propene, where no pollutants are emitted.

Conclusions

The cleanup of the flue gases from the regenerator of an FCCU has been investigated. Rh impregnated on γ-alumina and unpromoted γ-alumina were the catalysts for the SCR of NO_x by C_3H_6 or CH_3OH, respectively. Experimental results in a fixed-bed reactor signified that the use of the above catalysts with the appropriate reductants leads to NO_x reduction to N_2 even in the presence of SO_2 in the feed. Rh/alumina activated the reductant at significantly lower temperatures than the unpromoted alumina.

The removal of gaseous pollutants from the exit of a pilot-plant-scale FCCU operating under typical conditions was carried out in a deNO$_x$ unit connected to the exit of the regenerator. The loading of the fluidized-bed reactor was Rh/alumina, γ-alumina, and a 5% blend of Rh/alumina with FCC catalyst. The last sample was employed by aiming at the production of experimental data for the in situ NO_x reduction by the addition of a deNO$_x$ additive in the FCC inventory. Rh/alumina reduced more than 70% of the inlet NO_x to N_2 at ca. 300 °C. Alumina exhibited significant activity (max conversion 97%) at higher temperatures. Finally, the Rh/alumina−FCC blend converted about half of the incoming NO_x to N_2 in a relatively narrow temperature range (340−380 °C).

CO was efficiently (ca. 90%) oxidized to CO_2 over all three loadings used in this study. Rh impregnated on γ-alumina enhanced the CO oxidation. SO_2 was removed from the flue gases, and this was attributed to the alumina sulfation. In accordance with the CO oxidation data, Rh enhanced the SO_3 formation. Incomplete oxidation of methanol and formation of dimethyl ether hinder the potential use of alumina−methanol in tail-end deNO$_x$ units. Efficient reduction of the NO_x emitted from the regenerator by propene accompanied by CO oxidation and SO_2 adsorption was observed over Rh/alumina loaded in a fluidized-bed reactor. These results imply the potential of this system to be used in flue gas treatment units.

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