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Pt-loaded zeolites for reducing exhaust gas emissions at low temperatures and in lean conditions

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Abstract

In this study, pure and platinum-loaded zeolites, ZSM-5, Beta, zeolite Y and Ferrierite, were examined for the reduction of NO with propene in lean conditions and at low temperatures. The studies were carried out by utilising the FT-IR technique both in determination of surface species as well as concentrations in the gas flow at reactor outlet. The maximum in the intermediate formation can be observed at the light-off temperatures over all studied catalyst materials. The maximum conversions of NO were reached with 1 wt% Pt-loaded Beta and Y zeolites in excess oxygen. The lowest light-off temperatures of NO as well as propene can be detected also with Beta and Y zeolite catalysts.

Keywords: Activity; Propene; FT-IR; ZSM-5; Beta; Y zeolite; Ferrierite; HC–SCR; Platinum

1. Introduction

Zeolites and other microporous materials have been studied widely to find new catalysts for lean and diesel engines' exhaust gas purification. The large oxygen excess and lower temperature in the burning process make the mitigation of NO species from the exhaust gas more difficult with traditional three-way catalysts (TWC) [1]. Different metals (e.g. Cu, Co, Ga) and platinum group metals (PGM) have been tested on different zeolite materials.

Platinum-based zeolite materials have been found to be effective in the reduction of NO_x emissions and, at the same time, in the oxidation of unburned hydrocarbons and CO in oxygen-rich conditions [2–4]. The well-known undesired property of Pt catalysts is their tendency to convert NO to NO_2 and N_2O [5]. The formed NO_2 can also enhance other reactions like hydrocarbon oxidation and selective catalytic reduction by hydrocarbons (HC–SCR). However, Pt-loaded ZSM-5 has been found to show a stable performance in the presence of water vapour [6].

In this work, NO reduction by propene in the presence of excess oxygen over 1 wt% Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolites were studied. The catalytic activities and surface intermediate formation on catalyst surfaces have been examined in low temperature exhaust gas purification in lean conditions to understand the behaviour of the zeolite catalyst in diminishing the cold start emissions.

2. Experimental

2.1. Catalyst preparation and characterization

The studied catalysts were zeolites ZSM-5 (Z), Beta (B), Y (Y), and Ferrierite (F). The SiO_2/Al_2O_3 ratios were 29, 150, 80, and 20, respectively. Platinum was loaded to the zeolite materials by impregnation as described in [3]. Pt loading was 1 wt% on all zeolite materials except on Ferrierite (0.8 wt%). The desired 1 wt% loading of Ferrierite was not attained due to the used preparation method. The specific surface areas and pore sizes were measured by nitrogen adsorption at −196 °C with ASAP 2020 from Micromeritics.

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2.2. Activity measurements

The activities of catalysts were studied by using FT-IR as the analytical technique for gas compositions. The catalysts samples (0.1 g) in the form of powder mixed with quartz sand (~1 g) were inserted into the tubular (Ø 9 mm) quartz reactor. Quartz sand was set into the tube to keep the space velocity constant. The reactor was sealed by quartz wool. The samples were heated under N_2 flow from room temperature to 500 °C and oxidized by 5% O_2/N_2 at 500 °C for 15 min. Then the samples were cooled down to room temperature under oxygen flow and purged by N_2 to remove the excess oxygen from the reactor. The reaction gas mixture was inserted into the reactor and the activity measurements were done in the temperature range from room temperature to 550 °C by increasing temperature with the rate of 10 °C min^{-1}. The reaction gas mixture contained 1000 ppm NO, 1000 ppm propene, and 5% oxygen balanced by N_2. The total flow rate was 1000 $\mathrm{cm}^3\,\mathrm{min}^{-1}$, which corresponds to the space velocity of 26,500 h^{-1}. The temperature was measured inside the catalyst bed. The outlet concentrations of propene, NO, N_2O, NO_2, CO, and CO_2 were measured by GASMET$^{\mathrm{TM}}$ FT-IR analyzer.

2.3. Surface intermediates

An in situ DRIFT spectrometer, Perkin-Elmer 1760X with a heated reaction chamber, was used to examine the surface intermediates [3]. The pre-treatment was started by heating the powder zeolite catalyst samples under vacuum to 400 °C. Oxidation was done by 5% O_2/Ar at 400 °C and then the samples were cooled to room temperature under an oxidizing atmosphere. Finally, the samples were evacuated at room temperature for 20 min to remove the excess oxygen from the reaction chamber and to record the background spectrum. The vibrations of adsorbed surface components were detected in the range of 4000–800 cm^{-1}. The resolution of the measurements was 4 cm^{-1}, and the number of scans was 50, except in the case of Y zeolite when the number of scans was 100. The measurements were done at 25, 100, 150, 200, 250, 300, 350, and 400 °C. Propene (1000 ppm) adsorption in the presence of oxygen (5%), nitric oxide (1000 ppm), or both (1000 ppm NO + 5% O_2) was measured under a continuous reaction gas flow (150 $\mathrm{cm}^3\,\mathrm{min}^{-1}$). IR beam goes through the laboratory air, therefore, the band caused by carbon dioxide (at 2360 cm^{-1}) was not analysed. The wavenumbers between 1400 and 1300 cm^{-1} were omitted from analysis because of the strong vibration caused by the zeolite framework.

3. Results

3.1. Catalyst characterisation

The specific surface areas (Brunauer–Emmett–Teller, BET) of Pt-loaded zeolite catalysts were 349 $\mathrm{m}^2\,\mathrm{g}^{-1}$ (1 wt% Pt-ZSM-5), 485 $\mathrm{m}^2\,\mathrm{g}^{-1}$ (1 wt% Pt-Beta), 503 $\mathrm{m}^2\,\mathrm{g}^{-1}$ (1 wt% Pt-Y), and 289 $\mathrm{m}^2\,\mathrm{g}^{-1}$ (0.8 wt% Pt-Ferrierite). These measurements are in a good correlation with the literature [7,8]. The measured pore widths of studied Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolites were 2.8, 7.6, 3.7, and 2.7 nm, respectively, and the pore volumes were 0.25, 0.92, 0.47, and 0.20 $\mathrm{cm}^3\,\mathrm{g}^{-1}$, respectively. In the case of highly microporous materials, the numerical values determined by N_2 adsorption can have small errors [9]. In general, the values are in good correlation with the literature data and with the data obtained by the same method but another apparatus. Platinum dispersion was measured to be 11.6, 11.8, 12.1, and 33.3% over Pt-loaded ZSM-5, Beta, Y zeolite, and Ferrierite, respectively.

3.2. Activity measurements

Conversions of NO and C_3H_6, and light-off temperatures of the Pt-loaded zeolite catalysts in lean conditions are shown in Fig. 1. Propene reached 50% conversion over all of the studied catalysts at temperatures from 200 to 253 °C. The lowest light-off temperature of propene (198 °C) can be measured by Pt-Y zeolite catalyst. The light-off temperatures of Pt-loaded catalysts increased in the following order: Pt-Y ≤ Pt-Beta < Pt-Ferrierite < Pt-ZSM-5. The propene conversion above the light-off temperature was better than 99% with all studied catalysts. The formation of CO_2 from propene was detected to be at the maxima at the light-off

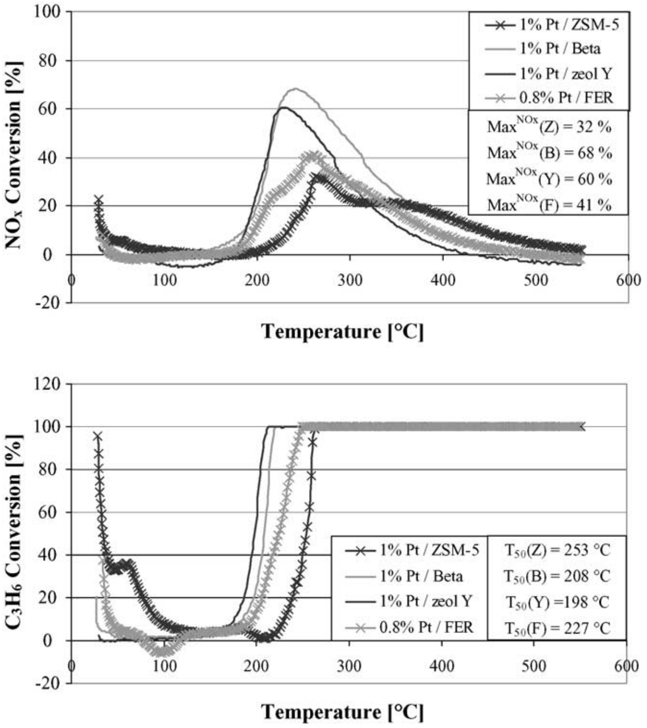

Fig. 1. NO and C_3H_6 conversions and light-off temperatures of Pt-loaded zeolites with a reaction gas mixture of 1000 ppm NO, 1000 ppm propene, and 5% oxygen balanced by N_2.

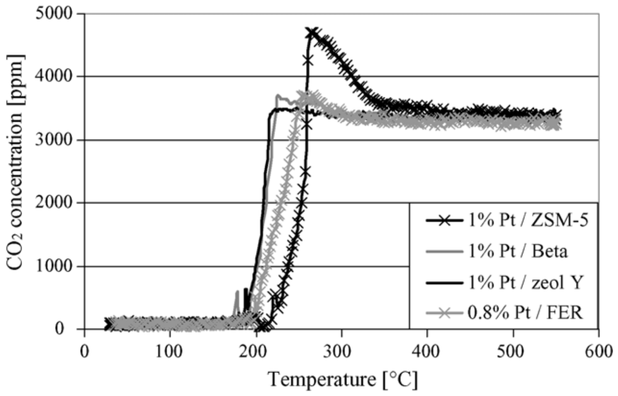

Fig. 2. CO_2 formation over Pt-loaded zeolites ZSM-5, Beta, Y, and Ferrierite. Inlet gas composition: 1000 ppm NO, 1000 ppm C_3H_6, and 5% O_2, N_2 as balance. The experimental error is 10% at the maximum at high temperatures.

temperature of each catalyst. (Fig. 2) The Pt-ZSM-5 zeolite seems to produce CO_2 just above the light-off temperature, which is most possibly caused by the oxidation of adsorbed C_3H_6 species on the catalyst surface. The highest adsorption of propene at temperatures below 70 °C was detected with the Pt-ZSM-5 catalyst. With the other studied samples, the oxidation of the carbon containing surface species to CO_2 was not detected to be as strong, while more CO_2, than can be formed from propene were measured with all catalysts after the light-off temperature was reached. The results correlate well with the results of Furusawa et al. [10].

NO conversions were observed to increase as a function of temperature up to 220–270 °C. The maximum conversions of NO_x over Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolites were achieved at 267, 245, 232, and 262 °C, respectively. At higher temperatures, the conversions decreased rapidly. This is due to the favourable propene oxidation by O_2 instead of NO [11,12]. NO_x conversion did not exceed 50% with Pt-ZSM-5 and Pt-Ferrierite catalysts, while the best conversions were observed over Pt-Beta and Pt-Y zeolites. The maximum conversion of NO_x was almost 70% with Pt-Beta and 60% with Pt-Y. NO started to react at above 150 °C over all catalysts except Pt-ZSM-5, which had an ignition temperature at 200 °C. The maximum NO conversions were measured just above the temperature where propene had reached the conversion over 99%. The conversion remained quite stable in the wide temperature area and also at temperatures above 350 °C with the 1 wt% Pt-ZSM-5 catalyst.

3.3. Surface intermediates

In Fig. 3, the DRIFT spectra of surface intermediate formation over pure (Fig. 3a) and platinum-loaded (Fig. 3b) zeolites are presented at temperatures of 100 and 200 °C with a $NO + C_3H_6 + O_2$ reaction gas mixture. The amounts of formed reaction intermediates and adsorbed hydrocarbon compounds on the catalyst surface were found to be in maximum near the light-off temperature when the reaction gas mixture contained propene and NO. The adsorption of reactants was almost undetectable on zeolite Y.

Propene adsorption can be detected as CH_x-surface species at 3100–2500 cm^{-1}. Propene adsorption increased when the zeolite material contained platinum. This can be detected with all studied zeolite materials. Nitrate and nitrite species on ZSM-5, Pt-ZSM-5, and Pt-Beta can be observed at 1295 and 1312 cm^{-1}. The band at 1830 cm^{-1} can probably be assigned to adsorbed NO on oxidised platinum. Weak band at 1654 cm^{-1} on all Pt-loaded zeolite catalysts can be assigned to the ν(C=C) vibration [13]. The band at 1595 cm^{-1} is assigned as COO^- or CO_2^- caused by the adsorbed acetates or formates [13]. Bands at 1458 and 1414 cm^{-1} on zeolite catalysts can be proposed to be cause by the propenal oxime intermediate formed in reaction between NO and propene [14].

By increasing the temperature to 200 °C (Fig. 3), the propene adsorption can be seen to increase significantly over Beta and Pt-Beta zeolites. With other zeolite catalysts, the propene adsorption does not increase at the same rate. Intermediate formation such as nitrate and nitrite species as well as CO on Pt-Ferrierite can also be detected to be more intensive at higher temperatures near the light-off temperature. These observations are in good agreement with the activity experiments.

4. Discussion

The most intensive adsorption of propene and NO on the surface can be detected with zeolites ZSM-5, Pt-ZSM-5, Beta, and Pt-Beta at low temperatures. The intensive propene adsorption on Pt-ZSM-5 can be due to a low silica-alumina ratio ($SiO_2/Al_2O_3 = 29$). The adsorbed propene was detected to convert fast to CO_2 over Pt-ZSM-5 at light-off temperature, and CO_2 overlapping was measured. However, propene light-off temperature initiates at the highest temperature (230–250 °C) on Pt-ZSM-5 catalyst, while with Pt-Beta and Pt-Y zeolites the light-off temperature initiation was the lowest (200–210 °C). Beta ($SiO_2/Al_2O_3 = 150$) and Y (80) are more hydrophobic and, therefore, should have a tendency to more strongly adsorb hydrocarbons. Adsorbed NO is assumed to react with excess oxygen and the reactions produce surface nitrate and nitrite species. The results of simultaneous NO and propene adsorption are in agreement with studies by Garetto et al. [15] and Guo et al. [16].

The adsorption on the Y zeolite is rather different than on the other studied catalysts. The possible reason for low adsorption capacity can be due to the zeolite framework structure and the high SiO_2/Al_2O_3 ratio of Y zeolite. The ion exchange ratio (IER) of platinum on Y zeolite is also high, which can block the adsorption on Al sites. To find the right explanation for this phenomenon, further studies are needed, e.g. study on the character of adsorption complexes and number of adsorption sites.

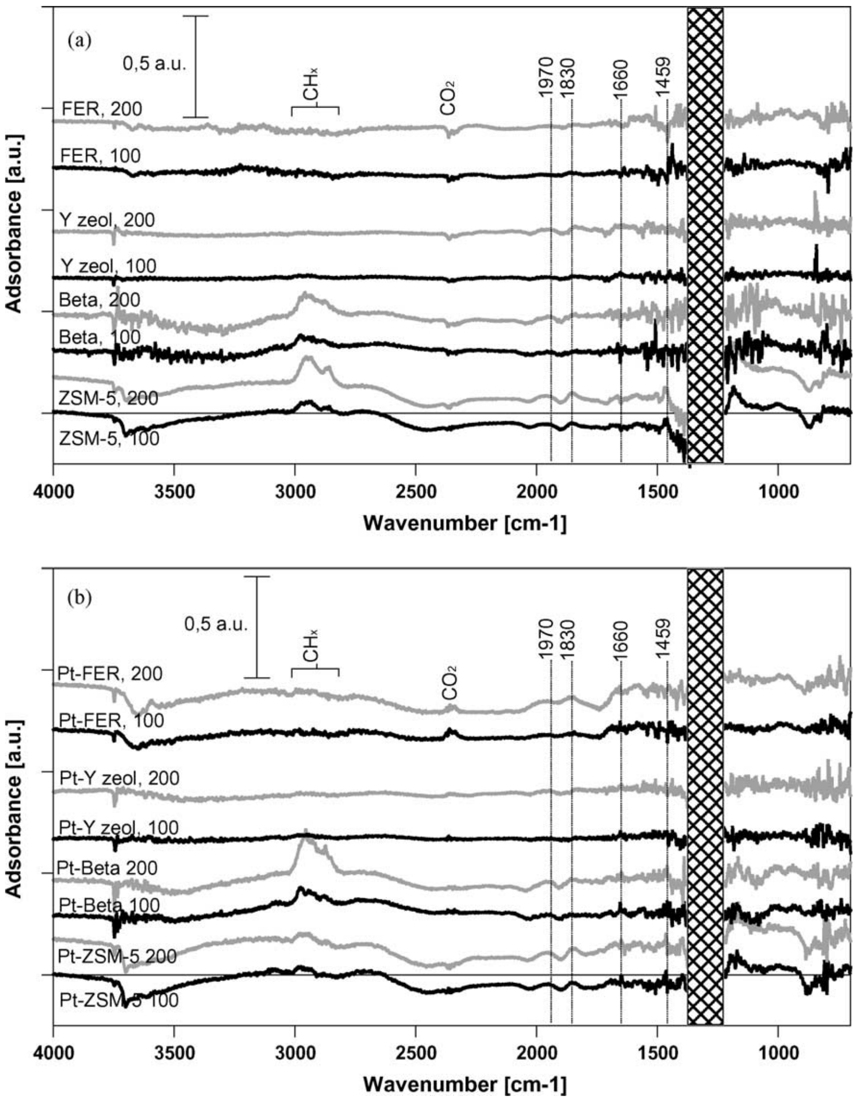

Fig. 3. DRIFT spectra of (a) parent zeolites and (b) Pt-loaded zeolites at 100 and 200 °C (gas mixture of 1000 ppm NO, 1000 ppm C_3H_6, and 5% O_2, Ar as balance).

As well, the small pore size (2.7 nm) of the Ferrierite zeolite could be one of the reasons for the low adsorption activity as discussed in our earlier studies [3]. The larger pores of Beta and Y with inter-connected pores can be features, which have a role in the detected HC activities and selectivities.

A reaction mechanism has been proposed, which is based on NO decomposition and hydrocarbon oxidation [17]. This is not in agreement with the NO_x surface intermediate detections, because in these compounds, a critical step is the breakage of N–O bonding before NO reduction could proceed. The most possible reaction route is the NO and propene adsorption to the support and platinum particles followed by the oxidation of the adsorbed species with excess oxygen to partially oxidized hydrocarbons, and nitrate and nitrite species. The oxygenated hydrocarbon intermediates on the surface react with gaseous nitric oxide as well with surface nitrites and nitrates to CO and CO_2. Excess oxygen in the reaction gas mixture can strongly enhance the formation of surface intermediate species (e.g. NO_3^-, NO_2^-, and $C_xH_yO_z$). Above the light-off temperature, propene was oxidized most probably purely by oxygen, which as a competing reaction decreases the NO conversion.

5. Conclusions

Y and Beta zeolites with 1 wt% Pt-loading have the lowest light-off temperatures, which provide the guidelines to develop catalysts based on zeolite materials for low temperature exhaust gas catalysis in lean conditions. The highest NO reduction by propene can be detected with Pt-Y and Pt-Beta zeolite catalysts. According to the results, zeolites Pt-Y and Pt-Beta with high Si/Al_2 ratio have been found to be the most promising and the most active catalysts for the simultaneous reduction of NO and propene in lean conditions.

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