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Selective catalytic reduction of NO_x with propylene in the presence of oxygen over Co–Pt promoted H-MFI and HY

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Abstract

Kinetic and in situ spectroscopic studies of Co–Pt/MFI and Co–Pt/HY catalysts for the selective reduction of NO_x with propylene in the presence of oxygen were carried out. The results of catalytic tests of Co–Pt/MFI showed that the addition of Pt to Co based catalyst improved the activity, but a small increase in selectivity to N_2O (15–20%) was observed. In the case of Co–Pt/HY catalyst, the addition of Pt improved the activity more significantly and however, a larger increase in selectivity to N_2O (6–72%) was obtained. It was also found from the results of FT-IR studies of Co–Pt/MFI that the reduction of NO to N_2 was as follows: firstly the oxidation of NO to NO_2 occurred over metallic Pt and NO_2 forms Co–NO_2, Co–ONO, and/or Co–ONO_2; secondly, the partial oxidation of C_3H_6 was happened over Brønsted acid sites and the reaction of NO_2 formed on Co sites with partial oxidized C_3H_6 produced organo-nitro species. These species were dehydrated and isomerized to form isocyanate. Finally, [NCO] type intermediates react with NO from gas phase to selectively yield N_2.

Keywords: deNO_x; SCR; C_3H_6; Co; Pt; H-MFI; HY

1. Introduction

Nitrogen oxides (NO_x) are byproducts of energy creation. They are hazardous to the environment we live in, causing problems such as smog, acid rain and contribute to global warming. Current strategies attempting at minimizing of fuel usage and emissions of CO_2 prompt use of lean (air rich) combustion. Thus, deNO_x strategies target NO_x to be reduced to N_2 in the presence of excess oxygen. Improvement in combustion technology is one of the options, but alone is not sufficient to meet legislation. Thus interest in developing new catalytic processes for the reduction of NO_x under conditions of excess oxygen such as needed for stationary sources, diesel engines and lean burn Otto engine is currently very high. Catalytic options (SCR; selective catalytic reduction) available include using reduction of NO_x by ammonia, however, the technology, though practiced extensively now, is not free of problems. The use of hydrocarbons (HC) as an alternative reductant is being intensively investigated currently and a large number of catalysts based on zeolites have been proposed [1–3].

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Even though HC-SCR is a promising method and was subject to intensive research during the last years, there are still many problems to be overcome. For instance, sensitivity towards water and sulfur compounds has been found to be prohibitive to a breakthrough. Pt based catalysts are very active and durable, however, during NO reduction they yield large amounts of N_2O [4,5]. Information available in the literature indicates that Co/ZSM5 catalysts are very selective in converting NO to N_2 [6,7], and they are also active in the reduction of N_2O to N_2 [8,9]. It was our intention to prepare a multi-component catalyst that will preserve the desired characteristics of the individual components with minimizing their negative aspects. In this paper, we describe a zeolite based catalyst, Co–Pt/MFI that is sulfur and water tolerant and considerably extends the limit of operation towards lower temperature. A Co–Pt/HY catalyst was also studied to investigate the influence of the zeolite type on the catalytic performances for HC-SCR. The roles of Pt and Co for the elementary steps of NO_x reduction and the implications for catalyst design are discussed.

2. Experimental

2.1. Catalysts preparation

Co/MFI (Si/Al = 38.5) catalyst was prepared by solid state ion exchange (SSIE) method. The method for preparation of Co/MFI catalyst is as follows: 5 g of NH_4-MFI and the required amount of $CoCl_2{\cdot}6H_2O$ were grinded to obtain mixture. The resulting mixture was heated to 773 K at $2\,K\,min^{-1}$ in He and was maintained at same temperature for 12 h. During the heating cycle, the sample was maintained for 3 h near the melting point (353 K) and boiling point (378 K) of $CoCl_2$. After this procedure, the catalyst was washed with de-ionized water and dried in air at 393 K for 8 h [10].

In the case of Co–Pt/MFI (Si/Al = 38.5) catalysts, a typical preparation procedure is as follows: 5 g of NH_4-MFI was thoroughly grinded with the required amounts of $CoCl_2{\cdot}6H_2O$ and $PtCl_4$. The resulting mixture was heated to 773 K at $2\,K\,min^{-1}$ in He and was maintained at this temperature for 12 h. During the heating cycle, the sample was maintained for 3 h near the melting point (353 K) and boiling point (378 K) of $CoCl_2$ and then near the melting point and decomposition point (643 K) of $PtCl_4$ for 3 h to allow slow diffusion of the metal ion into the zeolites [11].

In the case of the catalysts based on HY zeolites, the preparation of catalysts was carried out by conventional liquid state ion exchange (LSIE) method. The Co–Pt/HY (Si/Al = 2.55) catalysts were prepared by ion exchange of NH_4-Y with $Co(NO_3)_2$ and $Pt(NH_3)_4(OH)_2$ solutions. Both $Co(NO_3)_2$ and $Pt(NH_3)_4(OH)_2$ solutions used here were adjusted to required concentrations. The details are as follows: 5 g of NH_4-Y and $Co(NO_3)_2$ solution were stirred at room temperature for 8 h, then the solution of $Pt(NH_3)_4(OH)_2$ was introduced drop wise at room temperature. After introduction of platinum, the solution was maintained at room temperature with constant stirring for another 2 h, the temperature was then raised to 353 K and maintained at this point until all water gets evaporate. The solid was mounted on filter, rinsed with water and dried at 383 K overnight [12].

2.2. Characterization of catalysts

The IR measurements were performed in situ on a BRUKER IFS 88 FTIR spectrometer (resolution of $4\,cm^{-1}$) in a continuous gas flow mode using the transmission–absorption technique. The IR cell was equipped with a heatable sample holder and CaF_2 windows. The catalyst was pressed into a self-supporting wafer (2 mg) and activated in flowing He at 773 K for 1 h. The ion exchange level of acidic sites (–OH) was calculated by comparing spectra after normalizing the spectra using peaks for zeolite lattice vibrations [13]. AAS or XRF measurements were performed for determining the loading of Co, Pt, and Si/Al ratios for all catalysts [11,12].

A transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) was used to obtain the size of Pt particle (TEM) and to observe the location of Pt and Co species (TEM, EDX) for the selected sample areas. The catalyst samples were coated with carbon and supported on copper grid prior to the TEM analysis [11,12].

X-ray absorption spectra were measured at the SRS in Daresbury on beamlines 9.2 and 8.1. The spectra were collected in transmission mode, with a Si (2 2 0) monochromator detuned to 50% on beamline 9.2 and

70% on beamline 8.1, to remove high energy harmonies present in the beam. The analysis was carried out using standard analysis procedures [14]. The EXAFS spectra were collected at 170 K in flowing He. The catalysts were heated to 773 K in flowing He or H_2 to effect activation or reduction and XAFS spectra were taken during these processes.

2.3. Catalytic tests

The reactor used was U-shaped quartz tube with an internal diameter of 6 mm and the catalyst bed was supported by means of two plugs of quartz wool. The catalyst was palletized, crushed, and sieved to 0.3–0.6 mm before use. For testing, the catalyst was activated in situ by heating to 773 K for 1 h in flowing He. After activation, the flow was switched to a mixture of ($NO/O_2/C_3H_6/He$). The typical reactant gas mixture consisted of NO (0.1%), C_3H_6 (0.1, 0.2%), O_2 (5%) balancing with He to 100%. A total gas flow of 100 ml min^{-1} was passed through varying amounts of catalysts resulting in GHSV's between 15 000 and 45 000 h^{-1}, based on the apparent bulk density of the catalyst bed (0.5 g cm^{-3}). The temperature of the catalyst bed was controlled by a Eurotherm 903P temperature controller, the gas flow by four Brooks mass flow controllers. The products were analyzed simultaneously by gas chromatography (Varian 3700 equipped with a TCD detector and a molecular sieve 5A column for separation of N_2, O_2 and CO and porapak Q column for N_2O, C_3H_6, and CO_2 analysis) and a chemiluminescence $NO–NO_2–NO_x$ analyzer (Thermo Environmental Instrument, Model 42C, NO, NO_2 analysis).

2.4. In situ IR measurements

IR measurements were carried out as the same procedures as mentioned in Section 2.2. All IR spectra were recorded in the range from 3800 to 1300 cm^{-1} with a time resolution of 30 s. Difference spectra were obtained by subtracting the spectrum of the catalyst from the spectra measured during the reaction. Both spectra were collected at the same temperature. After activation of catalyst, the following series of experiments were performed: (i) C_3H_6 at 623 K; Co–Pt/MFI was heated to 623 K and a mixture of C_3H_6 (0.2%) in He was passed over the catalyst at rate of 10 ml min^{-1}. Spectra were collected every 2 min for 30 min. (ii) NO at 313 K; Co–Pt/MFI was heated to 313 K and NO (0.1%) in He was passed over the catalyst at rate of 10 ml min^{-1}. Spectra were recorded every 10 min for 1 h. (iii) NO and O_2 at 473 K; after (ii), the catalyst was heated to 473 K. The flow was switched to NO (0.1%), O_2 (5%) in He. Spectra were recorded every 10 min for 1 h and subsequently purged with O_2 (5%) at same temperature for 1 h. In this case, spectra were also recorded every 10 min for 1 h. (iv) NO, C_3H_6, and O_2 between 473 and 773 K. The catalyst was heated to 473 K in He. Then, a mixture of NO (0.1%), C_3H_6 (0.2%), and O_2 (5%) in He was passed over the catalyst. Spectra were recorded every 30 s for 10 min and then at intervals of 30 min. Subsequently, the temperature was increased linearly from 473 to 773 K and the IR spectra were measured at temperature intervals of 50 K.

3. Results

3.1. Characterization of Co and Pt catalysts based on H-MFI and HY

The results of characterization of Co–Pt/MFI have already been reported in detail elsewhere [11], thus only a summary of the results are mentioned in this paper. The result of high resolution TEM–EDX measurement of Co–Pt/MFI catalyst showed the three zones in the catalyst: (i) areas with large Co particles (maximal diameter approximately 5 nm), (ii) areas with highly dispersed Co, and (iii) areas with particles containing both Co and Pt. The results of EXAFS and XANES measurements for Co–Pt/MFI after activation in He showed that Pt was present in a metallic state and Co in an oxide state. It was also found from IR measurements that approximately 50% of Brønsted acid sites were exchanged with Co^{2+} and Pt^{4+} estimated by normalizing the spectra of H-MFI and Co–Pt/MFI catalysts for the lattice overtones at 2000 and 1880 cm^{-1} [13].

The results of characterization for Co–Pt/HY catalyst have been reported elsewhere [12]. The results of IR and TEM–EDX measurements showed that part of the Co were exchanged with Brønsted acid sites and exist as Co ions, however, most of Co exist as a Co oxide. Pt is present as metallic or partially reduced

Table 1
Catalytic performances of Co and Pt promoted MFI (Si/Al = 38.5) catalysts for the selective reduction of NO (0.1%) with propylene (0.2%) in the presence of oxygen (5%) at 623 K

Catalysts	Co (wt.%)	Pt (wt.%)	Rates of NO conversion[a,b] (mol s^{-1} g^{-1})	Rates of C_3H_6 conversion[a,b] (mol s^{-1} g^{-1})	Selectivity[b] (%)		
					N_2	N_2O	NO_2
H/MFI	–	–	0.08×10^{-7}	0.06×10^{-6}	100[c]	0	0
Pt/MFI	–	0.11	3.52×10^{-7}	1.03×10^{-6}	45	55	0
Co/MFI	2.8	–	1.28×10^{-7}	0.63×10^{-6}	85	15	0
Co–Pt/MFI	2.74	0.13	2.36×10^{-7}	1.04×10^{-6}	80	20	0

[a] Differential rates of conversion.

[b] At 30% NO conversion (by varying the contact time). Product NO_2 is observed only when C_3H_6 conversion reaches 100%.

[c] At 2% NO conversion.

Pt oxide particles, the size of which is approximately 4 nm.

3.2. Catalytic reduction of NO with C_3H_6 over MFI based catalysts

Table 1 summarizes the kinetic data for Co and Pt catalysts based on MFI for the selective reduction of NO (0.1%) with propylene (0.2%) in the presence of excess oxygen (5%) at 623 K. The rates of NO and propylene conversions were obtained at identical conditions for all catalysts and normalized to amounts of catalyst. It can be seen from Table 1 that Co/MFI showed the lowest activity (rates for NO conversion and C_3H_6 conversion) and highest selectivity to N_2 among the catalysts promoted by metals and Pt/MFI on the contrary showed high activity, but low selectivity to N_2. The addition of Pt to Co based catalyst improved the activity, however, resulted in a small increase in selectivity to N_2O (15–20%).

3.3. IR studies of the surface species during selective reduction of NO with propylene over Co–Pt/MFI

Fig. 1 shows the infrared spectra for Co–Pt/MFI catalyst after exposure to C_3H_6 (0.2%) in He at 623 K

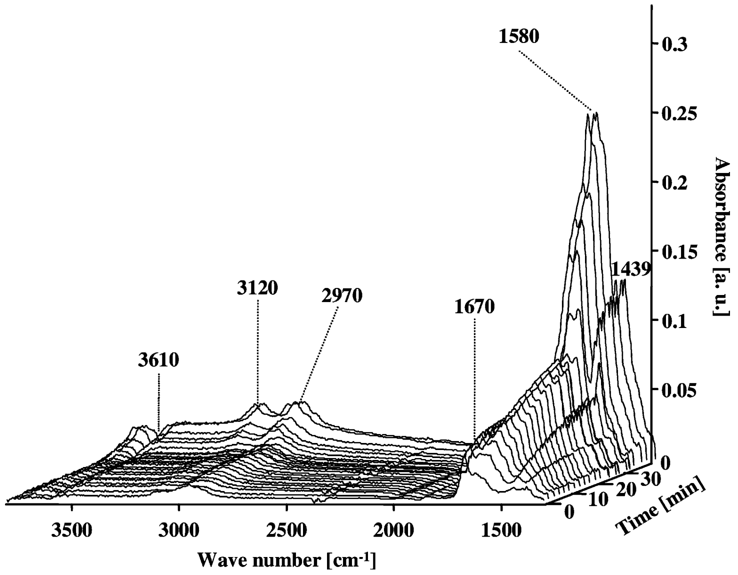

Fig. 1. Infrared spectra for Co–Pt/MFI catalyst after exposure to C_3H_6 (0.2%) in He at 623 K as a function of time.

as a function of time. After 1 min of reaction, the two peaks corresponding to OH bands (3740 cm^{-1} [terminal Si–OH] and 3610 cm^{-1} [Brønsted acid sites]) decreased with exposure. This is deduced from the appearance of two negative bands at these wave numbers. In the C–H stretching region (3200–2800 cm^{-1}), bands appear at 3100 (=CH$_2$), 3070 (=CH), 2956 (–CH$_3$), and 2917 cm^{-1} (–CH$_2$) [15–19]. These bands grew slowly and after 5 min they merge into two broad bands at 3120 and 2970 cm^{-1}. Bands also appear at 1670 (C=O), 1625 cm^{-1} (C=C) during 1 min. After 2 min of reaction, new bands appear at 1580 and 1540 cm^{-1}. After 30 min, the peak at 1670 cm^{-1} remained as a shoulder, while the peaks at 1580 and 1540 cm^{-1} became dominant. Additionally, band was observed at 1439 cm^{-1} corresponding to allylic species [15,20] and/or carbonates and/or formates [16–18]. After 19 h, the propylene stream was stopped and the catalyst was purged with He for 10 min at 623 K. The spectra did not indicate changes during that period. When a mixture of O$_2$ (5%) in He was passed over the catalyst at 623 K, these bands decreased only marginally and were visible even after 4 h. These observations indicate that the formation of propylene oligomers at the acid sites occurred and this is in line with the knowledge that Brønsted acid sites have strong tendency to adsorb and oligomerize olefins. Note that characteristic bands of C–H bonds in aromatic molecules (at 3120 and 2970 cm^{-1}) and of C=O and C=C groups (at 1670 and 1625 cm^{-1}, respectively) indicate a quite complex surface chemistry beyond oligomerization.

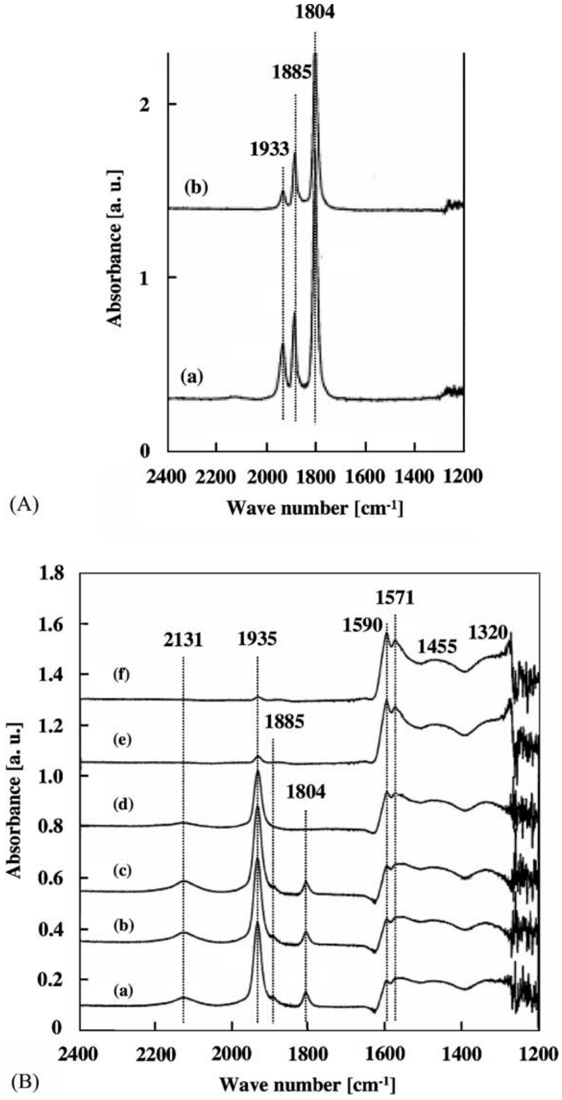

Fig. 2. Infrared spectra of (A) Co–Pt/MFI catalyst after NO adsorption at 313 K under the flow of NO (0.1%) in He and (B) Co–Pt/MFI catalyst after NO oxidation reaction at 473 K under the flow of NO (0.1%), O$_2$ (5%) in He [a–c] and subsequently followed by O$_2$ (5%) purging at 473 K [d–f].

Fig. 2A shows the infrared spectra of Co–Pt/MFI catalysts at 313 K under the flow of NO (0.1%) in He. Bands were observed at 1933, 1885, and 1804 cm^{-1}. Based on the previous reports, the band at 1933 cm^{-1} is assigned to Co(NO), that at 1885 and 1804 cm^{-1} to Co(NO)$_2$ [15,21–27]. Fig. 2B shows the infrared spectra of Co–Pt/MFI catalysts after NO oxidation reaction at 473 K under the flow of NO (0.1%), O$_2$ (5%), and He (balance) and subsequently followed purging by O$_2$ (5%) at 473 K. In the presence of oxygen (Fig. 2B and a–c), additional bands were observed at 1590, 1571, 1455, and 1320 cm^{-1}. The bands between 1600 and 1300 cm^{-1} appear to be related to Co–NO$_2$, Co–ONO, and/or Co–ONO$_2$ species [15,21–27]. However, during purging with O$_2$ (5%) at 473 K (Fig. 2B and d–f), the bands at 1933, 1885, and 1804 cm^{-1} decreased with time, on the contrary the bands at 1590, 1571, 1455, and 1320 cm^{-1} increased. These observation indicated that the oxidation of Co(NO) and Co(NO)$_2$ occurred and resulted in the formation of Co–NO$_2$, Co–ONO, and Co–ONO$_2$ species under the flow of O$_2$ (5%).

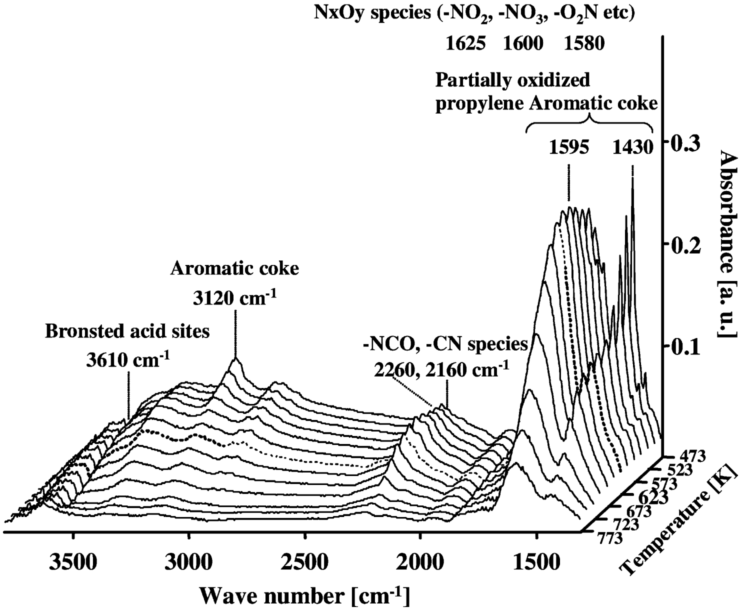

Fig. 3. Infrared spectra of Co–Pt/MFI catalyst after exposure to NO (0.1%), C_3H_6 (0.2%), O_2 (5%) in He for 30 min as a function of reaction temperature from 473 to 773 K.

Fig. 3 shows the infrared spectra of Co–Pt/MFI catalyst after exposure to NO (0.1%), C_3H_6 (0.2%), and O_2 (5%) in He for 30 min as a function of reaction temperature from 473 to 773 K. It was found that all bands in the region 3800–2800 and 1500–1300 cm^{-1} decreased, on the contrary, the bands at 2260, 2160 and at 1750–1500 cm^{-1} increased continuously with reaction temperature reaching a maximum at 573 K. All the bands, except those in 1600–1300 cm^{-1}, disappeared completely at 773 K. In a separate experiment (not shown here), the results of the exposure of Co–Pt/MFI to a mixture of NO (0.1%) and O_2 (5%) in He as a function of reaction temperature showed that no adsorbed species were observed above 723 K. This is in contrast to the results mentioned above (Fig. 3) indicating that the bands at 1600–1300 cm^{-1} are obviously related to propylene and the possible surface chemistry under these reaction conditions will be discussed below.

3.4. Catalytic reduction of NO with C_3H_6 over HY based catalysts

Table 2 summarizes the catalytic performances of Co and Pt catalysts based on HY for the selective reduction of NO (0.1%) with propylene (0.1%) in the

Table 2
Catalytic performances of Co and Pt promoted HY (Si/Al = 2.55) catalysts for the selective reduction of NO (0.1%) with propylene (0.1%) in the presence of oxygen (5%) at 498 K

Catalysts	Co (wt.%)	Pt (wt.%)	Rates of NO conversion[a,b] (mol s^{-1} g^{-1})	Rates of C_3H_6 conversion[a,b] (mol s^{-1} g^{-1})	Selectivity[b] (%)		
					N_2	N_2O	NO_2
Pt/HY	–	0.1	4.38×10^{-7}	7.50×10^{-7}	34	66	0
Co/HY	2.9	–	0.33×10^{-7}	0.31×10^{-7}	94	6	0
Co/Pt/HY	3.0	0.1	2.5×10^{-7}	3.75×10^{-7}	28	72	0

[a] Differential rates of conversion.

[b] At 30% NO conversion (by varying the contact time). Product NO_2 is observed only when C_3H_6 conversion reaches 100%.

presence of excess oxygen (5%) at 498 K. The rates of NO and propylene conversions were obtained at identical conditions for all catalysts and normalized to amounts of catalyst. It is seen from Table 2 that Co/HY showed the lowest activity (rates for NO conversion and C_3H_6 conversion) and highest selectivity to N_2 among the catalysts promoted by metals and Pt/HY on the contrary showed high activity, but lower selectivity to N_2. The addition of Pt to Co based catalyst improved the activity significantly, however, in a large increase in selectivity to N_2O (6–72%).

4. Discussions

4.1. Proposal of a reaction mechanism over Co–Pt/MFI catalyst during C_3H_6-SCR of NO

Fig. 1 shows the infrared spectra for Co–Pt/MFI catalyst after exposure to C_3H_6 (0.2%) in He at 623 K as a function of time. Several bands at 3100 ($=CH_2$), 3070 (=CH), 2956 ($–CH_3$), 2917 ($–CH_2$), 1670 (C=O), 1625 (C=C), 1580 (C=C; aromatic coke), 1540 (C=O; aromatic coke), 1439 (allylic species) cm^{-1} [15–20] were observed. Hayes et al. [15] showed that while passing propylene alone at 573 K over Cu/ZSM5 caused the appearance of 1670 cm^{-1} and they assigned it to the C=O stretching of acrolein. The oxygen necessary to form acrolein was proposed to originate from the oxo bridges between Cu^{2+} ions or hydroxyls species. Finocchio et al. [16] showed that Co_3O_{4+x} caused propylene oxidation to acrylate species already at RT indicating the consumption of lattice oxygen. It has been mentioned in Section 3.1 that Co oxide phase exist in the Co–Pt/MFI catalyst and this phase could be the source of oxygen needed for the formation oxygenate species from propylene. Furthermore, in the presence of oxygen both Pt and CoO_x catalyze this reaction. It is known from literature that oxidation of C_3H_6 proceeds via π-allyl complexes [20]. The π-allyl complexes may undergo selective oxidation of the methyl C–H allylic bond by nucleophilic oxygen to produce acrolein. At catalytic reaction temperature, we observed bands that could be assigned to allyl species (1439 cm^{-1}) and acrolein (1670, 1625 cm^{-1}). However, under reaction conditions the chances are that arolein, once formed, is an intermediate in the combustion of propylene.

The bands related to coke at 1580, 1540, and 1439 cm^{-1} increased with a function of time (Fig. 1) and in the present case the surface species were very stable and resisted purging with He at 623 K and even in the presence of oxygen (5%) in the feed stream. These observations indicate that the coke that is formed can partly be combusted unselectively, but most of it stays as spectator species over the acid sites during reaction.

Fig. 2 showed the infrared spectra of Co–Pt/MFI catalysts after NO adsorption at 313 K (Fig. 2A) and after NO oxidation reaction, and subsequently followed purging by O_2 (5%) at 473 K (Fig. 2B). We assigned the band at 1935 cm^{-1} to Co (NO) and 1896 cm^{-1} together with 1813 cm^{-1} to Co $(NO)_2$ [15,21–27] and the band at 1590, 1571, 1455, and 1320 cm^{-1} to Co–NO_2, Co–ONO, and Co–ONO_2. The formation of Co–NO_2, Co–ONO, and Co–ONO_2 species can be explained as follows by reaction of NO with surface oxygen to form NO_2 (Co–Pt/MFI is active in the oxidation of NO–NO_2 [11]). NO_2 reacts further over Co to form Co–NO_2, Co–ONO and/or Co–ONO_2 species. NO disproportionation at low temperature has also been suggested as reaction pathway for formation of NO_2 [23,25,28]. Furthermore, the more intense bands between 1700 and 1400 cm^{-1} indicate that formation of Co–NO_2, Co–ONO, and/or Co–ONO_2 compounds was significantly enhanced by the presence of oxygen.

Fig. 3 showed infrared spectra of Co–Pt/MFI catalyst after exposure to NO (0.1%), C_3H_6 (0.2%), and O_2 (5%) in He for 30 min as a function of reaction temperature from 473 to 773 K. It was found that all the bands in the region 3800–2800 and 1500–1300 cm^{-1} decreased, on the contrary, the bands at 2260, 2160 and 1750–1500 cm^{-1} increased continuously with reaction temperature reaching a maximum at 573 K. The bands in the region 3200–3100 cm^{-1} (aromatic =CH and $=CH_2$), 3000–2800 cm^{-1} (–CH, $–CH_2$, $–CH_3$), and 1500–1300 cm^{-1} (allylic, formate and/or carbonate species) decreased with reaction temperature indicating that these species disappeared. On the other hand, the bands in the region 1750–1635 cm^{-1} (C=C, C=O), 1635–1500 cm^{-1} (surface NO_x species, oxygenates, coke) and at 2260, 2160 cm^{-1} increased with temperature. Under similar conditions, peaks at 2260 and at 2160 cm^{-1} were assigned to isocyanate (–NCO) or nitriles (–CN) species [15,17,19,22].

Having established the presence of nitrile and isocyanate type species on the surface of the catalyst, we will try to trace its origin and its possible involvement in the formation of nitrogen. It has been shown that the absorption at 1439 cm^{-1}, when propylene was passed over the catalyst at 623 K, indicate the presence of allylic species derived from propylene. Further, during the NO oxidation, experiments species formed that were assigned to Co–NO_2, Co–ONO, and/or Co–ONO_2 species. These NO_x compounds can react with allylic species to form organo-nitro intermediates. In the presence of propylene and NO, organo-nitro/-nitroso species have been proposed [15,17,29]. The dehydration of nitro (R–CH_2–NO_2) fragments form R–CNO and may isomerize to isocyanate (R–NCO). The organo-nitroso species may isomerizes to an oxime (R–CH = NOH) [15,17,29] and subsequently dehydration of this oxime forms the nitrile (R–CN). The reaction of NO from gas phase with R–NCO species might be important pathway to generate N_2. The reaction of NO_2 from gas phase with R–CN seems to be also important pathway to generate N_2, however, this reaction is rather limited compared to the reaction of NO with R–NCO. During our experiments, the peaks assigned to nitrile (–CN) and isocyanate (–NCO) species grew as function of the temperature until 623 K. Note that this coincides with the temperature at which high SCR activity was observed [11,30]. More work, however, it is needed to unequivocally demonstrate the participation of the nitrile and isocyanate in the NO_x reduction.

4.2. Comparison of Co–Pt/MFI and Co–Pt/HY catalysts

It was found from Table 1 that Co/MFI showed the lowest activity (rates for NO conversion and C_3H_6 conversion) and highest selectivity to N_2 among the catalysts studied, Pt/MFI on the contrary showed high activity, but low selectivity to N_2. Similar tendency was also observed in the case of catalysts based on HY zeolites (Table 2). However, the addition of Pt to Co based catalysts resulted in differences for the two catalyst systems. The improvement of the activity was similar, however, in terms of selectivity to N_2O, the extent of increase was obviously different. In the case of Co–Pt/MFI, a small increase from 15 to 20% was obtained, on the other hand, a large increase from 6 to 72% was observed in the case of Co–Pt/HY. This difference seems to be attributed to the difference in the method of catalyst preparation and the state of Co species. Co–Pt/MFI catalyst prepared by SSIE method possesses highly dispersed Co^{2+} (50% of Brønsted acid sites, which is corresponding to half of the amount of Co loaded, were exchanged with Co^{2+} ions), large Co particles and particles where Co and Pt are both present. On the other hand, Co–Pt/HY catalyst prepared by LSIE method possesses minor extent of Co^{2+} ions and major extent of Co oxide. Co oxide is known as a promoter for the combustion of reductant, on the contrary Co^{2+} exchanged with Brønsted acid sites is useful for formation of Co–NO_2, Co–ONO, Co–ONO_2 species and can be reacted easily with partial oxidized HC activated on the Brønsted acid sites, which were not exchanged with any metal ions. This reaction pathway is important to produce N_2 mentioned in Section 4.1 and is related with obtaining higher selectivity to N_2O over Co–Pt/HY catalyst, which possess lower Co^{2+} ions than Co–Pt/MFI catalyst. However, different structure of zeolites cannot ruled out for explaining different tendency of the effect of the addition of Pt–Co based catalysts. More work, thus, is needed to explain these differences among two catalyst systems.

5. Conclusions

Catalytic tests and FT-IR studies of Co–Pt/MFI and Co–Pt/HY catalysts for the selective reduction of NO_x with propylene in the presence of oxygen were carried out. The results of catalytic tests of Co–Pt/MFI showed that the addition of Pt to Co based catalyst improved the activity, but a small increase in selectivity to N_2O (15–20%) was observed. In the case of Co–Pt/HY catalyst, the addition of Pt–Co based catalyst improved the activity more significant and larger increase in selectivity to N_2O (6–72%) was obtained. This difference might be attributed not only to the different preparation method of catalyst and the structure of zeolites, but also to the state of Co species (Co^{2+} vs. Co oxide) and their location. FT-IR studies on Co–Pt/MFI showed that the reduction of NO to N_2 followed the route. First, oxidation of NO to NO_2 occurred over metallic Pt and NO_2 forms Co–NO_2, Co–ONO, and/or Co–ONO_2. Second, the partial oxidation of C_3H_6 over Brønsted acid sites and the reaction of NO_2 formed on Co sites with partial oxidized C_3H_6 produced organo-nitro species. These species were dehydrated and isomerized to form isocyanate. Finally, [NCO] type intermediates react with NO from gas phase to selectively yield N_2.

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