Infrared study of acetone and nitrogen oxides on Cu-ZSM-5

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Surface species formed during co-adsorption of acetone and nitrogen oxides on Cu-ZSM-5 were studied by infrared spectroscopy to help address intermediacy during selective catalytic reduction of NO by hydrocarbons in excess oxygen (SCR-HC). NO plus acetone on Cu-ZSM-5 produced only marginal spectral differences compared to acetone on Cu-ZSM-5, indicating limited interaction between the adsorbates. Oxygen addition to NO plus acetone on Cu-ZSM-5 resulted in considerable NO_2 formation. Upon oxygen addition, bands assigned to surface carbonyls and carboxylates formed from acetone attenuated substantially, apparently due to a strong affinity of NO_2 for these ketone-derived surface oxygenates. Co-adsorbed NO_2 and acetone on Cu-ZSM-5 resulted in a weak band at 2590 cm^{-1}. The co-adsorption data show that interaction of acetone was greater with the NO_2 oxidant than with NO or oxygen. Addition of oxygen to NO plus acetone on Cu-ZSM-5 produced stronger interactions between oxidants and the organic reductant than those observed for the propene-containing system, especially at elevated temperatures (225°C). The results suggest that both oxygenate and NO_2 intermediacy may benefit SCR-HC.

Keywords: copper; ZSM-5 zeolite; acetone adsorption; nitric oxide adsorption; nitrogen dioxide adsorption; infrared spectroscopy

1. Introduction

The selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen (SCR-HC) is of great automotive interest. A suitable catalyst would facilitate the development of lean-burn engine technology which could significantly enhance fuel economy [1].

Cu-ZSM-5 catalysts have high initial activity for SCR-HC [2]. There have been some suggestions that oxygenated organic species may be intermediates during the reaction [2,3]. Montreuil and Shelef [3] found that the activity of oxygenates such as alcohols, aldehydes, and ketones for selective reduction of NO over Cu-ZSM-5 was similar to that of propene. However, they showed that for oxygenates, NO reduction did not require the presence of oxygen. In effect, the oxygenates could be viewed as pre-formed intermediates. With addition of oxygen, their activity advantage over propene diminishes due to partial oxidation of propene on the catalyst. For Cu-ZSM-5, Iwamoto and Mizuno [2] even suggested that the shift to lower temperature of the NO_X activity window observed when replacing NO by NO_2 during SCR-HC may be due to an oxygen- and nitrogen-containing organic intermediate ($C_XH_Y(O, N)$) rather than intermediacy of NO_2. Recent infrared work by Misono and co-workers [4–6] on Ce-ZSM-5 and Pt/SiO_2 has shown evidence of organic nitro and nitrite complexes during SCR-HC which they correlated with nitrogen formation. On the other hand, there are studies [7–9] which suggest that NO_2 formed through NO oxidation is the critical intermediate during SCR-HC. In this letter we consider the interactions between co-adsorbed acetone and nitrogen oxides (NO_X) on Cu-ZSM-5 by infrared spectroscopy and compare them to our previous results [10] on co-adsorbed propene and NO_X. Infrared band assignments are tentative.

2. Experimental

The Cu-ZSM-5 catalyst (CuHZSM5) was prepared [11] by copper ion exchange of HZSM-5 (PQ Corp., $SiO_2/Al_2O_3 = 80$, 460 m^2/g). Copper was exchanged from copper acetate (99.9%, Johnson Matthey). The sample was calcined at 400°C for 12 h. ICP analysis determined 1.78 wt% of copper. This corresponds to a nominal exchange of 147% copper as cupric ions.

Adsorption experiments were performed in situ using a high-vacuum IR cell (base pressure of 5×10^{-8} Torr) [11]. Oxygen (99.998%, Matheson) and acetone (99.6%, Fisher Scientific) were used without further purification. NO and NO_2 were purified by multiple freezing distillation [11]. During in situ catalyst pretreatment, the sample was evacuated at 400°C and treated at temperature in 100 Torr oxygen for 25 min. The sample was then cooled to the adsorption temperature in 100 Torr oxygen and evacuated at temperature for 1 h.

The reported spectra for acetone adsorption are difference spectra using the spectrum of the corresponding evacuated, calcined sample as a reference. For acetone adsorption, the sample was first exposed to 3 Torr of acetone for 10 min at a given temperature. The ketone was then evacuated for 30 min at temperature before the spectrum was obtained. The spectra reported for the

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subsequent additions of 15 Torr NO and 3 Torr oxygen to the acetone/catalyst systems are difference spectra with respect to the spectra of the samples after evacuation of the pre-adsorbed ketone. The spectra were obtained 15 min after the pressure change.

The co-adsorption experiments were limited to temperatures below 225°C since at higher temperatures ($\geqslant$300°C) the batch reaction tended toward completion which only reduced the opportunity to observe interactions between adsorbed reactant and intermediate species. Compared to the real SCR-HC application, a relatively low ratio of O_2/NO was used. This limited NO_2 formation in the batch infrared cell and allowed a measure of NO adsorption in the presence of NO_2 on the organic/catalyst system. As a consequence, deep NO oxidation may be limited. More complete experimental details can be found elsewhere [10].

3. Results and discussion

Fig. 1 shows spectra for acetone adsorption on CuHZSM5 at 25 and 225°C. Relevant band assignments are listed in table 1. The spectra show the typical envelopes due to adsorbed methyl groups in the 3000–2800 and 1600–1300 cm^{-1} ranges. As expected, the intensity for the methyls of ketone between 3000 and 2800 cm^{-1} (fig. 1) was somewhat less than that of propene [10]. A band between 1738–1726 cm^{-1} due to physisorbed ketone carbonyls was removed upon sample evacuation. The intense band at 1682 cm^{-1} was due to stretching of the carbonyl group of adsorbed acetone. In addition,

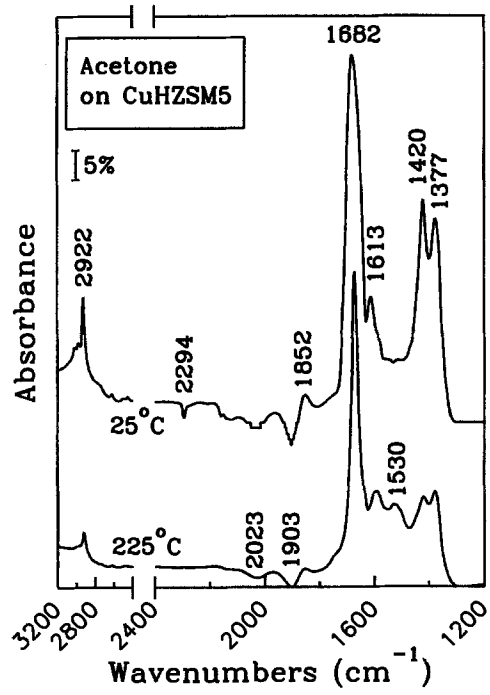

Fig. 1. Acetone on CuHZSM5 after sample evacuation.

Table 1
Approximate frequencies and tentative functional group assignments for bands observed upon adsorption of propene and acetone on CuHZSM5

Bands (cm^{-1})	Possible assignments	Ref.
2984	$\nu_s(=CH_2)$	[15]
2963–2956	$\nu_{as}(-CH_3)$	[15]
2934	$\nu_{as}(-CH_2-)$	[15]
2922–2890	$\nu_s(-CH_3)$	[15]
2865–37	$\nu_s(-CH_3)$	[15]
2158	$\nu_s(-CO)$	[16]
1726	ν(C=O), removed after evacuation	[13]
1682	ν_{as}(C=O)	[15,13]
1630	$\delta(H_2O)$	[15,17]
1625–1618	ν_s(C=C)	[15]
1613–1545	ν_{as}(carboxylate of acetate ion)	[15,17]
1610	ν_{as}(C=O)	[15]
1530–1520	ν(monodentate carbonate ion)	[15,17]
1510–1507	ν_{as}(carboxylate of formate ion)	[15]
1470–1467	ν(carboxylate ion)	[15]
1445–1420	$\delta_{as}(-CH_3)$	[15,13]
1440–1420	ν_s(carboxylate in acetate ion)	[15,17]
1388–1380	ν_s(carboxylate in formate ion)	[15,17]
1385–1346	$\delta_s(-CH_3)$	[13,15,17]

compared to propene adsorption [10], bands at 1613, 1420, and 1377 cm^{-1} attributable to carboxylate stretching also increased significantly, possibly indicating increased interaction with adsorbed oxygen or surface hydroxyls. It should be noted that the acetone remaining on the zeolite after the 30 min evacuation, particularly at 225°C, corresponds to strongly bound acetone which has been associated with strong Brønsted acidity [12,13].

Fig. 2A1, addresses the co-adsorption of NO on acetone/CuHZSM5 at 25°C. Relevant bands for NO_X adsorption are summarized in table 2. For comparison, fig. 3 shows corresponding spectra for propene and nitrogen oxides on CuHZSM5 from previous work [10]. The spectrum in fig. 2A1 resembles that of NO on propene/CuHZSM5 (fig. 3), except for some additional features at 1702 and 1640 cm^{-1}. Apparently, upon NO addition, a ketone carbonyl stretch at 1640 cm^{-1} attenuated but another one at 1702 cm^{-1} intensified. At 225°C (fig. 2B1), the intensity of the 3000–2800 cm^{-1} envelope

Table 2
Tentative band assignments for surface species formed during adsorption of nitrogen oxides on CuHZSM5 [10]

Band (cm^{-1})	Assignment	Ref.
2224	adsorbed N_2O	[8]
2133	adsorbed NO_2^+	[11]
1904	NO^+ on Cu^{2+}	[18]
1898, 1875, 1854	gaseous NO	[19]
1823	$(NO)_2^-$ on Cu^+, symm.	[18]
1811	NO^- on Cu^+	[18]
1744	adsorbed N_2O_4	[20]
1734	$(NO)_2^-$ on Cu^+, asymm.	[18]
1611	NO_2^-	[20]
1576	NO_3^-	[20]

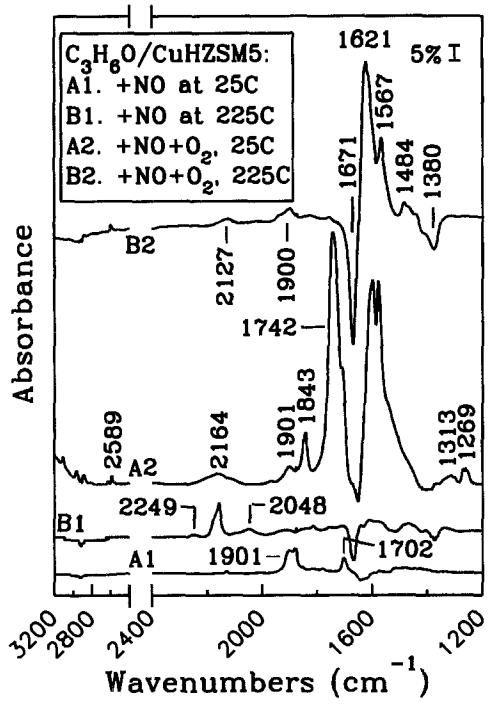

Fig. 2. Addition of 15 Torr NO followed by 3 Torr O_2 to acetone pre-adsorbed on CuHZSM5.

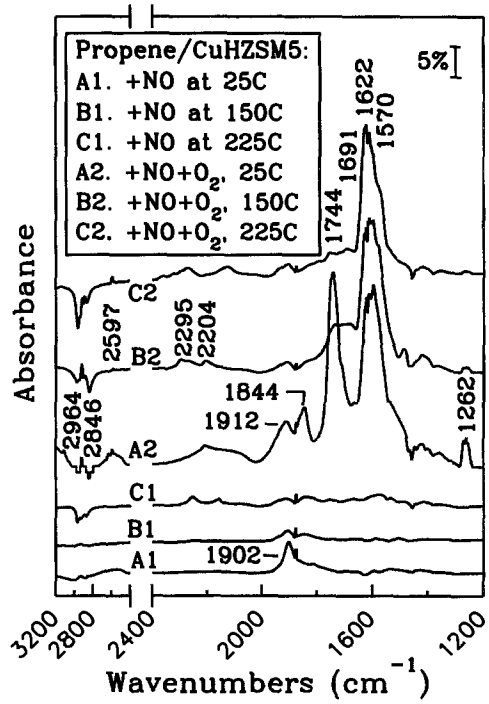

Fig. 3. Addition of 15 Torr NO followed by 3 Torr O_2 to propene pre-adsorbed on CuHZSM5 [10].

decreased and was comparable to that of the propene-containing system (fig. 3C1). At the higher temperature, CO was detected (2164 cm^{-1}). CO production was higher with acetone than with propene (fig. 3C1). The attenuation at 1660 cm^{-1} indicates a decrease in the carbonyl function of the adsorbed ketone.

Upon subsequent addition of oxygen to the NO–acetone/CuHZSM5 system at 25°C (fig. 2A2), adsorption of NO_2 and NO_3^- species increased sharply (1742, 1621, 1567, and 1269 cm^{-1}). The bands at 1901 and 1843 cm^{-1} may signify NO adsorption on the zeolite (cf. fig. 3A2). The intensities due to methyl groups (3000–2800 cm^{-1}) and that due to the carbonyl group (1670 cm^{-1}) decreased upon oxygen introduction. CO formation (2164 cm^{-1}) became apparent, and the band at 2589 cm^{-1} assigned to $(N_xO_y)_z$/Cu [14] appeared at greater intensity than was observed for the propene-containing system (see fig. 3A2).

At higher temperature (225°C, fig. 2B2), oxygen addition resulted in less adsorbed NO, NO_2, and NO_3^- species. The intensity at 2127 cm^{-1} due to adsorbed CO was comparable to that observed in the propene-containing system. The attenuation of the methyl envelope (3000–2800 cm^{-1}) was less with acetone than with propene (cf. fig. 3C2). On the other hand, bands at 1671 and 1380 cm^{-1} attributable to adsorbed ketone carbonyls and surface carboxylates decreased sharply. The band at 2589 cm^{-1} was slightly more intense than was observed with propene. However, it did attenuate with increased temperature (cf. fig. 2A2). Separate addition of oxygen to acetone/CuHZSM5 at 25°C (fig. 4A) attenuated the ketone carbonyl stretch at 1714 cm^{-1} and intensified the carboxylate band at 1619 cm^{-1}.

There has been some discussion on whether oxygenated species are intermediates during SCR of NO in the presence of organic species [2,3]. For co-adsorption of NO and acetone at 225°C, the conversion of the ketone was modest, and some of the ketone carbonyls trans-

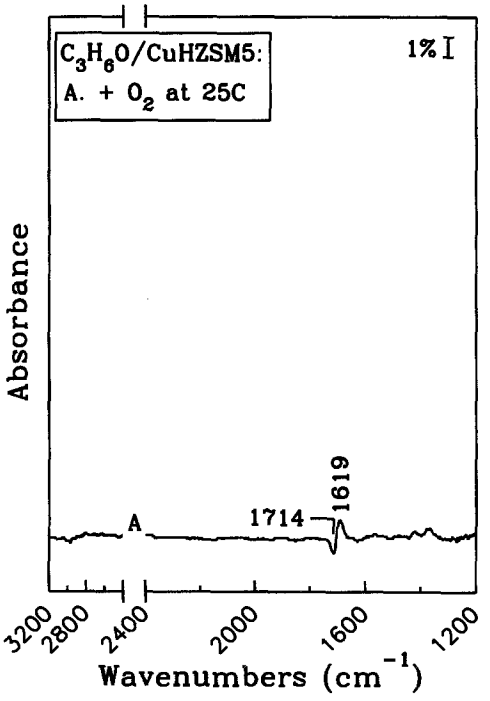

Fig. 4. Addition of 3 Torr O_2 to acetone pre-adsorbed on CuHZSM5.

formed to adsorbed CO (fig. 2B1). Also, as with NO–propene co-adsorption (fig. 3C1), some isocyanate formation was still evident (2249 cm^{-1}), in spite of CO formation. Addition of oxygen at 225°C (fig. 2B2) resulted in NO_2 formation (1621, 1567 cm^{-1}) and caused sharp decreases in ketone carbonyls (1671 cm^{-1}) and suface carboxylates (1380 cm^{-1}). Thus, it appears that NO_X reduction would benefit from both oxygenate and NO_2 intermediacy. Adsorbed CO, formed previously during co-adsorption of NO and acetone, actually declined upon oxygen introduction (fig. 2B2) even though CO_2 formation (2329 cm^{-1}) was not evident.

The nature of the products of the interaction between NO_2 and acetone was not obvious and may have been obscured by bands due to NO_X adsorption below 1700 cm^{-1}. No detectable amounts of isocyanates were formed (fig. 2A2, B2) as when propene was used (fig. 3). The only apparent product was the species at 2590 cm^{-1} previously assigned to $(N_xO_y)_z$/Cu [10,14]. Because of the formation of this product and since preadsorbed acetone was relatively strongly bound [13], it appears unlikely that the attenuations observed for the bands due to ketone-derived carbonyl and carboxylate species could be entirely due to simple displacement of adsorbed acetone by NO_2. It would be particularly difficult to envision how product surface carboxylates (1380 cm^{-1}) could result in such a reversible desorption of acetone. Even though not all products could be identified, the experiments clearly demonstrated that NO_2 interacted more strongly with acetone than with propene. Consequently, catalysts that form adsorbed oxygenated species from hydrocarbons may be more efficient in the O_2–NO–hydrocarbon reaction, especially if the reaction conditions also favor NO oxidation.

4. Concluding remarks

NO–acetone/CuHZSM5 produced only marginal spectral differences compared to acetone/CuHZSM5, indicating minimal interactions between the adsorbates. Oxygen addition to NO–acetone/CuHZSM5 resulted in considerable NO_2 formation. Upon oxygen addition, acetone adsorption decreased substantially, apparently due to a strong affinity of NO_2 for surface oxygenates derived from the ketone. For product NO_2 and acetone on CuHZSM5, a band appeared at 2590 cm^{-1}, possibly due to $(N_xO_y)_z$/Cu [14]. This band was also observed previously upon reaction of propene and NO_X on Cu-ZSM-5 [10,14]. The co-adsorption experiments suggest that the interaction of NO_2 with acetone was greater than that of NO or oxygen. Addition of oxygen to NO plus acetone on CuHZSM5 produced stronger interactions between oxidants and the organic reductant than those observed for the propene-containing system, especially at elevated temperatures (225°C). It was found that NO_2 formed from NO oxidation interacted strongly with adsorbed ketone carbonyls. The results suggest that both oxygenate and NO_2 intermediacy could benefit SCR-HC.

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