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Simultaneous $S0_2/N0_x$ Abatement Using Zeolite-Supported Copper

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ABSTRACT

We have begun the investigation of the adsorption of NO on the Cu/γ-alumina samples. The object of this aspect of the project is to investigate the modes of adsorption of NO on the Cu/γ-alumina sorbents, to investiagate the potential activity of these materials for the catalysis of the reduction of NO. Additionally, when subsequent measurements of NO interacting with a sulfated sorbent are investigated, a baseline of data will have been obtained which can be used to evaluate the effects of surface sulfation on the adsorption process in the absence of other competing effects.

Based on the current results and by comparing our results with those found by others, we have determined that the copper species exist predominantly as isolated copper atoms on the aluminum oxide surface, which behave chemically as copper aluminate. The copper species is responsible for the formation of an NO/Cu^{2+} complex which gives rise to an infrared absorption at 1863 cm^{-1}. There do exist some Cu^{+} species on the surface, which are formed only after some time by an interaction with NO, which give rise to an NO^{-}/Cu^{+} complex with an infrared absorption at approximately 1700 cm^{-1}. Additionally, an intense feature at 1640 cm^{-1} is observed which may be due to NO_2 on the surface, which is the expected oxidation product if NO reduces Cu from Cu^{2+} to Cu^{+}.

EXPERIMENTAL

The copper on γ-alumina catalysts were prepared using non-aqueous impregnation techniques. Copper acetylacetonate (Aldrich, used as received) was dissolved in acetonitrile (Fisher Scientific, dried with molecular sieves), γ-alumina (from Goodfellow, 99.995%, 150 m^2/g, < 0.1 µm particle size) was added, and the mixture was stirred at room temperature for 24 hours. The catalysts were then vacuum filtered and dried in a vacuum oven at 80 °C for 24 hours. The catalyst was then calcined in air at 500 °C for 2 hours. Elemental analyses of the catalysts were performed by Galbraith Laboratories, Knoxville, TN.

For the infrared spectroscopic studies, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used. A DRA-2C0 optical accessory from Harrick Scientific was used, with an associated controlled environment cell for the *in situ* studies. The sample was sieved using a 38 µm particle size sieve, mixed with dried, sieved KBr very gently (to avoid impregnating the sorbent with potassium) 20% by weight, placed in the DRIFTS sample cup, and carefully leveled with a spatula.

Before beginning the NO adsorption experiments, the catalyst/KBr was heated to 400 °C in slowly flowing oxygen to remove any water or organics adsorbed after calcination. The sample was then cooled to 30 °C and exposed to 20 torr of a flowing 4% NO (balance He) gas mixture (Specialty Gas Southeast). The infrared spectrum was measured at 1, 20, 40, and 60 minutes after the flow was begun. The final spectra were obtained by subtracting the contribution of gas-phase NO. Initial experiments using pure NO as the adsorbate failed due to the disproportionation reaction $3NO \rightarrow N_2O + NO_2$ which occurs rapidly in pure NO and which took place in the gas tank before use. Several experiments were carried out with this gas mixture before source of our novel results was determined.

RESULTS

The infrared spectra of NO adsorbed on Cu/γ-alumina catalysts containing 1.12, 2.35, and 5.78 wt % Cu are shown in Figures 1, 2, and 3, respectively. The results are plotted as a function of time to observe the formation of new species and changes in the intensities of the infrared bands with adsorption of NO. On the sample with 1.12 wt% copper, shown in Figure 1, after 1 minute of exposure to flowing NO, only a band at 1640 cm^{-1} was observed. Twenty minutes later, two new adsorption bands had developed at approximately 1865 cm^{-1} and 1702 cm^{-1} as well as a broad feature with an absorption maximum at approximately 1952 cm^{-1}. After 1 hr exposure time, the 1640 cm^{-1} peak had shifted to 1627 cm^{-1}. All the bands disappeared after evacuation.

On the catalysts containing 2.35 and 5.78 wt% copper, two new bands at approximately 1863 and 1640 cm^{-1} appear after 1 min. At the completion of 1 hr exposure to flowing NO, these two bands were still present and were accompanied by a new band at approximately 1703 cm^{-1} which began to appear after 20 min exposure time. Also, the 1640 cm^{-1} peak had shifted to approximately 1629 cm^{-1} at the end of one hour exposure. No significant adsorption band was observed in the neighborhood of 1952 cm^{-1} on either catalyst with higher copper content, Figures 2 and 3. Results from adsorption experiments carried out at 70 and 100 °C, though not shown, yielded a peak at approximately 1863 cm^{-1}. Upon brief evacuation, this peak disappeared.

The infrared spectrum of NO adsorbed on transition metals can be used to determine the oxidation state of the metal and the nature of NO bonding to the surface.[1] NO contains one electron in a π^* anti-bonding orbital. If this electron is transferred to the metal upon bonding, the NO vibrational frequency will increase, corresponding to an increased bond order for the N-O bond. On the other hand, the bonding of NO to some metals involves the transfer of an electron from the metal to NO, a situation which will result in a decrease in the NO vibrational frequency due to a decrease in the N-O bond order.[2] The gas-phase infrared absorption of NO is at 1876 cm^{-1}. Typical frequencies for the NO absorption which have observed for NO on Cu/ZSM-5 are: Cu^{2+}/NO^{+} - 1906 cm^{-1}; Cu^{+}/NO^{-} 1813 cm^{-1}.[2] The Cu/ZSM-5 system has been widely studied due to its importance as an NO reduction catalyst. Less well studied is the Cu/γ-alumina system. The Cu^{2+}/NO^{+} vibration has been assigned as occuring at 1875, 1900, and 1920 cm^{-1}.[3] The Cu^{+}/NO^{-} absorption has been assigned to bands observed at 1780 and 1800 cm^{-1}, while some suggest that these bands must be due to the neutral NO species and that the band for NO^{-} adsorbed on Cu should be observed at approximately 1700 cm^{-1}.[2] A band in the neighborhood of 1863 cm^{-1} has been assigned to NO adsorbed on copper aluminate ($CuAl_2O_4$), a Cu^{2+} species.[4]

Based on these previous studies, the results from the current work are interpreted a follows. The non-aqueous impregnation gives rise to isolated copper species on the alumina surface which behave chemically as copper aluminate. NO adsorbed on these sites gives rise to the adsorption at 1863 cm^{-1}. The interaction of NO with the copper sites results in the oxidation of NO to NO_2, which remains on the surface and is responsible for the absorption at 1640 cm^{-1}. The NO oxidation results in the formation of Cu^{+} species which adsorb NO to form NO^{-}/Cu^{+} complexes, which are responsible for the absorption at 1700 cm^{-1}. More work needs to be carried out to be completely confident in these assignments.

REFERENCES

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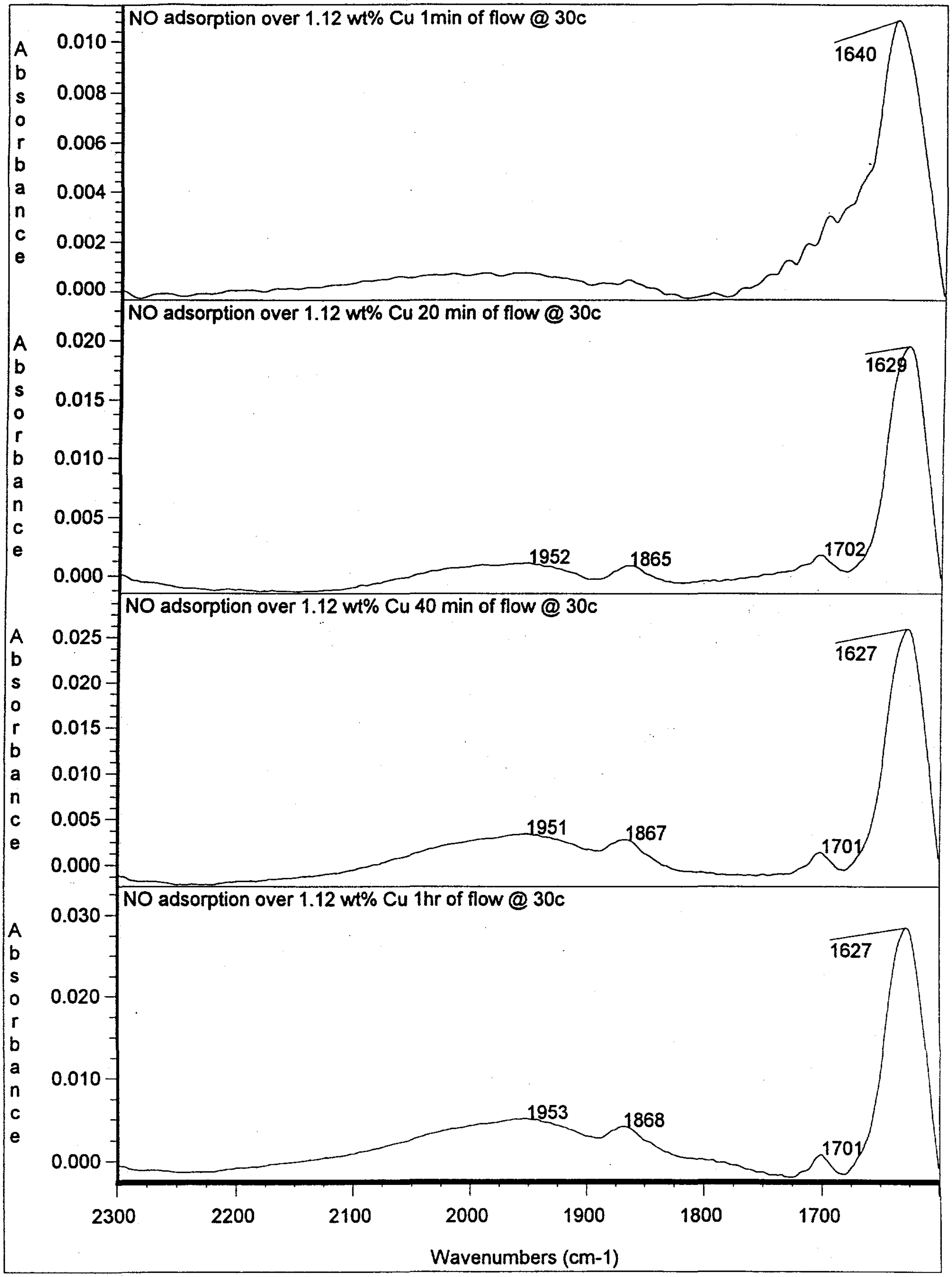

NO adsorption over 1.12 wt% Cu 1min of flow @ 30c
Absorbance
0.010
0.008
0.006
0.004
0.002
0.000
1640
NO adsorption over 1.12 wt% Cu 20 min of flow @ 30c
Absorbance
0.020
0.015
0.010
0.005
0.000
1952
1865
1702
1629
NO adsorption over 1.12 wt% Cu 40 min of flow @ 30c
Absorbance
0.025
0.020
0.015
0.010
0.005
0.000
1951
1867
1701
1627
NO adsorption over 1.12 wt% Cu 1hr of flow @ 30c
Absorbance
0.030
0.020
0.010
0.000
1953
1868
1701
1627
2300
2200
2100
2000
1900
1800
1700
Wavenumbers (cm-1)

Figure 1.

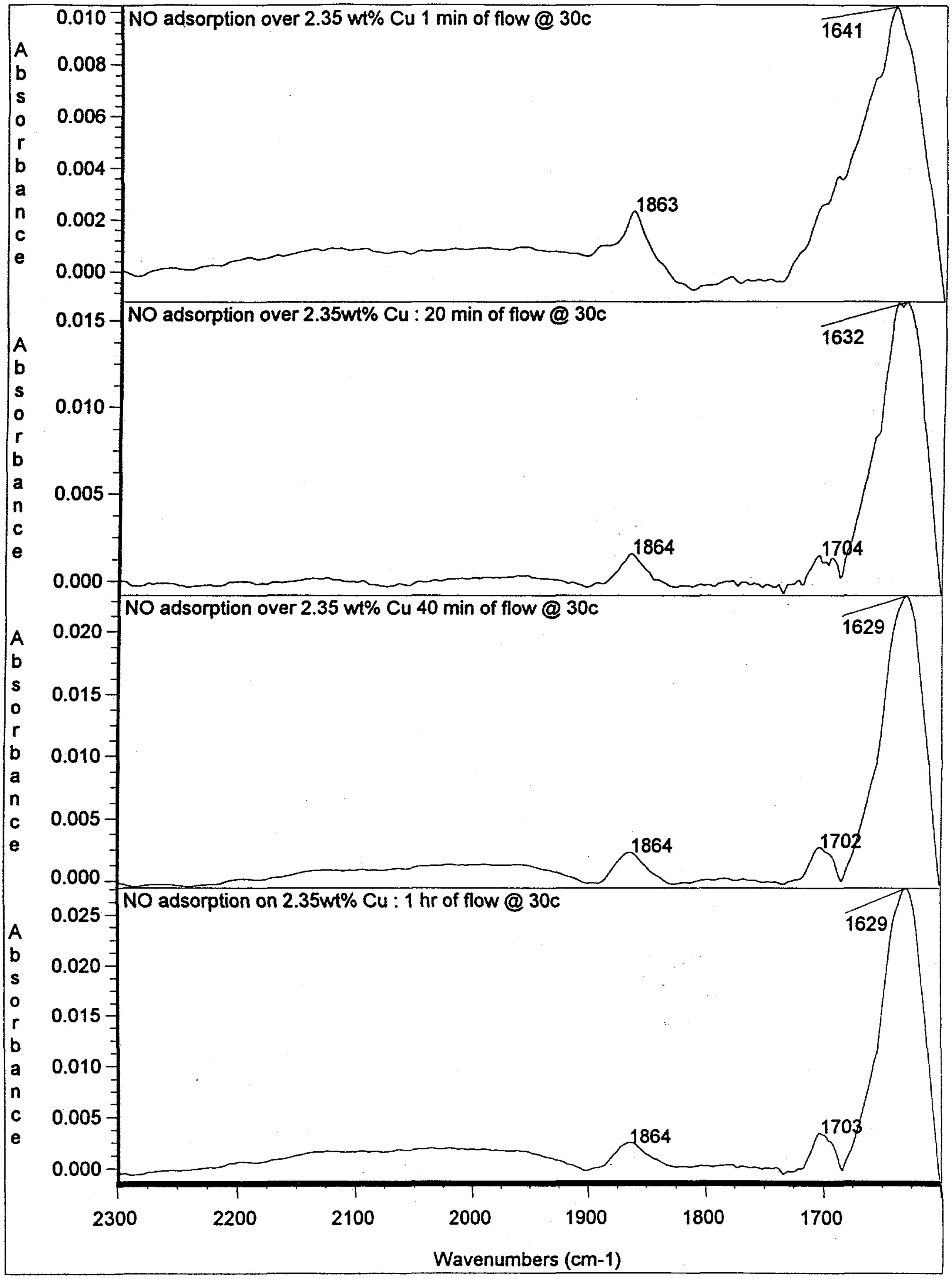
NO adsorption over 2.35 wt% Cu 1 min of flow @ 30c
1641
1863
NO adsorption over 2.35wt% Cu : 20 min of flow @ 30c
1632
1864
1704
NO adsorption over 2.35 wt% Cu 40 min of flow @ 30c
1629
1864
1702
NO adsorption on 2.35wt% Cu : 1 hr of flow @ 30c
1629
1864
1703
Absorbance
0.000
0.002
0.004
0.006
0.008
0.010
0.005
0.015
0.020
0.025
2300
2200
2100
2000
1900
1800
1700
Wavenumbers (cm-1)

Figure 2.

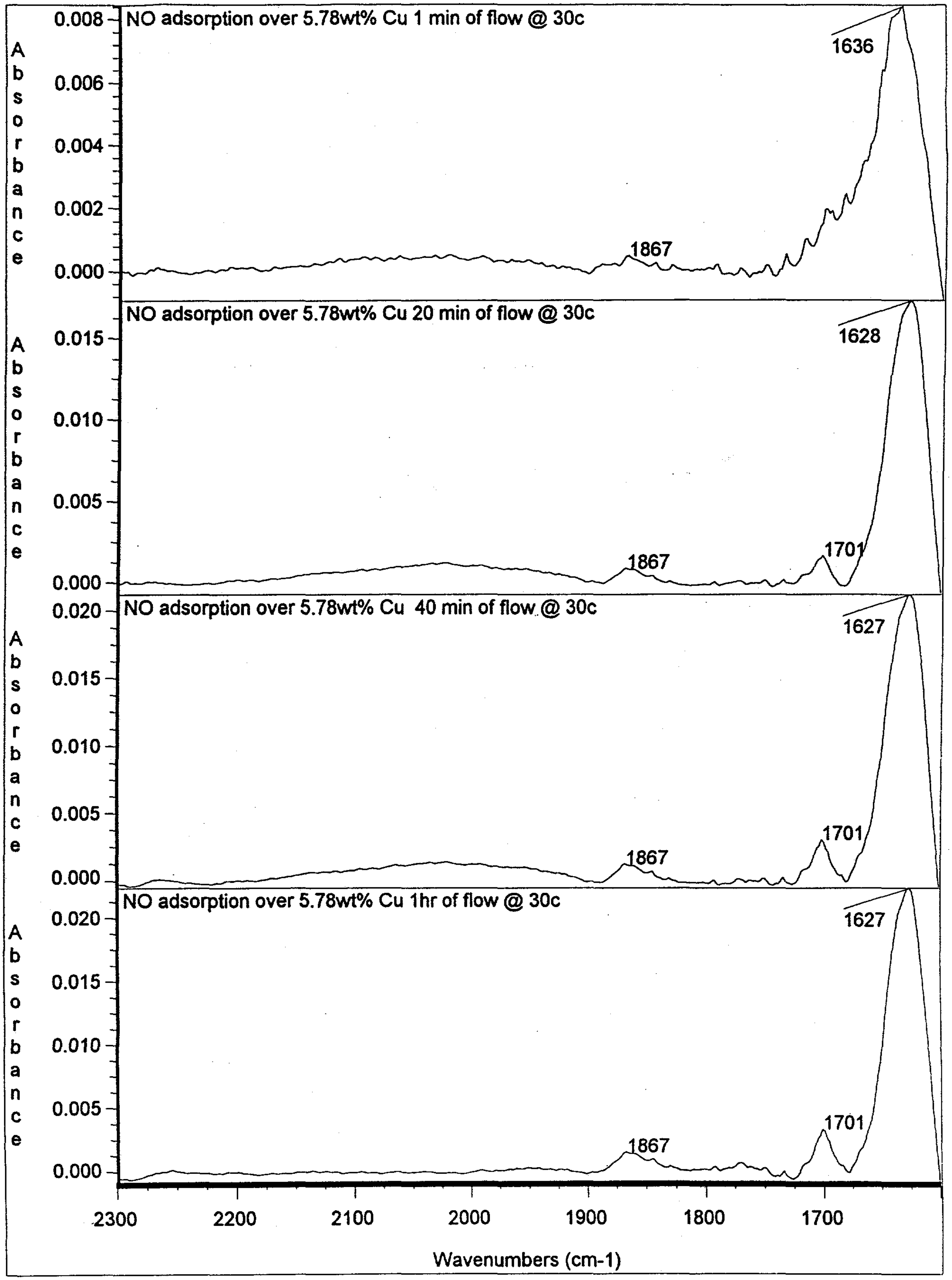
NO adsorption over 5.78wt% Cu 1 min of flow @ 30c
NO adsorption over 5.78wt% Cu 20 min of flow @ 30c
NO adsorption over 5.78wt% Cu 40 min of flow @ 30c
NO adsorption over 5.78wt% Cu 1hr of flow @ 30c
Absorbance
0.008
0.006
0.004
0.002
0.000
0.015
0.010
0.005
0.020
1636
1628
1627
1867
1701
2300
2200
2100
2000
1900
1800
1700
Wavenumbers (cm-1)

Figure 3.