JOURNAL OF CATALYSIS 83, 182–191 (1983)

Propene Metathesis over CoMo/Al_2O_3: Poisoning by NO to Determine Active Site Concentration

JOHN R. HARDEE[1] AND JOE W. HIGHTOWER[2]

Department of Chemical Engineering, Rice University, Houston, Texas 77251

Received January 24, 1983; revised April 11, 1983

The metathesis of propene over a reduced (with CO) CoO · MoO_3/Al_2O_3 catalyst has been studied in a batch recirculation reactor. Ethene plus *cis*- and *trans*-2-butene (in thermodynamic equilibrium) were the only products observed, and the reaction occurred at a moderate rate at 0°C. The kinetics could be described by adsorption on adjacent sites in a Langmuir–Hinshelwood rate model that had been corrected for the reversible nature of the reaction. Nitric oxide completely poisoned the reaction, and doses of various sizes were used to titrate the activity. The amount of NO required to eliminate totally the activity (the "lethal dose") decreased as the reaction temperature increased from 0 to 27°C. If the smallest value observed ($2.5 \times 10^{13}/cm^2$) is taken as an upper limit of the active site density, this corresponds to at most 14% of the total Mo atoms in the catalyst being active. The turnover frequency at 0°C and 1.33×10^4 N/m^2 propene pressure is 0.05 sec^{-1}. Infrared analysis of the adsorbed NO indicated three strong bands each with a unique thermal stability. The least thermally stable band (1875 cm^{-1}) is probably due to NO adsorbed on Co. The other two bands, 1796 and 1710 cm^{-1}, probably are due to NO adsorbed on Mo by coordinative covalent and covalent bonds, respectively.

INTRODUCTION

Many different techniques have been applied to characterize the oxides of CoMo/Al_2O_3. One of the most successful methods has been to study the behavior of probe molecules adsorbed on these materials and their effects on test catalytic reactions. Oxygen (*1, 2*), carbon monoxide (*3*), and nitric oxide (*4*) chemisorption have been used to measure the dispersion of molybdenum on alumina. Oxygen and hydrogen chemisorption have helped to characterize the sites of incompletely reduced MoO_3/Al_2O_3 that are active for propene hydrogenation (*5, 6*). The chemisorption of poisons has also been used to study the reactions of ethene (*7*), cyclopropane (*8*), and propene (*9*) over Mo/Al_2O_3. Tracer olefins have been employed as a diagnostic tool for the assay of supported molybdenum surfaces (*10–12*). This is possible because different reaction mechanisms of olefins can reflect different kinds of surface sites.

Nitric oxide has recently been used as a probe to study Co/Al_2O_3, Mo/Al_2O_3, and CoMo/Al_2O_3 (*13*). Specifically, changes in the infrared spectra of adsorbed NO were used to provide information about the effects of varying the Co loading, calcination temperature, and sample pretreatment conditions.

The purpose of this study was to use nitric oxide as a probe molecule to study the sites on CoMo/Al_2O_3 that are active for a specific reaction—olefin metathesis. Two groups (*9, 14*) have used indirect evidence to speculate that the concentration of sites on supported molybdenum for olefin metathesis is only a small fraction of the molybdenum atoms present. Since NO poisons the metathesis reaction over our catalyst, one of our objectives was to measure directly the density of active sites of CoMo/Al_2O_3 for olefin metathesis by titrative poisoning.

---

[1] Present address: Department of Sciences, Louisiana State University, Eunice, Eunice, Louisiana 70535.

[2] To whom correspondence should be addressed.

0021-9517/83 $3.00

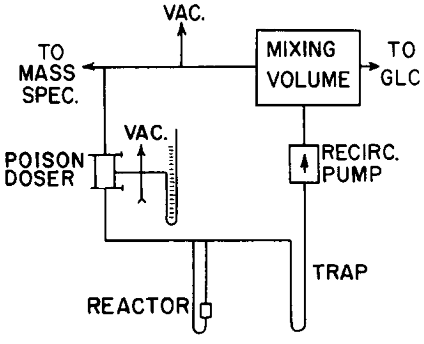

FIG. 1. Recirculation reactor system.

EXPERIMENTAL

All reactions were carried out in an all-Pyrex recirculation system shown in Fig. 1. The volume of the system was about 400 cm^3, depending on which reactor was used. The system had a 2.23 cm^3 doser through which known amounts of gases could be added at any time to the recirculating gases in the system. A mercury diffusion pump routinely gave pressures of 1.3×10^{-4} N/m^2 or lower in noncondensables as measured by a McLeod gauge. Separation of the reactants and products was achieved with a gas–liquid chromatograph system which consisted of a helium carrier gas stream, a 4-m, 0.95-cm-diameter propylene carbonate column thermostated at 0°C, and a thermal conductivity cell detector.

The catalyst used in this work was supplied by Haldor Topsøe A/S in Copenhagen, Denmark. It contained 1.6 wt% CoO and 10.7 wt% MoO_3 on γ-alumina. It had 50–100 ppm Na and a maximum of 30 ppm Cl^-. The catalyst was received in 3 mm extrusions which were ground and sieved to 20–40 mesh particles that were used in all the kinetic experiments. The surface area (measured by BET nitrogen adsorption) was 248 m^2/g. With a pore volume of 0.350 cm^3/g (measured by mercury porosimetry), the catalyst had a particle density of 1.50 g/cm^3.

The propene (Phillips Research Grade) had a listed purity of 99.99 mol% and was subjected to four freeze-pump–thaw cycles before use. Nitric oxide (Matheson Gas Products) was purified by freezing it into a trap at liquid nitrogen temperature and retaining only the center portion of a distillation cut. This center cut of NO was again frozen at −195°C and degassed for 1 min. The solid NO was warmed slowly until the liquid phase formed, at which time the pumping was stopped. After the liquid N_2 bath was replaced with a dry ice–acetone bath, the NO was distilled into another trap held at −195°C. The contents of the dry ice–acetone trap were discarded. This procedure was repeated four times before the NO was ready for use.

Labeled ^{15}NO was obtained from Prochem B.O.C. Limited and had a listed purity of 97.2 at% nitrogen 15; mass spectral analysis confirmed this purity. No attempt was made to purify this gas further.

O_2 and CO (Matheson Gas Products) were passed through traps at liquid nitrogen temperature before being used.

The infrared spectra were recorded with a Perkin Elmer Model 21 instrument operated in a double-beam mode with air as the reference. Scans were made at the slowest practical speed with maximum recorder gain and programmed slit setting. Other instrument controls were set to give the highest resolution and signal-to-noise ratio attainable with the expanded transmittance scales required for the spectra.

The ir cell contained an upper portion made of Pyrex while the lower part was made of 2.54-cm^2 quartz tubing. The cell could be attached to the recirculation system. The heated region of the cell consisted of a 10-cm section of tubing which was wrapped with asbestos paper tape and wound evenly with nichrome heating wire. The wire was wrapped with asbestos and connected to a Hewlett-Packard 240 temperature programmer. An iron-constantan thermocouple was placed in the thermowell, the bottom tip of which was located near the midpoint of the heated region. Oval holes were cut in the quartz tubing

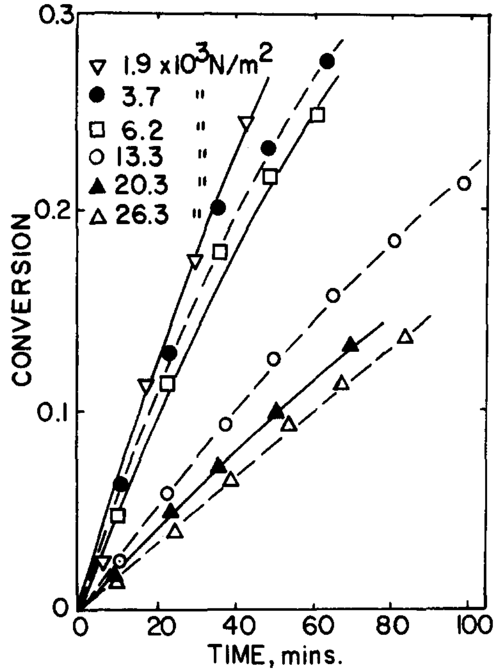

FIG. 2. Fractional conversion of propene at various initial pressures (0°C, 50 mg reduced CoMo/Al_2O_3).

1.25 cm from the bottom, and 0.3-cm-thick polished sodium chloride windows were sealed with epoxy over the holes.

For ir measurements, catalyst samples in the form of circular wafers were prepared by pressing 40–75 mg of finely ground (<300 mesh) CoMo/Al_2O_3 in a 1.9-cm-i.d. hardened steel die to a pressure of 3×10^8 N/m². By manipulation of a wire cranking device, the disk was shifted between the heated region for pretreatment and the spectral region between the NaCl windows for ir measurements.

The "standard" catalyst pretreatment consisted of circulating 2.0×10^4 N/m² of O_2 over the catalyst at 500°C for 30 min, evacuating to below 1.3×10^{-3} N/m², and then circulating 2.0×10^4 n/m² of CO over the catalyst for 1 hr. It was then evacuated at 500°C until the system pressure reached 1.3×10^{-4} N/m². This pretreatment resulted in a consistent high catalyst activity.

The test reaction was propene metathesis to ethene and butenes. *cis*- and *trans*-2-butene were the only observed butene products, and they were formed in equilibrium ratios.

RESULTS

Kinetic Measurements

Propene conversion data are shown in Fig. 2 for the reaction run at 0°C over 50 mg of catalyst. The initial rate of disappearance of propene versus propene pressure is shown in Fig. 3. The fact that the initial rate approaches zero order at high propene pressure suggests that the kinetics of propene metathesis can be described by a Langmuir–Hinshelwood model, e.g., rate $= k_f(\Theta_{C_3})^2$. The integrated Langmuir–Hinshelwood equation (15) which takes into account the reversibility of the metathesis reaction is

$$\sqrt{K_{eq}}\,\ln\frac{\left(2x-\dfrac{x}{2K_{eq}}-2-\sqrt{\dfrac{1}{K_{eq}}}\right)\left(-2+\sqrt{\dfrac{1}{K_{eq}}}\right)}{\left(2x-\dfrac{x}{2K_{eq}}-2+\sqrt{\dfrac{1}{K_{eq}}}\right)\left(-2-\sqrt{\dfrac{1}{K_{eq}}}\right)}=\frac{2k_fK_3^2(C_3)_0t}{[1+K_3(C_3)_0]^2} \qquad (1)$$

where x is the conversion of propene, K_{eq} is the equilibrium constant for the metathesis reaction, k_f is the forward reaction rate constant, K_3 is the adsorption equilibrium constant for propene, $(C_3)_0$ is the initial pressure of propene, and t is time. A plot of the left side of this linear Eq. (1) versus time is shown in Fig. 4.

Poisoning

Although CO, O_2, and NO were tested as potential poisons for the metathesis reac-

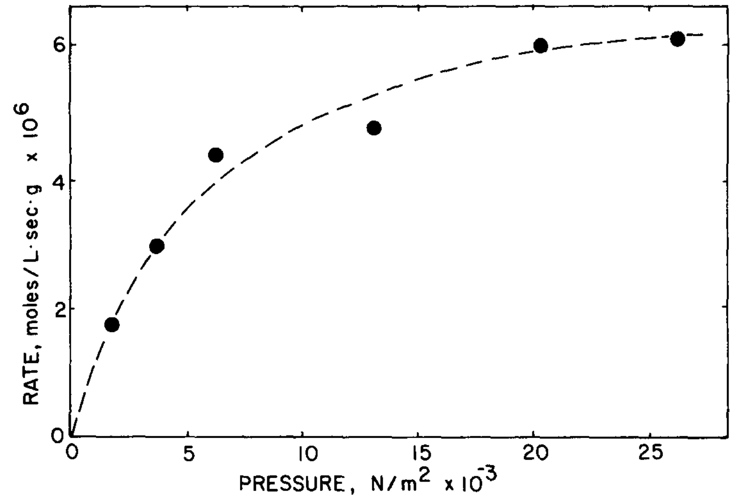

FIG. 3. Initial reaction rates for metathesis at various pressures of propene (0°C, 50 mg reduced $CoMo/Al_2O_3$).

tion, only NO actually decreased the reaction rate. Varying amounts of NO were added to the system after the propene metathesis reaction had begun, and its effect on the catalyst activity was measured in each case. For low conversions (<15% conversion) the kinetics of the metathesis reaction can be described adequately by an irreversible Langmuir–Hinshelwood equation. The integrated form of this equation is

$$2K_3(C_3)_0 \ln\left(\frac{1}{1-x}\right) + K_3(C_3)_0^2 x - \frac{1}{1-x} = 2k_f K_3(C_3)_0 t \quad (2)$$

where the terms have the same meaning as in Eq. (1). Since the slope of a plot of the left-hand side of this linear Eq. (2) versus time is proportional to the reaction rate constant k_f, any abrupt change in the cata-

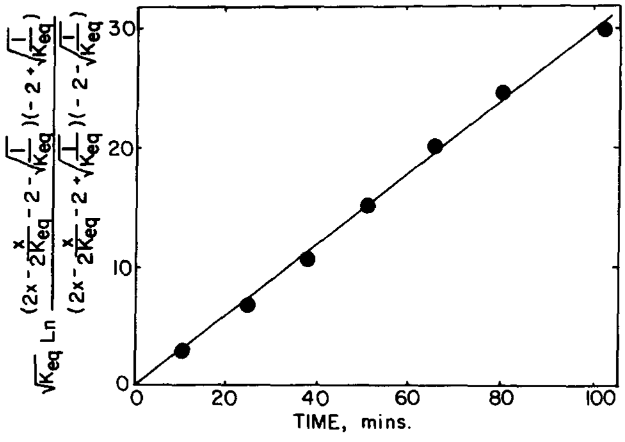

FIG. 4. Conversion data for propene metathesis plotted according to integrated linear rate Eq. (1) (0°C, 50 mg reduced $CoMo/Al_2O_3$, 1.33×10^4 N/m^2).

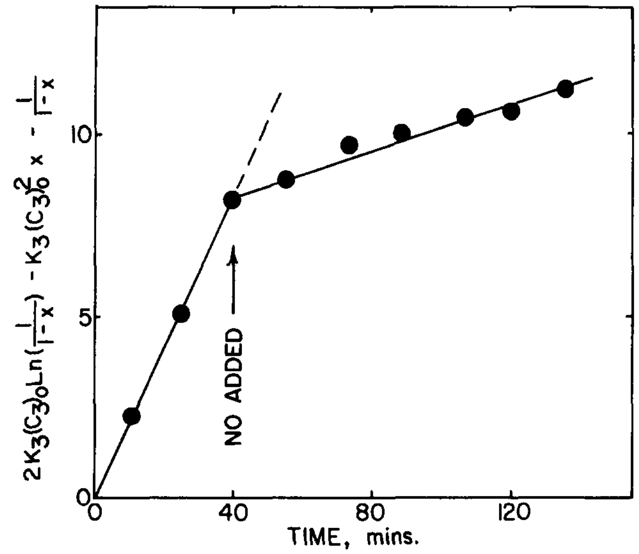

FIG. 5. Effect of NO poisoning on propene metathesis (8.2×10^{13} NO/cm^2 introduced at 40 min, 0°C, 50 mg reduced CoMo/Al_2O_3, 2.0×10^4 N/m^2 initial propene pressure).

lyst activity should be reflected in an abrupt change in the slope of such a plot. This is shown in Fig. 5 where 8.24×10^{13} NO molecules/cm^2 total surface were added 40 min after the reaction began. The reaction rate constants can be determined from the slopes of the two straight-line portions of this plot. The ratio of the reaction rate constant after the poison was added to the rate constant before the poison was added, k_p/k_0, is a measure of how much a given amount of NO poisons the reaction. An estimate of the active site density may be determined by plotting the ratio k_p/k_0 versus the amount of poison added per cm^2 of the catalyst. Figure 6 shows that the extrapolated site densities are 7.5×10^{13}/cm^2 at 0°C and 2.5×10^{13}/cm^2 at 27°C. Since no residual gas phase NO was ever seen by GLC during these poisoning experiments, we assume that all NO added was adsorbed.

Adsorption Isotherms

Figure 7 shows an isotherm of NO on CoMo/Al_2O_3 at 27°C. The catalyst was given the "standard" pretreatment and was then cooled to room temperature under vacuum. The triangles in Fig. 7 represent the amounts of NO adsorbed both chemically and physically on the catalyst for increasing pressures of NO. After these data were taken, the system was evacuated at room temperature and additional NO was added to determine if any more NO could be adsorbed. Some additional NO was adsorbed, as indicated by the circles in Fig. 7. The solid line is simply the difference be-

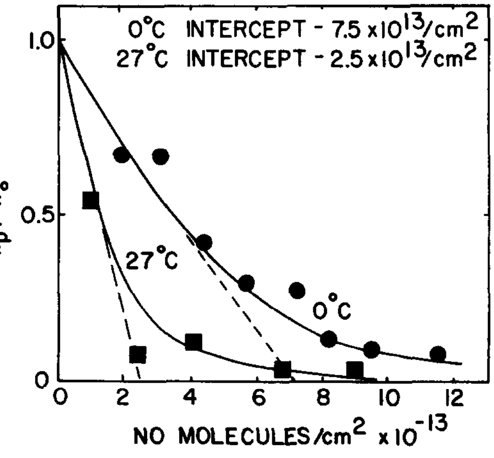

FIG. 6. Titration plots showing NO poisoning of propene metathesis at 0 and 27°C (50 mg reduced CoMo/Al_2O_3, 2.0×10^4 N/m^2 initial propene pressure).

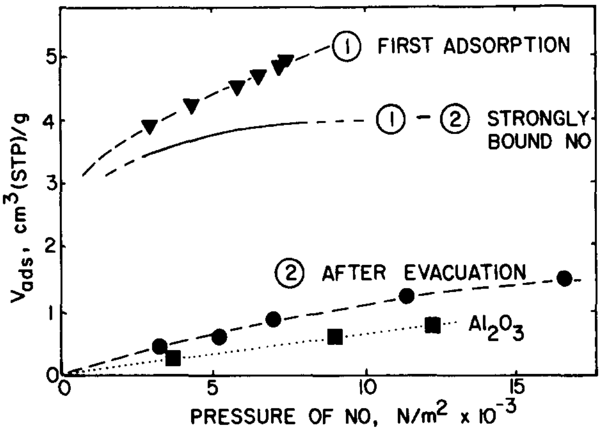

FIG. 7. Adsorption isotherms of NO on reduced CoMo/Al$_2$O$_3$ and on the support Al$_2$O$_3$ at 0°C.

tween the amount of NO adsorbed initially and the amount of NO adsorbed after the system had been evacuated. The line appears to become constant at about 4.0 cm^3 (STP)/g, which represents the NO that was strongly adsorbed on the catalyst. NO was also adsorbed on the Al$_2$O$_3$ support, as indicated by the squares in Fig. 7; this amount varied linearly with the pressure of NO.

Infrared Spectra of Adsorbed NO

NO was allowed to contact a 75 mg pressed disc of CoMo/Al$_2$O$_3$ at a pressure of 3.3 × 10^3 N/m^2 and 27°C. The gas phase was evacuated and the cell was removed from the system. Figure 8 shows the spectrum that was obtained, along with the spectrum of the sample before NO was added. The adsorbed NO produced three intense bands at 1875, 1796, and 1710 cm^{-1}. In an attempt to determine if these three bands are due to more than one monomeric surface species, the ir spectrum of ^{15}NO and the spectrum of a 50–50% mixture of ^{15}NO and ^{14}NO were also recorded. These are shown in Fig. 9. The dotted line is ^{14}NO on CoMo/Al$_2$O$_3$, the dashed line is for adsorbed ^{15}NO, and the solid line is the spectrum of the mixture of ^{14}NO and ^{15}NO. Notice that the spectrum of the mixture is to a first approximation the sum of the individual spectra of ^{14}NO and ^{15}NO adsorbed on the same catalyst. In all cases the catalyst was reduced.

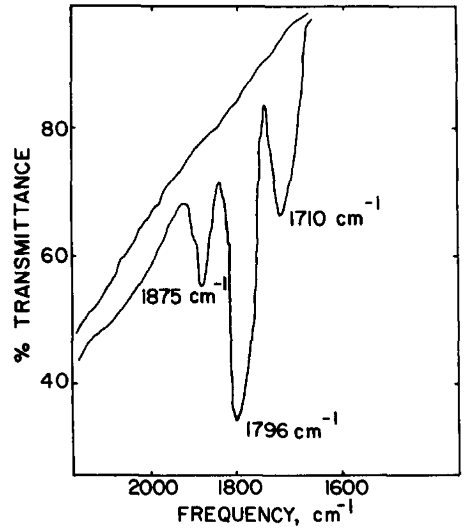

FIG. 8. Infrared spectrum of NO adsorbed on reduced CoMo/Al$_2$O$_3$ at 27°C.

Experiments were run to test the thermal stability of the adsorbed species. Figure 10 shows the results. The dotted line is NO adsorbed on CoMo/Al$_2$O$_3$ at room temperature. The solid line spectrum resulted when the sample was heated to 150°C and evacuated for 30 min. The band at 1875 cm^{-1} disappeared while the bands at 1796 and 1710 cm^{-1} remained. A 200°C evacuation for 30 min (dashed line) almost removed the 1796 cm^{-1} band but did not cause much change in the 1710 cm^{-1} band.

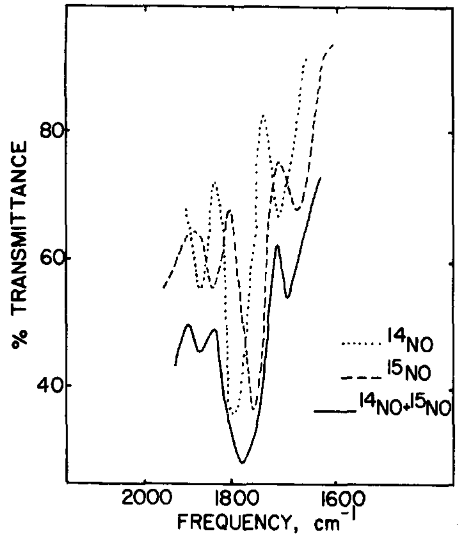

FIG. 9. Infrared spectra of ^{14}NO, ^{15}NO, and (^{15}NO + ^{14}NO) mixture adsorbed on reduced $CoMo/Al_2O_3$ at 27°C.

Another catalyst that contained 8.1 wt% MoO_3 on the same γ-Al_2O_3 (no CoO was present) was similarly treated with 3.3×10^3 N/m^2 of NO at room temperature; its ir spectrum is shown in Fig. 11. The band at 1875 cm^{-1} was not present on this sample. To serve as a blank, a 75-mg Al_2O_3 pellet was prepared and contacted with the same pressure of NO. After evacuation, no bands that could be attributed to adsorbed NO were seen in the ir spectrum.

DISCUSSION

Attempts to explain the kinetics of olefin metathesis have employed both Eley–Rideal (*17*) and Langmuir–Hinshelwood models (*15, 16, 18, 19*). In Fig. 12 we have compared both models using our data. Clearly the Langmuir–Hinshelwood equation satisfies our data better than does the Eley–Rideal equation.

Lombardo *et al.* (*9*) reported NO to be a poison for propene hydrogenation but not for propene metathesis. Their results are in sharp contrast with our own. Perhaps the difference may lie in the fact that the catalyst used in this study was about 40 times more active than the catalyst used by Lombardo. If the sites on Lombardo's catalyst were not activated or were already poisoned by something, then NO would probably not show any effect on the already slow metathesis reaction.

Figure 6 shows that there is a marked dependence of the measured site density on

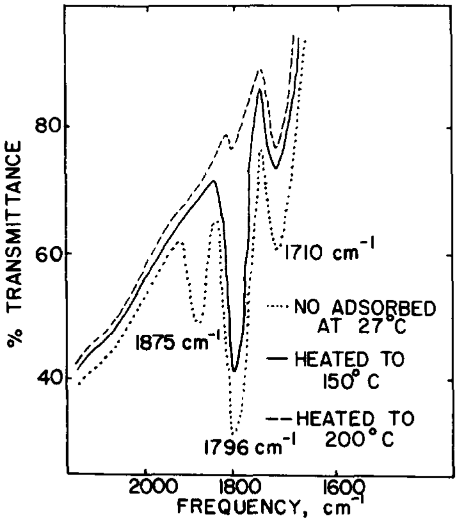

FIG. 10. Thermal stability of bands: effect of evacuation at elevated temperatures on the infrared spectrum of NO adsorbed on reduced $CoMo/Al_2O_3$.

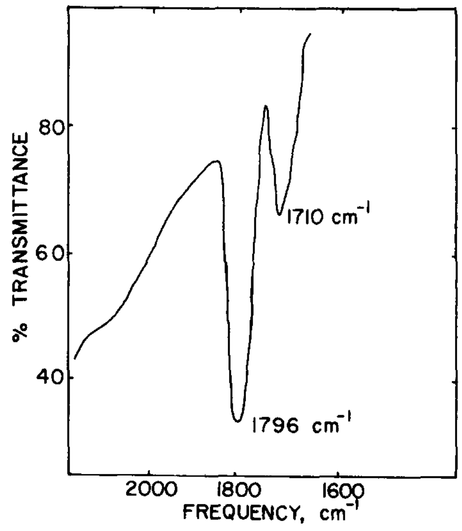

FIG. 11. Infrared spectrum of NO adsorbed on reduced Mo/Al_2O_3 at 27°C.

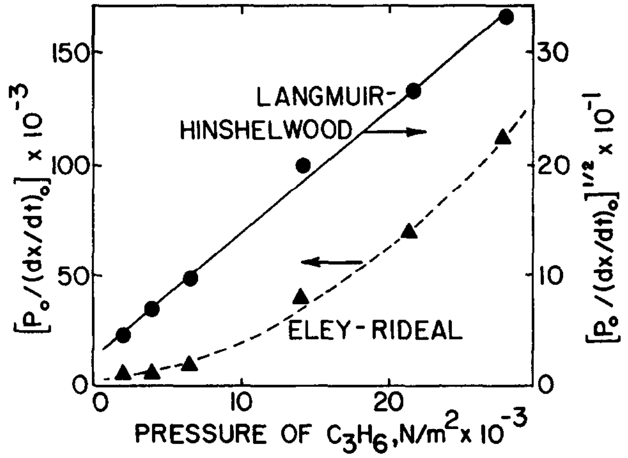

FIG. 12. Tests of initial propene metathesis rate data according to Langmuir–Hinshelwood and Eley–Rideal models. Both models predict linear plots.

temperature. A similar dependency was observed by Rosynek and Hightower (*20*) for the poisoning of D_2/C_6H_6 exchange sites by CO_2 on an alumina catalyst. Even though the two systems are quite different, we suggest that the explanation for the temperature dependence may be the same. A decrease in site density with temperature may indicate that the poison molecules are adsorbed on other sites in addition to those that are active for olefin metathesis. If the poison molecules are adsorbed more strongly on the active metathesis sites than on the "other" sites, then at the higher temperature the poison will have more surface mobility and can seek out these sites with the higher heat of adsorption. This would result in fewer poison molecules being required to have an effect on the catalyst activity, since the poison is more selective for the active sites. A lower "site density" would be observed at the higher temperatures, as was the case. For this reason, the quantity $2.5 \times 10^{13}/\text{cm}^2$ (the intercept at the highest temperature used) is at best an upper limit of the active site density of CoMo/Al$_2$O$_3$ for propene metathesis.

Assuming that only the Mo atoms are active for the metathesis reaction, this density corresponds to 14% of the total Mo atoms in the catalyst being utilized. For this site density, the turnover frequency is 0.05 sec^{-1} at 0°C and 1.33×10^4 N/m^2 olefin pressure. Of course this is a lower limit of the turnover frequency since in reality a much smaller fraction of the total Mo atoms may be responsible for this reaction.

The isotherms of NO adsorbed on this catalyst indicate that the volume of NO chemisorbed is about 4.0 cm^3 (STP)/g of catalyst. This number is the equivalent of 1.08×10^{20} molecules of NO/g, which is 1.7 times greater than the measured lethal dose for propene metathesis. This is consistent with the suggestion that NO is adsorbed on additional sites beyond those active for the metathesis reaction and that the poisoning molecules are *selectively* seeking out the active sites for reaction at the higher temperature.

The ir spectrum of NO on Mo/Al$_2$O$_3$ has been attributed to a dinitrosyl complex (*21–23*). The ir spectrum of the 50–50% mixture of ^{14}NO and ^{15}NO (Fig. 9) along with the difference in thermal stability of the 1796 cm^{-1} band and the 1710 cm^{-1} band (Fig. 10) indicate that at least two monomeric NO species give rise to these absorption bands rather than a dinitrosyl complex. The band at 1875 cm^{-1} may be due to NO adsorbed on cobalt since it is completely missing from the ir spectrum on the catalyst that lacked cobalt (Fig. 11).

By comparing the absorption frequency of adsorbed NO molecules with the stretching frequency of NO in various complexes, one may obtain information about the type of bonding that is taking place during chemisorption. Terenin and co-workers (*24–26*) have investigated in considerable detail the infrared spectra of NO adsorbed on transition metals. Their results support our claim that the band at 1875 cm^{-1} is due to NO on cobalt, with a double ionic bond between cobalt and NO. The bands at 1796 and 1710 cm^{-1} are less clearly identified but may be due to NO adsorbed on Mo by coordinative covalent and covalent bonds, respectively. The assignment of these bands is in agreement with the thermal stability observed for the three species. One would expect that a residual repulsion between the cobalt cation and the nitrosonium ion would result in a weak ionic bond. This species was the least stable of the three. Also, one would expect the covalent bond to be stronger than the coordinative covalent bond, in agreement with the observed order of stability when the sample was heated and evacuated.

CONCLUSIONS

Propene metathesis has been found to follow Langmuir–Hinshelwood kinetics. From titrative poisoning with dosed amounts of NO, the active site density for the reaction on $CoMo/Al_2O_3$ is $2.5 \times 10^{13}/cm^2$. This is an *upper limit* to the active site density and represents at most only 14% of the total molybdenum atoms in the catalyst. The turnover frequency calculated from this active site concentration is 0.05 sec^{-1} at a pressure of 1.33×10^4 N/m^2 at 0°C.

The ir spectrum of NO adsorbed on $CoMo/Al_2O_3$ shows three strong bands which have distinctly different thermal stabilities and are likely due to three different species. The species responsible for the least thermally stable 1875 cm^{-1} band is probably NO adsorbed via a double ionic bond to Co atoms. The 1796 and 1710 cm^{-1} bands may possibly arise from NO bonded to Mo by coordinative covalent and covalent bonds, respectively.

ACKNOWLEDGMENTS

The authors are grateful to Haldor Topsøe A/S (Copenhagen, Denmark) and the Robert A. Welch Foundation for financial support.

REFERENCES

1. Parekh, B. S., and Weller, S. W., *J. Catal.* **47,** 100 (1977).
2. Liu, H.-C., Yuan, L., and Weller, S. W., *J. Catal.* **61,** 282 (1980).
3. Ramakrishnan, N. R., and Weller, S. W., *J. Catal.* **67,** 237 (1981).
4. Yao, H. C., *J. Catal.* **70,** 440 (1981).
5. Millman, W. S., and Hall, W. K., *J. Catal.* **59,** 311 (1979).
6. Hall, W. K., and Millman, W. S., *Proc. 7th Inter. Congr. Catal.* 1304 (1980).
7. Lombardo, E. A., Houalla, M., and Hall, W. K., *J. Catal.* **51,** 256 (1978).
8. Lombardo, E. A., Lo Jacono, M., and Hall, W. K., *J. Catal.* **51,** 243 (1978).
9. Lombardo, E. A., Lo Jacono, M., and Hall, W. K., *J. Catal.* **64,** 150 (1980).
10. Goldwasser, J., Engelhardt, J., and Hall, W. K., *J. Catal.* **70,** 275 (1981).
11. Goldwasser, J., Engelhardt, J., and Hall, W. K., *J. Catal.* **71,** 381 (1981).
12. Engelhardt, J., Goldwasser, J., and Hall, W. K., *J. Catal.* **76,** 48 (1982).
13. Topsoe, N., and Topsoe, H., *J. Catal.* **75,** 354 (1982).
14. Brenner, A., and Burwell, R. L., *J. Catal.* **52,** 364 (1978).
15. Moffat, A. J., and Clark, A., *J. Catal.* **17,** 264 (1970).
16. Moffat, A. J., Johnson, M. M., and Clark, A., *J. Catal.* **22,** 379 (1971).
17. Begley, J. W., and Wilson, R. T., *J. Catal.* **9,** 375 (1967).
18. Lewis, M. J., and Wills, G. B., *J. Catal.* **15,** 140 (1969).
19. Lewis, M. J., and Wills, G. B., *J. Catal.* **20,** 182 (1971).
20. Rosynek, M. P., and Hightower, J. W., *Proc. 5th Inter. Congr. Catal.* 851 (1972).
21. Millman, W. S., and Hall, W. K., *J. Phys. Chem.* **83,** 427 (1979).

22. Kazusaka, A., and Howe, R. F., *J. Catal.* **63,** 447 (1980).
23. Okamoto, Y., Katoh, Y., Mori, Y., Imanaka, T., and Teranishi, S., *J. Catal.* **70,** 445 (1981).
24. Terenin, A. N., and Roev, L. M., *Actes Deuxieme Congr. Inter. Catal.* **2,** 2183 (1961).
25. Roev, L. M., and Terenin, A. N., *Opt. Spectroskip.* **7,** 756 (1959).
26. Roev, L. M., and Alekseev, A. V., *in* "Elementary Photoprocesses in Molecules" (B. S. Neporent, Ed.), p. 260 (Engl. trans.). Consultants Bureau, New York, 1968.