

## CH<sub>3</sub>NO<sub>2</sub> Addition to CO Hydrogenation over a Ru/KY Catalyst

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CH<sub>3</sub>NO<sub>2</sub> addition to CO hydrogenation over Ru/KY led to the formation of partially dehydrogenated CH<sub>x</sub> groups, which became indistinguishable from CH<sub>x</sub> groups derived from CO hydrogenation. Random reaction of these groups provided hydrocarbon formation along the same reaction pathway that normally occurs during CO hydrogenation over Ru/KY. The additional CH<sub>x</sub> groups from CH<sub>3</sub>NO<sub>2</sub> enhanced the rates of chain initiation and propagation to similar extents, leading to increases in the rates of formation of C<sub>2</sub><sup>+</sup> hydrocarbons. Some of these CH<sub>x</sub> groups were further dehydrogenated and formed surface carbon, resulting in the incorporation of some carbon from CH<sub>3</sub>NO<sub>2</sub> into CO<sub>2</sub>, an increase the rate of catalyst deactivation, and suppression of secondary reactions on the support. © 1991 Academic Press, Inc.

### I. INTRODUCTION

In previous work our group has reported on the addition of probe molecules containing alkyl groups to CO hydrogenation reactions over Ru catalysts (1-3). Recently, results from our studies involving CH<sub>3</sub>NO<sub>2</sub> (2) and C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> (3) addition to CO hydrogenation over Ru/SiO<sub>2</sub> indicated that adsorbed C<sub>y</sub>H<sub>x</sub> groups derived from these nitroparaffins were incorporated into hydrocarbon formation through their interaction with other surface species generated from CO. This occurred without any major disturbance to the intrinsic hydrocarbon formation from CO hydrogenation which allowed us to make mechanistic inferences about the reaction pathway.

The work presented here extends these studies of CH<sub>3</sub>NO<sub>2</sub> as a probe molecule to CO hydrogenation over a Ru/KY catalyst. This catalyst differs significantly in terms of its product selectivity from the Ru/SiO<sub>2</sub> catalyst previously studied. The CH<sub>3</sub>NO<sub>2</sub> addition data presented here and elsewhere (2) contribute to our understanding of the intrinsic differences in the catalytic behav-

ior of these two catalysts during CO hydrogenation.

### II. EXPERIMENTAL

*Catalyst preparation and characterization.* The KY support used in this work was prepared by ion exchange of NaY zeolite (Strem Chemicals) with KNO<sub>3</sub> (Alpha Products, ultrapure). The preparation procedure consisted of a three-step exchange in which the ion-exchange solution containing a two-fold equivalent excess of KNO<sub>3</sub> was replenished three times while being stirred with NaY at 333 K over a period of 72 h. This procedure led to a K : Na molar ratio in the zeolite of 65 : 1 as determined by atomic absorption (AA).

The Ru-loaded zeolite catalyst was prepared by a further ion exchange of the KY zeolite with Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (Strem Chemicals). The weight loading of Ru was a nominal 3 wt%. After a reduction pretreatment the catalyst was analyzed by inductively coupled plasma (ICP) for Ru and AA for K giving 2.47 and 6.76 wt%, respectively. More detailed procedures for the preparation and pretreatment of this catalyst have been described elsewhere (4). In our previous work (1), the Ru/KY catalyst used here was designated as Ru(KK).

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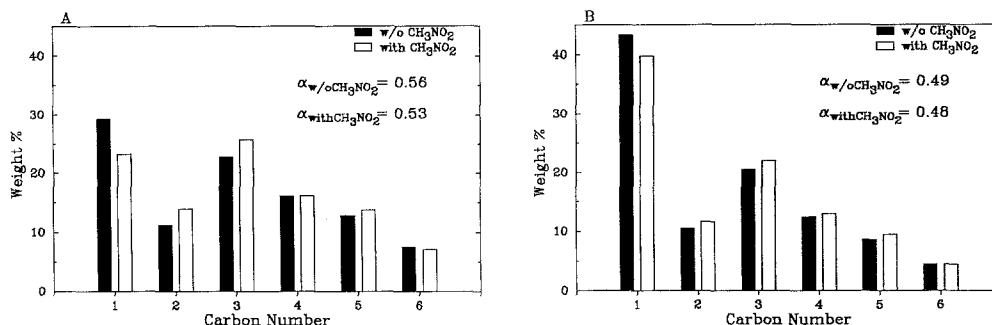


FIG. 1. Product distribution for CO hydrogenation on Ru/KY in the absence and presence CH<sub>3</sub>NO<sub>2</sub>. (A)  $T = 523$  K, He:CO:H<sub>2</sub> = 1:2:2. (B)  $T = 523$  K, He:CO:H<sub>2</sub> = 1:1:3.

**Reaction studies.** CO hydrogenation reactions were carried out in a downflow quartz tubular microreactor of 1-cm diameter. Prereduced catalyst, 0.25 g, was loaded on a porous ceramic frit in the center of the reactor where it was reduced under a H<sub>2</sub> stream of 3 liter/h at 673 K for 2 h. Ultrahigh purity He (Linde), H<sub>2</sub> (Linde), and CO (Matheson) were further purified by flowing through molecular sieve traps. The H<sub>2</sub> stream was also passed through a Deoxo unit prior to the molecular sieve trap while the CO stream was further purified by an activated carbon hydrocarbon trap (Scott).

Reaction conditions for CO hydrogenation were 101 kPa, 523 K, 1:2:2 (condition A) or 1:1:3 (condition B) mixtures of He:CO:H<sub>2</sub> flowing at 3 liter/h. Nitromethane addition was accomplished by passing part of the reactants through a saturator containing CH<sub>3</sub>NO<sub>2</sub> (Aldrich, 99+% purity) which was kept at 313 K. A hydrogen bracketing technique was used during these experiments in which the catalyst was "cleaned" with H<sub>2</sub> at 673 K for 1 h after every reaction period of 5 min. It was then flushed with He for 30 min at the reaction temperature prior to the start of a new CO hydrogenation reaction. Product analysis was carried out using a Perkin-Elmer Sigma 300 gas chromatograph fitted with thermal conductivity (TCD) and flame ionization (FID) detectors. Product separation was accomplished by use of either a 2 m × 1/8 in. o.d. GP 80/100 Carbopack c/0.19% Picric

Acid column or by a 6 ft × 1/8 in. Porapak R in series with a 6 ft × 1/8 in. Porapak Q column. Peak areas were determined by Varian 4270 and Hewlett-Packard 3380S integrators.

CO hydrogenation in the presence of <sup>13</sup>C-labeled CH<sub>3</sub>NO<sub>2</sub> (Aldrich, 99% atom <sup>13</sup>C) was also studied. Reaction products were collected for injection into and analysis by a GC-MS system (Extrel Series 800) using the same columns described above.

### III. RESULTS

*CO hydrogenation over Ru/KY in the absence and presence of CH<sub>3</sub>NO<sub>2</sub>.* Comparisons of the rates of formation of the products observed during CO hydrogenation in the absence and in the presence of CH<sub>3</sub>NO<sub>2</sub> are shown in Table 1, while Fig. 1 shows the carbon fraction selectivities. Table 1 indicates that the rate of formation of the higher hydrocarbons increased upon CH<sub>3</sub>NO<sub>2</sub> addition while a smaller increase was observed in the rate of formation of CH<sub>4</sub>. The results shown in Fig. 1 indicate that there were only slight changes in the overall product selectivity caused by CH<sub>3</sub>NO<sub>2</sub> addition, which was also reflected in the invariance of the calculated values of  $\alpha$ , the chain growth probability. The amount of CH<sub>3</sub>NO<sub>2</sub> present in the reactants for both conditions was 2.7 vol% and the amount of unreacted CH<sub>3</sub>NO<sub>2</sub> in the products did not exceed 2% of the original amount added.

Table 2 shows a comparison of the olefin-

TABLE 1

Product Distributions CO Hydrogenation over Ru/KY in the Absence and Presence of CH<sub>3</sub>NO<sub>2</sub>

Carbon fraction	Condition A		Condition B	
	W/o CH <sub>3</sub> NO <sub>2</sub> ( $\mu\text{g}/\text{min}$ )	With CH <sub>3</sub> NO <sub>2</sub> ( $\mu\text{g}/\text{min}$ )	W/o CH <sub>3</sub> NO <sub>2</sub> ( $\mu\text{g}/\text{min}$ )	With CH <sub>3</sub> NO <sub>2</sub> ( $\mu\text{g}/\text{min}$ )
C1	38.9	41.8	156.5	165.4
C2	15.0	25.0	38.0	48.1
C3	30.3	46.4	74.4	91.3
C4	21.4	29.0	44.9	53.9
C5	17.0	24.8	31.3	39.4
C6	10.1	12.9	16.4	18.6
Total	132.7	179.9	361.5	416.7
CO conv., % <sup>a</sup>	1.1		5.9	
TON, <sup>b</sup> CH <sub>4</sub>	1.2	1.3	4.9	5.2
TON, <sup>b</sup> C <sub>2</sub> <sup>+</sup> hyd.	3.3	4.9	7.3	9.0
CO <sub>2</sub> <sup>c</sup>	6.6	564.9	9.4	464.3

Note. Reaction conditions: 523 K; 101 kPa; GHSV = 12 liter/h\*g cat.; 2.7 vol% CH<sub>3</sub>NO<sub>2</sub> in reactants. (A) He:CO:H<sub>2</sub> = 1:2:2. (B) He:CO:H<sub>2</sub> = 1:1:3.

<sup>a</sup> CO conversion into hydrocarbon products.

<sup>b</sup> Turnover frequency, s<sup>-1</sup> × 10<sup>3</sup>.

<sup>c</sup>  $\mu\text{g}/\text{min}$ .

to-paraffin molar ratios of the C2 and C3 carbon fractions. It can be seen that there were small increases in the production of olefins in the presence of CH<sub>3</sub>NO<sub>2</sub>. Analysis of the C4 hydrocarbon selectivity shown in Fig. 2 demonstrates that an increase in the selectivity for the linear  $\alpha$ -olefin, 1-butene, occurred during CH<sub>3</sub>NO<sub>2</sub> addition. This C4 selectivity change took place, however, at a

constant overall olefin/paraffin ratio, as a result of a decrease in the selectivity for linear  $\beta$ -olefins rather than as a result of changes in the selectivity for the linear or branched paraffin products. Longer reaction times resulted in even more pronounced increases in the linear  $\alpha$ -olefins selectivity. These observations also apply for the C5 hydrocarbon fraction.

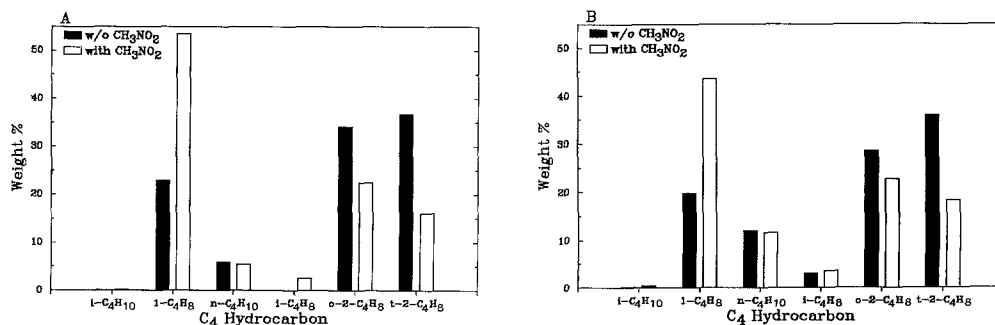


FIG. 2. Distribution of C4 products for CO hydrogenation on Ru/KY in the absence and presence of CH<sub>3</sub>NO<sub>2</sub>. (A)  $T = 523$  K, He:CO:H<sub>2</sub> = 1:2:2. (B)  $T = 523$  K, He:CO:H<sub>2</sub> = 1:1:3.

TABLE 2

Olefin: Paraffin Molar Ratios for CO Hydrogenation over Ru/KY in the Absence and Presence of  $\text{CH}_3\text{NO}_2$ 

Olefin: paraffin	Condition A		Condition B	
	W/o $\text{CH}_3\text{NO}_2$	With $\text{CH}_3\text{NO}_2$	W/o $\text{CH}_3\text{NO}_2$	With $\text{CH}_3\text{NO}_2$
$\text{C}_2\text{H}_4 : \text{C}_2\text{H}_6$	3.6	6.1	0.9	1.3
$\text{C}_3\text{H}_6 : \text{C}_3\text{H}_8$	21.6	28.2	8.6	12.0

Note. Reaction conditions: 523 K; 101 kPa; GHSV = 12 liter/h\* $\text{g}$  cat; 2.7 vol%  $\text{CH}_3\text{NO}_2$  in reactants. (A) He: CO:  $\text{H}_2$  = 1:2:2. (B) He: CO:  $\text{H}_2$  = 1:1:3.

The extent of  $^{13}\text{C}$  incorporation into C1–C3 hydrocarbons when  $^{13}\text{CH}_3\text{NO}_2$  was used is shown in Table 3. Higher hydrocarbons have more complex fragmentation patterns which preclude any quantitative analysis. However, the extent of  $^{13}\text{C}$  incorporation into higher hydrocarbons is qualitatively illustrated in Fig. 3 for 1-butene. Table 3 and Fig. 3 indicate clearly that addition of  $^{13}\text{CH}_3\text{NO}_2$  resulted in extensive and random  $^{13}\text{C}$  incorporation in all the hydrocarbons produced. This is the same observation that was made for  $^{13}\text{CH}_3\text{NO}_2$  incorporation during CO/ $\text{H}_2$  reactions over Ru/ $\text{SiO}_2$  (2).

The incorporation of  $^{13}\text{C}$  into the hydrocarbon products appears to be directly responsible for the increase in hydrocarbon products which was observed during addi-

tion of the probe molecules. For condition A, the amount of  $^{13}\text{C}$  found in the C1–C3 fraction was 3.11  $\mu\text{mol}/\text{min}$ . This corresponds to an average of 41% of the carbon being present as  $^{13}\text{C}$ . If we assume a similar  $^{13}\text{C}$  incorporation for the C4–C6 products, we calculate the total amount of  $^{13}\text{C}$  present in the products to be 5.1  $\mu\text{mol}/\text{min}$ . This number may be compared to the overall increase in total carbon in the products during  $\text{CH}_3\text{NO}_2$  addition, 3.35  $\mu\text{mol}/\text{min}$ . From these numbers we find that the actual CO conversion has changed only slightly from 1.1 to 0.89% upon addition of the probe molecule. A similar calculation for the reaction under condition B reveals that the amount of CO converted to products changed from 5.9 to 5.3% when  $\text{CH}_3\text{NO}_2$  was added. The fact that the  $\text{CH}_3\text{NO}_2$  has

TABLE 3

 $^{13}\text{C}$  Distribution in Products of CO Hydrogenation over Ru/KY in the Presence of  $^{13}\text{CH}_3\text{NO}_2$ 

Product	Condition A		Condition B	
	$^{13}\text{C}$ mol%	$\mu\text{mol } ^{13}\text{C}/\text{min}$	$^{13}\text{C}$ mol%	$\mu\text{mol } ^{13}\text{C}/\text{min}$
$\text{CH}_4$	35	0.91	20	2.06
$\text{C}_2\text{H}_4$	51	0.77	26	0.50
$\text{C}_2\text{H}_6$	30	0.07	30	0.42
$\text{C}_3\text{H}_6$	42	1.35	24	1.44
Total	—	3.11	—	4.42
$^{13}\text{CO}_2$	17	2.19	7	0.74

Note. Reaction conditions: 523 K; 101 kPa; GHSV = 12 liter/h\* $\text{g}$  cat.; 2.7 vol% (55.6  $\mu\text{mol}/\text{min}$ )  $^{13}\text{CH}_3\text{NO}_2$  in reactants. (A) He: CO:  $\text{H}_2$  = 1:2:2. (B) He: CO:  $\text{H}_2$  = 1:1:3.

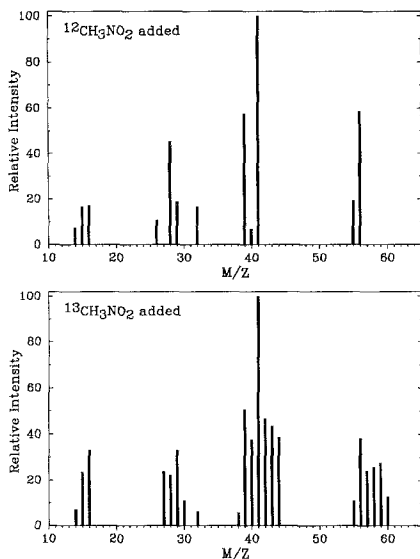


FIG. 3. MS Spectra obtained for 1-butene with <sup>13</sup>C-labeled and nonlabeled CH<sub>3</sub>NO<sub>2</sub> (Condition A).

such a small effect on the reactivity of CO suggests that the presence of the probe molecule did not significantly perturb the intrinsic behavior of the catalyst for CO hydrogenation.

Table 1 also shows that there were increases of nearly two orders of magnitude in the amount of CO<sub>2</sub> produced caused by CH<sub>3</sub>NO<sub>2</sub> addition. Interestingly, <sup>13</sup>CH<sub>3</sub>NO<sub>2</sub> addition showed that this large increase in CO<sub>2</sub> resulted not from extensive incorporation of <sup>13</sup>C from the probe molecule, but from increased consumption of <sup>12</sup>CO. Less than 20% of the CO<sub>2</sub> product formed during addition of <sup>13</sup>CH<sub>3</sub>NO<sub>2</sub> contained <sup>13</sup>C. This corresponds to less than 4% of the original carbon from CH<sub>3</sub>NO<sub>2</sub> in the reactants. There was no evidence using FID, TCD, and GC-MS of any compounds containing nitrogen atoms, such as HCN, NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub>CN, and NO<sub>2</sub>, in the products with the possible exception of N<sub>2</sub> and NO which could not be separated from CO in the columns used.

This information obtained from the <sup>13</sup>C-labeled nitromethane experiments may also be used to establish a material balance and

determine the fate of the probe molecule. All the <sup>13</sup>C incorporated in the hydrocarbon products and in the CO<sub>2</sub>, as well as the unreacted nitromethane, accounts for less than 20% of the total nitromethane added. This indicates that a substantial amount of the added probe molecule was continually being retained on the catalyst surface. The experiments discussed below involving CH<sub>3</sub>NO<sub>2</sub> reactivity on the support alone confirm this suggestion that the support can act as a "sink" for the probe molecule in the form of surface carbon, irreversibly adsorbed CH<sub>3</sub>NO<sub>2</sub>, or some intermediate species.

The degree of <sup>13</sup>C incorporation in the products was observed to increase with reaction time. The rate of catalyst deactivation increased by about 27% upon CH<sub>3</sub>NO<sub>2</sub> addition but the original catalyst activity could be easily restored by the hydrogen bracketing procedure used in between reaction periods.

*CH<sub>3</sub>NO<sub>2</sub> reactivity under various conditions other than CO hydrogenation.* The reaction of CH<sub>3</sub>NO<sub>2</sub> (1.4 vol%) in He and H<sub>2</sub> (1:1, 2.4 liter/h) in the absence of CO at 523 K over Ru/KY was also studied. Under these conditions less than 2% of the original CH<sub>3</sub>NO<sub>2</sub> in the reactants was found unreacted in the products. About 97+ wt% of the hydrocarbon products was CH<sub>4</sub>, about 2 wt% was C<sub>2</sub>H<sub>6</sub>, and there were traces of C<sub>3</sub>H<sub>8</sub> and *n*-C<sub>4</sub>H<sub>10</sub> (less than 1 wt% combined). No compounds other than these hydrocarbons were found by FID. Only about 80% of the original carbon atoms in CH<sub>3</sub>NO<sub>2</sub> were present in the hydrocarbons in the products again suggesting that the catalyst surface may retain significant amounts of the probe molecule.

The same experimental conditions described above were used to study CH<sub>3</sub>NO<sub>2</sub> decomposition in He and CO (1:1) over Ru/KY in the absence of H<sub>2</sub>. Under this gas feed composition, less than 3% of the CH<sub>3</sub>NO<sub>2</sub> in the reactants was found unreacted in the products. The amount of carbon in the hydrocarbons in the products accounted for less than 0.3% of the carbon

originally present in  $\text{CH}_3\text{NO}_2$ . Hence, in this case the catalyst "consumed" nearly all the  $\text{CH}_3\text{NO}_2$ .

The reactivity of  $\text{CH}_3\text{NO}_2$  with the zeolite support was investigated in similar CO hydrogenation reactions over the KY zeolite support in the absence of Ru. The behavior of the probe molecule toward the support was similar to its interaction with RuKY in that all was retained by the support. Less than 4% of the  $\text{CH}_3\text{NO}_2$  in the reactants appeared unreacted in the products. The only hydrocarbons detected in the products were traces (less than 50-ppm vol each) of  $\text{CH}_4$  and  $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ . Traces of two compounds that GC-MS analysis indicated could possibly be HCN (less than 30 ppm vol) and  $\text{CH}_3\text{ONO}$  (less than 800 ppm vol) were found. No other compounds containing nitrogen atoms were detected by FID, TCD, or GC-MS analysis although the presence or absence of  $\text{N}_2$  and NO could not be determined because of their overlap with CO in the columns used. A very small amount of  $\text{CO}_2$  was present in the products at levels of about 0.4% vol.

#### IV. DISCUSSION

Although the addition of  $\text{CH}_3\text{NO}_2$  to CO hydrogenation over Ru/KY had only minor effects in the carbon fraction selectivity, the total rate of formation of hydrocarbons was significantly enhanced by  $\text{CH}_3\text{NO}_2$  addition. The latter observation requires that the rates of chain initiation,  $R_i$ , and chain growth,  $R_p$ , increased as a result of  $\text{CH}_3\text{NO}_2$  addition. Furthermore, since the values of  $\alpha$  were not changed by the addition of  $\text{CH}_3\text{NO}_2$  it can also be inferred that the increases in  $R_i$  and  $R_p$  were of similar magnitudes.  $\text{CH}_3\text{NO}_2$  also caused small increases in the olefinic character of the products for the C2 and C3 carbon fractions, suggesting that the surface coverage of hydrogen,  $\theta_{\text{H}}$ , was slightly reduced upon  $\text{CH}_3\text{NO}_2$  addition. The observed incorporation of  $^{13}\text{C}$  from labeled  $\text{CH}_3\text{NO}_2$  into the hydrocarbon products was

substantial, took place in conjunction with chain growth involving surface species originating from CO hydrogenation, and involved hydrocarbons of all chain lengths. At least two-thirds of the  $\text{CH}_x$  groups derived from  $\text{CH}_3\text{NO}_2$  which were incorporated into products ended up in higher hydrocarbons rather than in  $\text{CH}_4$ .

Some important comparisons can be noted between these results and those for  $\text{CH}_3\text{NO}_2$  addition to Ru/ $\text{SiO}_2$  (2). For both catalyst systems, the significant increase in the overall production of hydrocarbons observed during  $\text{CH}_3\text{NO}_2$  addition suggested extensive incorporation of  $\text{CH}_x$  units from the probe molecule into hydrocarbon products. However, for Ru/ $\text{SiO}_2$ , large shifts in selectivity toward higher hydrocarbons were manifested by significant increases in  $\alpha$ ; hence the value of  $R_i$  increased much less than did  $R_p$  for Ru/ $\text{SiO}_2$ , compared to equal increases in the two rates observed here for Ru/KY. The increase in the rate of C2 hydrocarbon formation caused by  $\text{CH}_3\text{NO}_2$  addition to Ru/ $\text{SiO}_2$  was much smaller than that observed for the increase in the production of the  $\text{C}_3^+$  hydrocarbons, compared to similar rate increases for each carbon fraction for Ru/KY. This suggests a possible association between the rate of C2 hydrocarbon formation and  $R_i$ . A special role of a  $\text{C}_2$  surface species in chain initiation has been previously proposed by a number of other workers based on theoretical (5, 6) and experimental (7, 8) considerations. Furthermore, results indicating that  $\text{C}_2$  fragments derived from  $\text{C}_2\text{H}_5\text{NO}_2$  (3),  $\text{C}_2\text{H}_4$  (9), or from  $\text{C}_2\text{H}_5\text{OH}$  (10, 11) can be incorporated in the hydrocarbon formation pathway through chain initiation also offer additional indirect support for this proposal.

Why the  $\text{CH}_x$  groups derived from  $\text{CH}_3\text{NO}_2$  participate to different extents in the enhancement of the rate of chain initiation for these two catalysts is an interesting question. Comparison with the data of Ref. (2) shows that a more significant suppression of  $\text{H}_2$  surface coverage occurred during

CH<sub>3</sub>NO<sub>2</sub> addition for Ru/SiO<sub>2</sub>. It may be suggested that CH<sub>x</sub> groups originating from CH<sub>3</sub>NO<sub>2</sub> were more dehydrogenated on Ru/KY than on Ru/SiO<sub>2</sub>. This is supported by the differences in the olefin/paraffin ratios between the two catalysts during probe molecule addition as well as by several other observations. CH<sub>3</sub>NO<sub>2</sub> addition to the reactants had no effect on the deactivation rate of Ru/SiO<sub>2</sub> while it caused Ru/KY to deactivate faster. Facile restoration of activity following hydrogen treatment suggested that the faster deactivation rate on the Ru/KY catalyst was the result of additional surface carbon build up from CH<sub>3</sub>NO<sub>2</sub> and not from some irreversible poisoning. Also, the <sup>13</sup>C-labeled CH<sub>3</sub>NO<sub>2</sub> experiments indicated that the probability that a labeled <sup>13</sup>C atom from CH<sub>3</sub>NO<sub>2</sub> would end up in the C<sub>2</sub> and C<sub>2</sub><sup>+</sup> hydrocarbons was higher for Ru/KY than for Ru/SiO<sub>2</sub>. These observations may be interpreted as an indication that the rate of C<sub>2</sub> hydrocarbon formation, and possibly the rate of chain initiation, depends at least in part on the presence of a CH<sub>x</sub> surface species that is more dehydrogenated than methylene. Our results are consistent with a recent suggestion (12) that an adsorbed vinyl species, (CH<sub>2</sub> = CH-M), formed by the reaction between adsorbed methylene and methyne, CH, species play a special role in initiating hydrocarbon growth during CO hydrogenation.

Joyner (6) proposed recently that the rate-determining step in the formation of higher hydrocarbons is the formation of the C<sub>2</sub> surface intermediate ethylidyne by the reaction of two methylene groups. Once this species is formed chain growth proceeds rapidly by the addition of CH<sub>2</sub> to the growing chains. If one uses Joyner's proposed mechanism to build a kinetic model for the concentration of surface species it follows that the rate of formation of the C<sub>2</sub> species is proportional to [CH<sub>2</sub>]<sup>2</sup>, whereas the rate of formation of chains of *n* carbons atoms, C<sub>*n*</sub> (*n* ≥ 3), is proportional to [CH<sub>2</sub>]<sup>*n*</sup>. Assuming that the hydrocarbon products are formed by the de-

sorption of these species, increasing the concentration of CH<sub>2</sub> groups on the surface should always increase the rate of formation of higher hydrocarbons proportionally more than the rate of formation of C<sub>2</sub> hydrocarbons. Indeed, this was the case for CH<sub>3</sub>NO<sub>2</sub> addition to CO hydrogenation over Ru/SiO<sub>2</sub>, but the results presented here for Ru/KY also indicate that it is possible to increase the rates of formation of C<sub>2</sub> and higher hydrocarbons by similar amounts by the addition of CH<sub>x</sub> groups.

Even in the absence of CH<sub>3</sub>NO<sub>2</sub>, Ru/SiO<sub>2</sub> and Ru/KY differed greatly in their capacities to hydrogenate surface carbon species. Olefin/paraffin ratios were an order of magnitude lower for Ru/SiO<sub>2</sub> (2). Perhaps the nature of the C<sub>2</sub> fragment formed, vinyl vs ethylidyne, is related to the availability of surface hydrogen, and perhaps this parameter in some way dictates the relative rates of formation of C<sub>2</sub> and higher hydrocarbons (or *R<sub>i</sub>* compared to *R<sub>p</sub>*). Another way of stating this hypothesis is that any process which augments hydrocarbon production rates on a hydrogen-starved surface such as Ru/KY will enhance equally *R<sub>i</sub>* and *R<sub>p</sub>*; by contrast, on a hydrogen-rich surface such as Ru/SiO<sub>2</sub>, *R<sub>p</sub>* will be enhanced more than will *R<sub>i</sub>*.

The large increase in the rate of formation of CO<sub>2</sub> with addition of the probe molecule was also noted for Ru/SiO<sub>2</sub>. In that case, all of the carbon in the CO<sub>2</sub> originated from CO and not from CH<sub>3</sub>NO<sub>2</sub>. It was suggested that NO<sub>2</sub> groups from the probe molecule reacted with hydrogen to yield N<sub>2</sub> and H<sub>2</sub>O. The water reacted with the abundant "spectator" CO on the surface to produce CO<sub>2</sub> and H<sub>2</sub> in the water-gas shift reaction. Most of the CO<sub>2</sub> produced during probe molecule addition over Ru/KY was probably formed by the same mechanism, but the observation that some CO<sub>2</sub> produced during <sup>13</sup>CH<sub>3</sub>NO<sub>2</sub> addition was <sup>13</sup>C-labeled suggested a second mechanism involving complete dehydrogenation of some of the CH<sub>x</sub> groups derived from CH<sub>3</sub>NO<sub>2</sub>. The surface carbon thus formed could then react with H<sub>2</sub>O to form

CO<sub>2</sub> (2). This CO<sub>2</sub> formation mechanism is also supported by the results which show no CO<sub>2</sub> formation when the reaction of CH<sub>3</sub>NO<sub>2</sub> was carried out in the absence of H<sub>2</sub>.

The large degree of disappearance of CH<sub>3</sub>NO<sub>2</sub> without the formation of products containing carbon during its reaction over the support alone indicates that CH<sub>3</sub>NO<sub>2</sub> can interact extensively with the zeolite support. Furthermore, the lower selectivity toward  $\beta$ -olefins production appears to be the result of interactions between CH<sub>3</sub>NO<sub>2</sub> and the weak Brønsted acid sites on the zeolite support. Results on 1-butene isomerization reactions carried out over the KY support used in this work and results reported by Oukaci *et al.* (13) for the same reaction over various Y zeolites indicate that the selectivity for  $\beta$ -olefins during CO hydrogenation over Y-supported Ru catalysts is very similar to that obtained during 1-butene isomerization on the support alone. Thus, it appears that CH<sub>3</sub>NO<sub>2</sub> interacted with the zeolite support to neutralize the acid sites involved in double-bond shift and *cis-trans* isomerization reactions that lead to the production of  $\beta$ -olefins. The nature of this interaction is not known yet but our previous work (2, 3) and that of Ponec (14) have shown that nitroparaffins can strongly interact with other supports.

#### V. CONCLUSION

The addition of CH<sub>3</sub>NO<sub>2</sub> to CO hydrogenation over a Ru/KY catalyst resulted in an increase in the overall rate of higher hydrocarbon formation. This occurred without the significant changes in the carbon fraction distribution or the olefin : paraffin ratios that were observed previously for Ru/SiO<sub>2</sub>. This reflected similar increases in the rates of chain initiation and propagation due to the incorporation of CH<sub>x</sub> groups derived from CH<sub>3</sub>NO<sub>2</sub> into the normal hydrocarbon formation pathway involving surface species generated from CO hydrogenation. These observations appear to be related to the intrinsically low, as compared to Ru/SiO<sub>2</sub>,

hydrogenation ability of the Ru/KY catalyst during CO hydrogenation which resulted in extensive dehydrogenation of CH<sub>x</sub> groups derived from CH<sub>3</sub>NO<sub>2</sub>. They also support a proposed hydrocarbon formation mechanism that postulates that the formation of a C<sub>2</sub> surface intermediate that initiates chain growth involves the reaction of CH and CH<sub>2</sub> surface species.

The interaction of CH<sub>3</sub>NO<sub>2</sub> with the support resulted not only in the "disappearance" of large amounts of CH<sub>3</sub>NO<sub>2</sub> but also in the neutralization of acidic sites. The incorporation of carbon from CH<sub>3</sub>NO<sub>2</sub> into the additional CO<sub>2</sub> produced appeared to be related to the deposition of surface carbon due to extensive dehydrogenation of CH<sub>3</sub>NO<sub>2</sub>-derived CH<sub>x</sub> groups.

These results indicate once again the usefulness of CH<sub>3</sub>NO<sub>2</sub> as a probe molecule capable of providing information about the mechanistic features of the hydrocarbon formation pathways during CO hydrogenation.

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