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Probe Molecule Studies of CO Hydrogenation over Ru/SiO_2

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The effects of the addition of small amounts of CH_3NO_2 to the reactants during CO hydrogenation were investigated under various reaction conditions. The major changes in the product distribution of CO hydrogenation on Ru/SiO_2 caused by CH_3NO_2 addition to the reactants included substantial reduction of CH_4 production, increased production of hydrocarbons in the C3 to C6 carbon fractions, and enhanced selectivity toward linear olefinic products. A substantial incorporation of carbon originating from the added CH_3NO_2 into these hydrocarbon products was observed. Changes in the product distribution took place without significant disturbance of the main reaction pathways leading to hydrocarbon formation, offering great potential for the use of CH_3NO_2 as a probe molecule in the study of the mechanism of CO hydrogenation.

I. INTRODUCTION

Attempts at elucidating the mechanism of CO hydrogenation over supported metal catalysts by adding probe molecules can be traced back to at least as early as 1951 (*1*, *2*). Although use of this technique is an indirect way of studying surface reaction mechanisms, it allows for *in situ* studies under conditions which usually cannot be probed by more direct instrumental methods such as surface spectroscopic techniques. Different probe molecules, ranging from alcohols (*1–4*), to open chain olefins (*4–6*) and cycloolefins (*6*, *7*), to CH_2N_2 (*8*, *9*), and to alkyl halides (*10*, *11*) have been used for these studies. A similar concept of "chemical trapping" was proposed by Deluzarche and co-workers (*12*) and involves the use of alkylating agents, such as methyl iodide and dimethyl sulfate, to generate alkyl groups which attack the bonds between an adsorbed species and the surface of the catalyst; an alkyl group is postulated to insert at each former place of attachment to the surface, and the original surface species is deduced from the product which is formed. This technique was first used in static systems under conditions of temperature and pressure far removed from those of CO hydrogenation reactions. It was later expanded in this laboratory to *in situ* conditions by the addition of CH_3I during CO hydrogenation over RuKY catalysts (*11*). This work provided strong evidence for chemical trapping of active surface species by methyl groups. However, addition of CH_3I also had the undesirable result of poisoning the catalyst.

In an attempt to better understand the role and interactions of adsorbed alkyl groups presumably involved in hydrocarbon production during CO hydrogenation over a Ru/SiO_2 catalyst, we have searched for compounds with the potential for generating alkyl groups while not poisoning the catalyst. Nitromethane, CH_3NO_2, appeared promising since the C–N bond dissociation energy is comparable to the C–I bond dissociation energy in CH_3I. There is considerable evidence from gas-phase decomposition studies (*13*) that, for CH_3NO_2, the first step in the decomposition in scission of the C–N bond. There have also been some studies of the decomposition of CH_3NO_2 on a Ni (111) surface (*14*), and of CH_3NO_2 and $C_2H_5NO_2$ on Rh (111) and Pt (111) single crystals (*15*), indicating that the decompo-

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sition of nitroparaffins may proceed through pathways ranging from an initial scission of both the C–N and N–O bonds (on Rh) to an initial scission on the N–O bond only (on Ni). It is also known that primary and secondary mononitroparaffins in solution are acidic substances which exist in equilibrium with nitronic acids (aci-form), their tautomeric isomers (*16*). As with CH_2N_2, the aci- form of CH_3NO_2 has a CH_2 group, making it a potential source of methylene groups. Although caution is warranted in extrapolating results from gas-phase pyrolysis, decomposition on single crystals, and solution chemistry to heterogeneous catalytic systems; these studies provided incentive for an investigation of CH_3NO_2 as a potential source of methyl and/or methylene groups. It appeared that NO_2 or other by-products from the scission of the C–N and N–O bonds would be less harmful to the catalyst's overall behavior and activity than other groups containing elements such as halogens or sulfur.

In this paper we report observations and interpretations of the effects of the addition of small amounts of CH_3NO_2 to the reactants during CO hydrogenation over a Ru/SiO_2 catalyst, and how they can be used to better understand the mechanism of hydrocarbon formation during CO hydrogenation.

II. EXPERIMENTAL

Catalyst preparation and characterization. The Ru/SiO_2 catalyst used in this study was prepared by ion exchange using $RuCl_3 \cdot 1.5H_2O$ (Strem Chemicals) and SiO_2 (Strem Chemicals, large pore). Details of the preparation procedure are given elsewhere (*17*). After drying in air at 373 K, the catalyst precursor was decomposed in flowing He at 673 K for 4–5 hr. This pretreatment was followed by a 2-hr reduction by H_2. The metal loading of the catalyst was determined by atomic absorption and found to be 1.8 wt% Ru. The catalyst dispersion and average particle size determined from H_2 chemisorption were found to be 53% and 16 Å. Details of the catalyst characterization are also given in Ref. (*17*).

Reaction studies. CO hydrogenation reactions were carried out in a quartz tubular microreactor of 1 cm diameter. A sample (0.25 g) of the prereduced catalyst was loaded into the reactor where it was reduced under a H_2 stream of 3 liters/hr at 673 K for 2 hr. Ultrahigh purity He (Linde), H_2 (Linde), and CO (Matheson) were further purified by flowing through molecular sieve traps. The H_2 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 or 533 K, and 1 : 2 : 2 or 1 : 1 : 3 mixtures of He : CO : H_2 flowing at 3 liters/hr. Nitromethane addition was accomplished by passing He through a saturator containing CH_3NO_2 (Aldrich, 99+% purity) which was kept at 313 K. A H_2 bracketing technique was used during these experiments in which the catalyst was "cleaned" with H_2 at 673 K for 1 hr 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. Effluent gas analysis was carried out using a Perkin–Elmer Sigma 300 gas chromatograph fitted with thermal conductivity and flame ionization detectors. Product analysis was accomplished by the use of either a 2 m × $\frac{1}{8}$ in. o.d. GP 80/100 Carbopack C/0.19% picric acid column or by a 6 ft × $\frac{1}{8}$ in. Porapak R in series with a 6 ft × $\frac{1}{8}$ in. Porapak Q column. Peak areas were determined by Varian 4270 and Hewlett–Packard 3380S integrators.

CO hydrogenation in the presence of ^{13}C-labeled CH_3NO_2 (Aldrich, 99% atom ^{13}C) was also studied. Reaction products were collected for injection into and analysis by a GC-MS system (Extrel Series 800) using the columns described above.

Finally, a number of tests were also carried out to determine the reactivity of CH_3NO_2 under various conditions of feed composition and time of CH_3NO_2 addition, and on the catalyst support by itself.

III. RESULTS

Effect of CH_3NO_2 addition on CO hydrogenation. Figure 1 shows the carbon fraction distributions for CO hydrogenation in the absence and in the presence of CH_3NO_2 for two experimental conditions: (**A**) T = 523 K, He : CO : H_2 = 1 : 2 : 2; (**B**) T = 523 K, He : CO : H_2 = 1 : 1 : 3. Comparison of the rates of formation of individual carbon fractions are shown in Table 1. CO conversion into hydrocarbons when no CH_3NO_2 is added and turnover frequencies based on the estimated site concentration provided by hydrogen chemisorption measurements are also included in Table 1. From both Fig. 1 and Table 1 clear differences can be distinguished in the distributions due to CH_3NO_2 addition: (i) The weight percent and rate of formation of CH_4 in the products were greatly reduced upon CH_3NO_2 addition; (ii) the weight percent and rates of

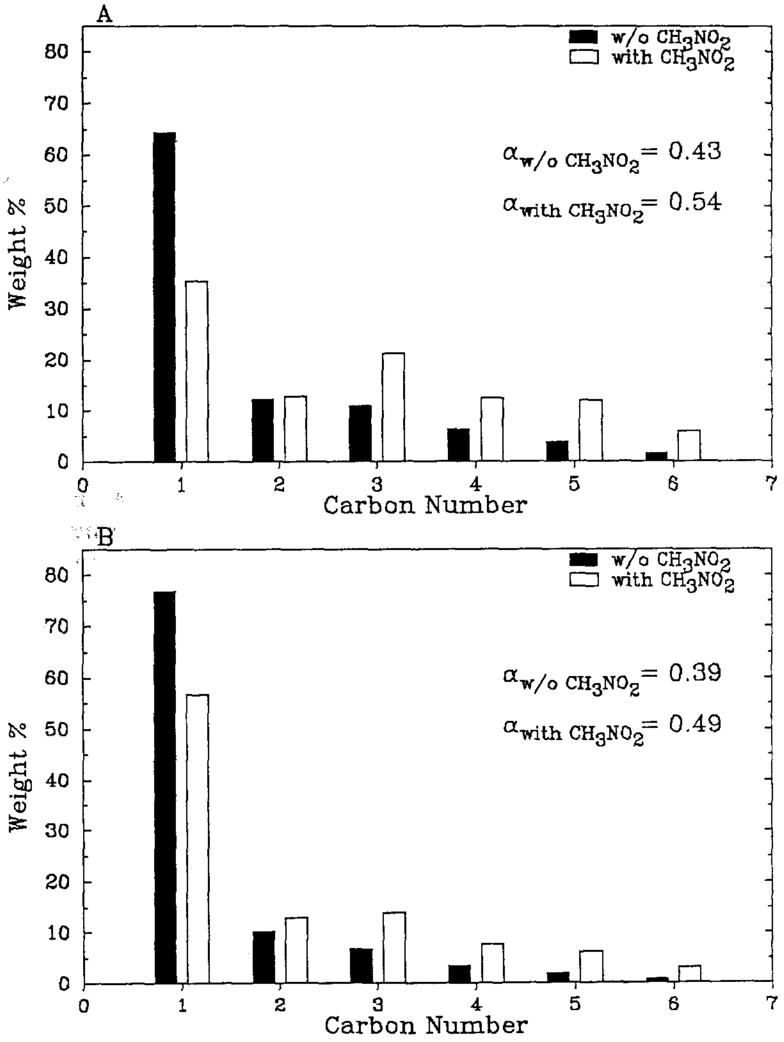


FIG. 1. Product distribution for CO hydrogenation on Ru/SiO_2 with and without CH_3NO_2. (**A**) T = 523 K, He : CO : H_2 = 1 : 2 : 2; (**B**) T = 523 K, He : CO : H_2 = 1 : 1 : 3.

TABLE 1

Activity and Selectivity of Ru/SiO_2 for CO Hydrogenation in the Absence and Presence of CH_3NO_2

Carbon fraction	Condition **A**[a]		Condition **B**[a]	
	Without CH_3NO_2 ($\mu g \cdot min^{-1}$)	With CH_3NO_2 ($\mu g \cdot min^{-1}$)	Without CH_3NO_2 ($\mu g \cdot min^{-1}$)	With CH_3NO_2 ($\mu g \cdot min^{-1}$)
C1	104.3	73.1	274.5	258.5
C2	20.0	26.6	36.1	58.6
C3	18.0	43.9	24.3	63.0
C4	10.5	25.9	12.5	34.6
C5	6.4	25.0	7.0	27.5
C6	2.9	12.5	4.1	13.3
Total	162.1	207.0	358.5	455.5
CO Conversion (%)[b]	1.3	—	5.5	—
TOF ($s^{-1} \times 10^3$)	7.6	—	16.5	—
CO_2[c]	10.5	385.6	8.8	312.5

Note. Reaction conditions: 523 K; 101 kPa; GHSV = 3800 hr^{-1}; 1.2 vol% CH_3NO_2 in reactants.

[a] (**A**) He : CO : H_2 = 1 : 2 : 2; (**B**) He : CO : H_2 = 1 : 1 : 3.

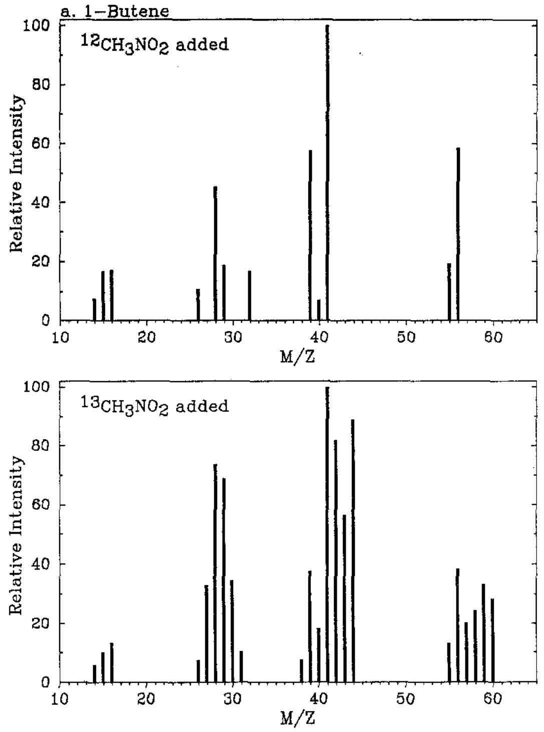
[b] CO conversion into hydrocarbon products.

[c] $\mu g \cdot min^{-1}$.

formation of the C3 through C6 carbon fractions were in general at least doubled when CH_3NO_2 was added to the reactants; (iii) in comparison to the changes in the other carbon fractions, there were only minor increases, if any, in the weight percent of the C2 fraction upon CH_3NO_2 addition, although its rate of formation increased. These trends were also observed when the same experiments were carried out at a reaction temperature of 533 K (*18*). In addition, the product distribution for the $CO/H_2/CH_3NO_2$ reaction remained the same whether the probe molecule was added with, prior to, or subsequent to, the CO/H_2 mixture.

The effect of addition of CH_3NO_2 on the production of higher hydrocarbons during CO hydrogenation can also be seen from the calculated chain growth probabilities, α, for the product distributions shown in Fig. 1. For all conditions studied, CH_3NO_2 caused significant increases in the value of α. Table 1 also shows that there were order-of-magnitude increases in the amount of CO_2 in the products when CH_3NO_2 was added. However, no compounds containing nitrogen atoms, such as HCN, NH_3, NO_2, and CH_3NH_2, were observed in the products with the possible exception of N_2 or NO. These two compounds could not be positively identified due to their overlap with CO in the columns used for GC analysis. Finally, there was no significant amount of unreacted CH_3NO_2 in the products.

For all conditions studied GC-MS analysis of the products when ^{13}C-labeled CH_3NO_2 was used indicated that from 28 to 56% of the carbon atoms in the CH_4 produced were labeled. Similar ranges of labeled carbon atoms for C_2H_6 and C_3H_6 were obtained. Furthermore, the extent of ^{13}C incorporation into other hydrocarbons is illustrated qualitatively in Fig. 2. This clearly indicates that there was substantial random incorporation of ^{13}C from the labeled CH_3NO_2 in all the hydrocarbon products. However, although addition of CH_3NO_2 resulted in a large increase in the amount of CO_2 produced, this CO_2 contained virtually no carbon from CH_3NO_2 as



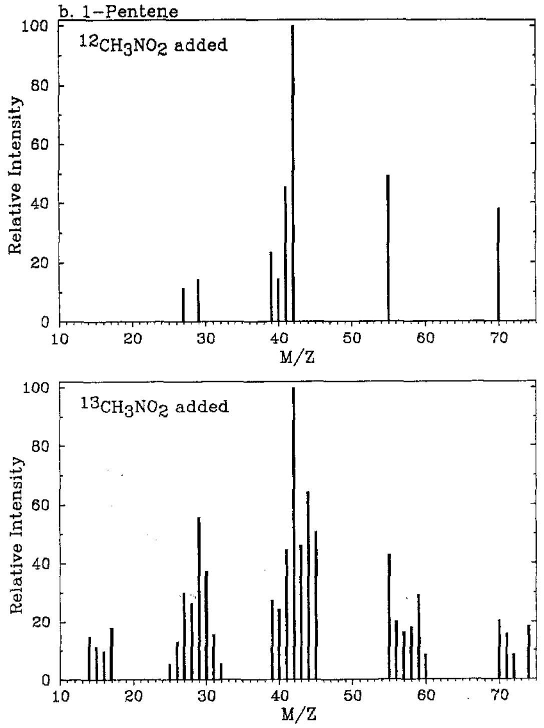


FIG. 2. ^{13}C incorporation into hydrocarbon products for CO hydrogenation with ^{13}C-labeled CH_3NO_2. $T = 523$ K, He : CO : H_2 = 1 : 2 : 2.

TABLE 2

Olefin-to-Paraffin Molar Ratios for CO Hydrogenation on Ru/SiO_2

	Condition **A**		Condition **B**	
	Without CH_3NO_2	With CH_3NO_2	Without CH_3NO_2	With CH_3NO_2
C_2H_4/C_2H_6	0.042	0.611	0.006	0.039
C_3H_6/C_3H_8	0.784	9.032	0.083	1.072
1-C_4H_8/*n*-C_4H_{10}	0.261	3.755	0.081	0.392
1-C_5H_{10}/*n*-C_4H_{12}	0.149	2.984	0.096	0.511

Note. Reaction conditions: 523 K; 101 kPa; GHSV = 3800 hr^{-1}; 1.2 vol% CH_3NO_2 in reactants. (**A**) He : CO : H_2 = 1 : 2 : 2. (**B**) He : CO : H_2 = 1 : 1 : 3.

evidenced by the lack of $^{13}CO_2$ in the products from ^{13}C-labeled CH_3NO_2 addition.

Table 2 shows a comparison of the olefin-to-paraffin molar ratios of the C2 through C5 fractions. There was a major shift toward the production of linear olefins when CH_3NO_2 was added. However, the analysis of the C4 and C5 isomers showed that CH_3NO_2 addition had no major effect on the total fraction of branched products.

CH_3NO_2 reactivity under various conditions other than CO hydrogenation. A study of the decomposition of CH_3NO_2 in the presence of H_2 and He and in the absence of CO over the Ru/SiO_2 catalyst revealed that at least 68% of the CH_3NO_2 in the reactants (always about 1.2 vol%) was converted into hydrocarbons after an initial period of CH_3NO_2 disappearance with only a small CH_4 formation. A minimum of 91 wt% of the hydrocarbons formed was CH_4, the balance being C_2H_6 and traces of C_3H_8 and *n*-C_4H_{10}. The amount of CH_4 in the products showed virtually no dependence on the H_2 partial pressure (varied from 75 to 8 vol% in the reactants, the balance being He) and on the reaction temperature. In addition, N_2 was the only nitrogen-containing compound detected, and no CO_2 was produced. Due to the analysis conditions used, the presence of H_2O in the products could be neither confirmed nor excluded.

The reactivity of CH_3NO_2 with predeposited surface carbon was studied by first depositing carbon either by 5 min of CO hydrogenation at 533 K and He : CO : H_2 of 1 : 2 : 2, or by 5 min of CO disproportionation at 533 K and He : CO of 3 : 2, followed by a He flush for 4 min. This was then followed by exposure of the catalyst to H_2 in a mixture of He : H_2 or 3 : 2 in the absence or presence of CH_3NO_2. The results of these experiments clearly indicated that the hydrocarbons produced from the hydrogenation of the surface carbon in the presence of CH_3NO_2 are essentially the result of the addition of two independent processes: (i) hydrogenation of the surface carbon; and, (ii) decomposition of CH_3NO_2 in H_2. Again, no CO_2 was detected in the products during hydrogenation of the surface carbon in either the absence or the presence of CH_3NO_2.

Finally, the possibility of reactions occurring on the support was examined in experiments in which the previously described CO hydrogenation conditions in the absence or presence of CH_3NO_2 were performed over the same SiO_2 used in the preparation of the Ru catalyst. For various reaction times and for all conditions studied, up to about 50% of the CH_3NO_2 present in the reactants was consumed. However, less than 10 ppm of hydrocarbons or of any other compounds was detected, with a maximum of 0.1 vol% CO_2 being the sole significant C-containing compound in the product.

IV. DISCUSSION

Higher hydrocarbon formation during CO hydrogenation can be viewed as a polymerization process consisting of initiation, propagation, and termination steps. There is considerable evidence (*6–11, 19–22*) in support of the proposal that methylene groups are the chain-propagating species and that their polymerization leads to a hydrocarbon product distribution described by the Anderson–Schulz–Flory (ASF) equation (*23*). It can be seen from Table 1 that CH_3NO_2 addition to the reactants causes large increases in both the weight fraction and the rates of formation of the C3 to C6 carbon fractions. These observations can be explained only if the chain initiation and propagation rates, R_i and R_p, respectively, are *both* enhanced as a result of CH_3NO_2 addition. However, Fig. 1 also indicates that α increased upon CH_3NO_2 addition, indicating that it causes a relatively larger enhancement of the chain propagation rate, R_p.

The increase in linear olefins, along with the marked decrease in CH_4 production, indicates a smaller hydrogenation capability of the catalyst, suggesting that the surface coverage of hydrogen, θ_H, is also significantly reduced. The rate of chain termination, R_t, should increase, since CH_3NO_2 addition causes R_i to increase, and since $R_i = R_t$ for a steady product distribution (*24*). These two effects, i.e., a decrease in θ_H and an increase in R_t, are taken as evidence against a chain termination step that involves the sequential hydrogenation of growing chains as suggested by McCandlish (*21*). Since the termination step does not appear to involve the direct participation of hydrogen, it could consist either of an intramolecular hydrogen transfer (*20*) or of the β-elimination of hydrogen (*23, 25*). These effects also support the view that linear α-olefins are the primary hydrocarbon products formed by CO hydrogenation and that paraffin production is the result of secondary reactions involving the hydrogenation of readsorbed olefins (*23, 26, 27*).

MS results indicated that CH_x groups originating from CH_3NO_2 were incorporated into the products. This incorporation was substantial, and it occurred at random; i.e., there was no concentration of CH_x groups derived from CH_3NO_2 in a particular carbon fraction or specific reaction product. CH_x incorporation from CH_3NO_2 took place in conjunction with, rather than in parallel to, chain growth involving surface species originating from CO hydrogenation. These observations, as well as changes in the product distribution caused by CH_3NO_2 addition, are similar to those reported by Brady and Pettit for CH_2N_2 addition to CO hydrogenation on a Co catalyst (*9*). This suggests that a significant fraction of the CH_3 groups in CH_3NO_2 was converted mostly into CH_2 groups. This conversion would account for the increases in R_p and α. The decreased hydrogenation capability of the catalyst may have been the result of the favorable competition of the additional CH_2 groups and other fragments derived from CH_3NO_2 for the sites normally occupied by hydrogen during CO hydrogenation.

These results contrast with those reported for CH_3I addition to CO hydrogenation over RuKY catalysts in which case GC-MS analysis of the products indicated that the CH_3 groups derived from CH_3I acted as chain terminators and were preferentially found in isobutene rather than in linear olefins (*11*). The observed difference in the fate of CH_3 groups generated from CH_3NO_2 and CH_3I is likely to be the result of the greater influence of the halogen atoms compared to NO_2 groups on the overall behavior of the catalyst. Further support for this explanation is available from reports that addition of CH_2N_2 and CH_2Cl_2 to CO hydrogenation over Co catalysts resulted in contrasting decreases (*9*) and increases (*10*), respectively, in CH_4 production.

The observed reduction in CH_4 formation upon CH_3NO_2 addition can be viewed as the direct result of the much lower hydrogenation ability of the catalyst. Furthermore, GC-MS analysis of the products when ^{13}C-labeled CH_3NO_2 was used suggests that the extent of carbon incorporation from CH_3NO_2 into the various hydrocarbon products appears to be similar for all the carbon fractions. For conditions **A** and **B** this means that approximately 33 and 54%, respectively, of the carbon originating from CH_3NO_2 ends up as CH_4. This indicates that a CH_3 group from CH_3NO_2 has an equal or a lesser probability of being hydrogenated to give CH_4 than of appearing in higher hydrocarbon products. Previously reported results (*19, 20*) have been used to propose that the rate-determining step (RDS) in CH_4 formation involves the hydrogenation of the CH_3 group. There also have been reports (*28*) and experimental results (*29*) that suggest that the $CH_3 \Leftrightarrow CH_2$ interconversion should be facile. The relatively low selectivity for the direct hydrogenation of CH_3 groups originating from CH_3NO_2 to produce CH_4 under CO hydrogenation conditions observed in this study is consistent with these proposals.

CH_3NO_2 addition to CO hydrogenation has less of an effect on the C2 carbon fraction compared to the C3 to C6 fractions, suggesting that the rate of C2 formation is distinct from that of other higher hydrocarbons. Whereas both R_p and R_i increase upon CH_3NO_2 addition, the latter does not increase as much as the former as evidenced by the observed increase in the value of α. Perhaps C2 formation is related to the chain initiation rate and C3 to C6 formation to the rate of chain propagation. There are experimental results for CO hydrogenation on Ru (*22, 30*) and theoretical studies (*21, 31*) that also postulate a special role for a C2 surface intermediate in the initiation of chain growth and as the RDS in the production of higher hydrocarbons.

Analysis of the products for CH_3NO_2 reaction in H_2 with and without CO showed that no compounds containing an intact C–N bond, such as CH_3NH_2, HCN, or CH_3CN, were detected. It is likely that the fate of the NO_2 groups produced as a result of the scission of the C–N bond in CH_3NO_2 is associated with the observed large increase in CO_2 production. During CH_3NO_2 hydrogenation, the only observed product that contained nitrogen atoms was N_2. In contrast to other transition metals, Ru-containing catalysts have been found to have a pronounced selectivity for the formation of N_2, rather than NH_3, during the reduction of NO and NO_x by H_2 and/or CO (*32–35*). Although the experimental setup used in the present study did not allow us to check the products for the presence of water, Uchida and Bell found that it was the major O-containing product during the temperature-programmed reaction of NO with H_2 over a Ru/Al_2O_3 catalyst (*32*). It is possible that the NO_2 groups from CH_3NO_2 follow a decomposition pathway involving their reduction to yield N_2 and H_2O. In the presence of H_2 only, these are the sole products. During CO hydrogenation, this additional H_2O may react with adsorbed CO by the water–gas shift reaction to form the excess CO_2 observed during CH_3NO_2 addition. This explains why no CO_2 is detected in the products when CH_3NO_2 is reacted with H_2 only, and why, during CO hydrogenation, the CO_2 produced during ^{13}C-labeled CH_3NO_2 addition contained no ^{13}C.

Another potential origin of the higher CO_2 production is the direct reaction between CO and NO to form CO_2 and N_2. This reaction is also known to take place easily on Ru (*33*). It is important to note that this enhanced CO_2 production, resulting from the reaction of adsorbed CO with additional H_2O or NO originating from CH_3NO_2, by no means appears to disturb the main reaction pathways leading from CO to hydrocarbons. This suggests that the CO molecules involved in these reactions are not participating to a great extent in the synthesis of hydrocarbons. This supports suggestions by Dalmon and Martin (*36*) and by Winslow and Bell (*37*) that, even if the catalyst surface is virtually saturated with adsorbed CO, only a small fraction of it participates actively in CO hydrogenation reactions.

V. CONCLUSIONS

When CH_3NO_2 was added to the reactants during CO hydrogenation over a

Ru/SiO_2 catalyst under various reaction conditions, carbon from CH_3NO_2 was incorporated into the CO hydrogenation pathway leading to hydrocarbon formation according to the mechanism suggested in Fig. 3. Some of the CH_3 groups are directly hydrogenated to form CH_4 but a large fraction forms mostly CH_2 groups which enhance preferentially the rate and probability of chain growth. Surface coverage of hydrogen was reduced as a result of CH_3NO_2 addition resulting in an overall decrease in CH_4 production and in an increase in the olefin-to-paraffin ratios due to less secondary hydrogenation of the primary olefinic products. The experiments involving ^{13}C-labeled CH_3NO_2 and the hydrogenation of predeposited surface carbon in the presence of CH_3NO_2 indicated that the CH_x groups derived from CH_3NO_2 are interacting exclusively with active surface species directly involved in the formation of higher hydrocarbons. In the presence of CH_3NO_2, large amounts of CO_2, derived not from CH_3NO_2 but from CO, were formed, supporting suggestions that only a small fraction of the adsorbed CO participates actively in the formation of Fischer–Tropsch products.

This study has also demonstrated that CH_3NO_2 is an effective probe molecule that can be used as a source of CH_x groups. Changes in the product distribution of CO hydrogenation over Ru/SiO_2 brought about by CH_3NO_2 addition took place without any significant disturbance of the main reaction pathways that lead to hydrocarbon formation. Unlike probe molecules containing halogen or sulfur atoms, the decomposition of CH_3NO_2 leads to fragments that appear

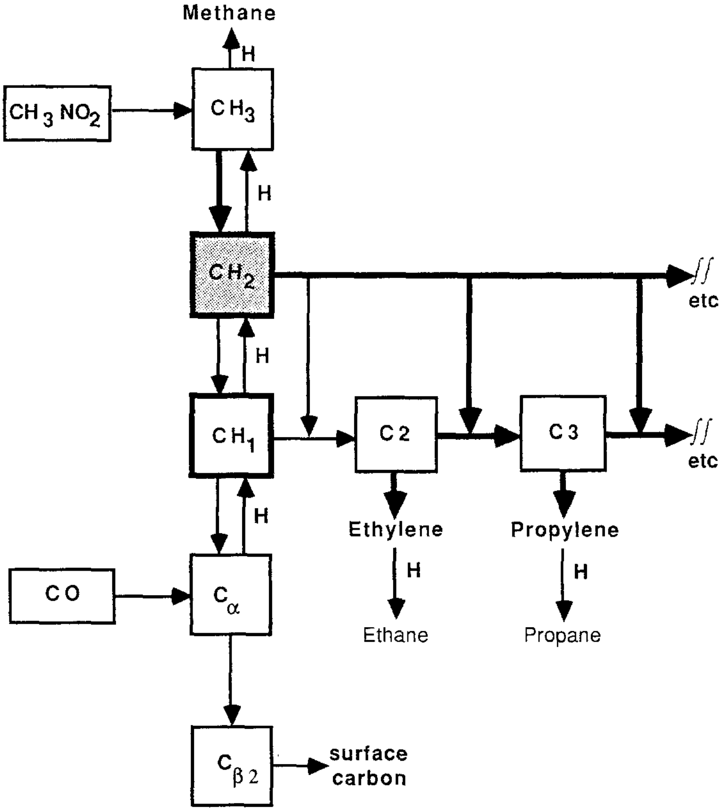


FIG. 3. Effect of CH_3NO_2 addition on CO hydrogenation pathway on Ru/SiO_2.

not to cause secondary changes in the hydrocarbon formation pathway. Also, CH_3NO_2 seems to decompose selectively at the C–N bond leading to simple fragments. These characteristics offer great potential for the use of CH_3NO_2 as probe molecule in the study of CO hydrogenation over other transition metals and in the formation of other families of compounds during Fischer–Tropsch synthesis.

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