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# *In Situ* Chemical Trapping of $CO/H_2$ Surface Species

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CO hydrogenation reactions over RuKY catalysts were monitored *in situ* using a novel chemical trapping technique to identify surface species. Study of alterations in the product distribution upon addition of the trapping agent led to a good prediction of the type of reactive surface species thought to be present on the surface of these catalysts. This work represents the first evidence that this chemical trapping technique selectively traps active surface intermediate species. A number of other significant changes in the surface chemistry of the catalysts occurred upon addition of the trapping agent, indicating that the action of the trapping agent appears to be more complex than had previously been suggested. Although these results have uncovered interesting and revealing phenomena, it is evident that additional investigations are needed before the full value and import of this technique as a means of identifying reactive surface species can be fully assessed. © 1988 Academic Press, Inc.

## INTRODUCTION

Understanding the nature of active intermediate species present on the surface of supported metal catalysts has long been a goal of catalytic scientists. The rich chemistry of the reactions that carbon monoxide (CO) and hydrogen ($H_2$) may undergo on different transition metals leads to a wide spectrum of products depending on the reaction conditions, the characteristics of the support, and the type of transition metal itself. Although many different techniques have been used to probe the surface chemistry of catalysts *in situ* during CO hydrogenation reactions, much remains to be learned about the nature of the surface species and the mechanisms by which they participate in catalytic reactions.

This paper reports investigations of CO hydrogenation over supported Ru catalysts using a novel chemical trapping technique proposed by Deluzarche and co-workers (*1*, *2*). They have reported the use of this technique to identify surface species under conditions quite far removed from those of conventional CO hydrogenation reactions. We have extended the chemical trapping technique for the first time for *in situ* use during CO hydrogenation reactions over Ru catalysts.

Two important questions remain to be addressed from the previous work on this technique. First, what is the nature of the interaction between the trapping agent and the adsorbed species? While the Strasbourg group has reported identification of an extensive number of surface species using this technique, to date the work has not focused in detail on the mechanism(s) by which the trapping agents react. Of great interest also is the question of whether the trapping agent can selectively trap *active* surface

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species, or if it merely acts as a nonselective alkylating agent for any and all species on the surface.

## BACKGROUND

Since the early work of Emmett and co-workers (*3*, *4*), a number of studies have attempted to identify reaction intermediates using tracer or probe molecules added to the reaction mixture (*5*–*9*). Other kinds of experiments have involved generating $CH_x$ species on the surface to confirm their role in CO hydrogenation reactions (*10*–*14*). Biloen *et al.* (*15*) and others (*16*, *17*) have performed elegant tracer experiments in which a steady-state CO hydrogenation reaction is suddenly subjected to a switch of one of its reactive components to an isotopic analog of that component ($D_2$ substituted for $H_2$, or $^{13}CO$ for $^{12}CO$, for example). The transient period in which the surface changes to species rich in the new isotopic component is then monitored.

Other imaginative experiments have involved the scavenging of surface species by reaction with molecules not part of the reaction scheme (*18*, *19*). A novel variation on this theme was developed by Deluzarche and co-workers (*2*) in which alkylating agents such as methyl iodide ($CH_3I$) have been used in attempts to chemically "trap" species on the surface by selectively attacking metal–adsorbate bonds. They proposed that an alkyl group inserts at each former place of attachment of the species to the surface. The nature of the original surface species is then deduced from analysis of the product which is formed in this trapping reaction. Figure 1 illustrates the manner in which this chemical trapping reaction is thought to occur.

Deluzarche and co-workers (*1*, *2*) have exploited this technique in extensive work suggesting that a wide array of surface species present on different catalyst surfaces could be identified. However, their work was carried out under static adsorption and under temperature and pressure conditions far removed from those of actual catalytic reactions. The need for identification of surface species under dynamic conditions is emphasized by recent work (*15*, *16*) indicating that in many cases only a small fraction of the surface sites actually participate in the CO hydrogenation reactions. Being able to identify these sites and distinguish them from inactive adsorbed species is important to our overall understanding of how catalytic reactions take place. Our group has undertaken investigations to explore the use of this trapping technique under dynamic conditions.

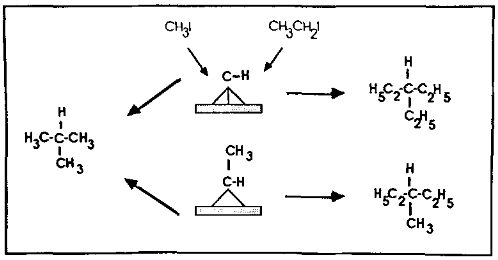

FIG. 1. The proposed mechanism of chemical trapping of surface species (*1*). An alkylating agent attacks bonds between an adsorbed species and the surface of a catalyst. An alkyl group is inserted at each former place of attachment to the surface. The original surface species is deduced from the gaseous product which is formed. Reagents with different alkyl groups may be employed for unambiguous determination of the identity of the surface species.

In the present study, two supported Ru catalysts exhibiting slightly different Fischer–Tropsch (F–T) product distributions were exposed to the trapping agent $CH_3I$ *in situ* during the CO hydrogenation reaction. The results have allowed us to make suggestions about the nature of the interactions between the trapping agent and the surface species. For this system, it appears that chemical trapping involves reactions which proceed along with and compete with the CO hydrogenation reaction steps. While chemical trapping is overlaid on the existing reacting system, it also perturbs the system causing irreversible poisoning of some sites. Thus, while chemical trapping may provide useful information about the nature of surface reactions, its influence on the main reaction pathways must be considered before it may be used as a method of studying reactive surface species.

## EXPERIMENTAL

*Catalyst preparation.* The KY support used in this work was prepared by ion exchange of NaY zeolite (Strem Chemicals) with potassium nitrate (Alpha Products, ultrapure). Two different procedures were used to carry out the ion exchange: a one-step procedure in which the solution containing the $KNO_3$ and the support was stirred at ambient temperature for 24 hr, and a three-step exchange procedure in which the ion-exchange solution was replenished three times while being stirred over a period of 72 hr. This second procedure causes more complete replacement of Na with K, yielding a zeolite with fewer acid sites *(20, 21)*.

After the support was dried overnight at 110°C, the Ru-loaded catalyst was then prepared by a further ion exchange of the KY zeolite with $Ru(NH_3)_6Cl_3$ (Strem Chemicals). The weight loading of Ru was a nominal 3% for both catalysts. More detailed procedures for the preparation and pretreatment of the RuKY catalyst are described elsewhere *(22)*.

*Reaction studies.* Fischer–Tropsch synthesis was carried out in a stainless-steel tubular microreactor of $\frac{3}{8}$ in. (0.95 cm) diameter. Approximately 0.25 g of prereduced catalyst was loaded into the reactor. Under a hydrogen stream of 3 liters/hr, the catalyst was heated to 673 K at 2 K/min and held there for 2 hr. Ultrahigh-purity $H_2$ (Linde) and CO (Matheson) were further purified by passage through molecular sieve traps. The $H_2$ stream was passed over a Deoxo unit prior to the molecular sieve trap.

Reaction temperature was controlled by a thermocouple inserted into the catalyst bed. Reaction conditions were 101 kPa and 523 K using a 1 : 1 mixture of $H_2 : CO$ flowing at 2.4 liters/hr. During trapping experiments, the CO stream was diverted through a saturator containing $CH_3I$ (Aldrich, 99% purity) which was kept in a Dewar flask filled with a 32 wt% $CaCl_2$ solution maintained at 227 K to provide approximately 3.7 vol% $CH_3I$ in the reactant stream. Under these conditions CO conversions were less than 3%. Effluent gas analysis was carried out on line using a Perkin–Elmer Sigma 300 gas chromatograph fitted with thermal conductivity and flame ionization detectors. Product analysis from reactions with the Ru(K) catalyst was made using a 12-m SP-1700 column maintained at 343 K. A 2-m 0.19% picric acid column packed with 80/100 Carbopak C was used for analysis of products from reactions with Ru(KK). Peak areas were determined by an electronic integrator (Varian CDS 111). A hydrogen bracketing technique was used during these experiments in which the catalyst surface was flushed with $H_2$ at reaction temperature for 40 min after every 5 min of reaction.

Trapping reactions on Ru(KK) were also carried out with $^{13}C$-labeled $CH_3I$ (Aldrich, 99.55% $^{13}C$) as the trapping agent. Reaction products were collected for injection into and analysis by a GC-MS system (Finnegan) using the picric acid column described above.

1-Butene (Matheson) isomerization reactions were carried out over fresh and used catalysts in the same microreactor system.

## RESULTS

CO hydrogenation reactions were performed over the two RuKY catalysts in both the absence and the presence of $CH_3I$ in the reactant mixture. Ru catalysts prepared from the extensively exchanged KY (Ru(KK)) gave an overall product distribution similar to the lesser exchanged Ru(K) catalyst, but they showed decreased hydrogenation capability, with a higher $C_3^{=}/C_3^{-}$ ratio. The parent NaY support possesses only weak acid sites; the exchange of Na for K decreases the number of these weak acid sites to a greater extent on the exten-

TABLE 1

Fischer–Tropsch Product Distributions for Ru(K) and Ru(KK) Catalysts[a] in the Absence and Presence of $CH_3I$ Trapping Agent

| Catalyst | Step 1 without $CH_3I$ | | Step 2 with $CH_3I$ | |
|---|---|---|---|---|
| | Ru(K) | Ru(KK) | Ru(K) | Ru(KK) |
| CO conversion (%) | 2.3 | 1.3 | 0.8 | 0.3 |
| Activity (μmol/hr * g cat.) | 4.7 | 2.5 | 1.5 | 0.5 |
| Turnover frequency ×1000 ($s^{-1}$) | 6.4 | 3.3 | 2.0 | 0.7 |
| Propylene/propane ratio | 5.7 | 18.2 | 24.3 | 55.7 |
| Selectivity (wt%) | | | | |
| $C_1$ | 33.4 | 36.5 | 19.1 | 53.2 |
| $C_2$ | 13.2 | 10.4 | 4.7 | 8.0 |
| $C_3$ | 20.8 | 20.6 | 8.3 | 9.9 |
| $C_4$ | 10.6 | 13.8 | 32.0 | 10.4 |
| $C_5$ | 8.6 | 11.2 | 18.9 | 6.7 |
| $C_6$[b] | 13.4 | 7.5 | 17.0 | 11.8 |
| Selectivity in $C_4$: fraction (wt%) | | | | |
| Isobutane | 0.2 | 0.3 | 28.8 | 0.0 |
| *n*-Butane | 16.3 | 6.9 | 0.3 | 1.0 |
| 1-Butene | —[c] | 18.5 | —[c] | 0.0 |
| Isobutene | 23.9 | 3.6 | 54.8 | 57.7 |
| *trans*-2-Butene | 18.4 | 42.0 | 9.6 | 26.9 |
| *cis*-2-Butene | 41.2 | 28.7 | 6.5 | 14.4 |

[a] Reaction conditions were 523 K and 101 kPa; details given in text. Details of catalyst characterization given in Ref. (*18*).

[b] Indicates a combination of the $C_6$ fraction and all higher hydrocarbons.

[c] Isobutene and 1-butene were not separated by analysis for Ru(K). The number given for isobutene is actually isobutene + 1-butene.

sively exchanged Ru(KK) than on the Ru(K) catalyst. The more basic the nature of the support, the more olefinic is the product distribution (*20*). Table 1 gives kinetic data for the two catalysts during reactions without and with the addition of $CH_3I$.

Table 1 and Figs. 2–5 compare hydrocarbon product distributions in the presence and absence of the trapping agent. When $CH_3I$ was added to the reaction mixture, the products changed dramatically from a characteristic F–T distribution. Ru(K) exhibited a strong shift to higher carbon numbers upon addition of $CH_3I$ while for Ru(KK) the major effect was an increase in the amount of methane. Both catalysts showed alterations in the distribution of products within a particular carbon number, as is shown for the $C_4$ fraction in Figs. 4 and 5. After addition of $CH_3I$ the $C_4$ fraction was lower in *n*-butane and *cis*- and *trans*-2-butene for both Ru(K) and Ru(KK). The most significant change upon $CH_3I$ addition was a dramatic increase in branched $C_4$ products: Ru(K) showed a strong increase in the amount of isobutane formed while isobutene increased substantially over Ru(KK). Product analysis for the Ru(K) catalyst showed an increase in a combined peak for 1-butene and isobutene which could not be separated by the column used. It is likely but not certain that an increase in isobutene occurred for Ru(K) as well as for Ru(KK) during trapping.

The conversion of CO decreased by at least a factor of 3 for both catalysts during the period in which $CH_3I$ was added to the reactant mixture. However, even after tak-

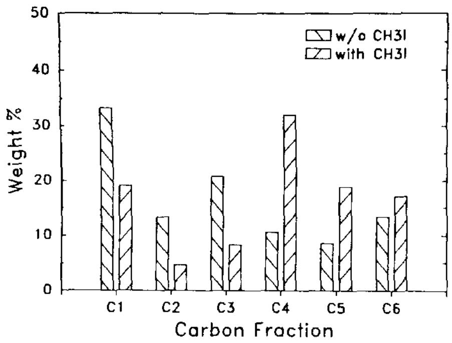

FIG. 2. Ru(K) catalyst. Comparison of the total hydrocarbon product distributions from $CO/H_2$ reaction in the absence and in the presence of $CH_3I$, a chemical trapping agent. *Note*: $C_6$ represents $C_6$ and higher hydrocarbons.

ing this activity decrease into account, quantitative analysis of the products showed absolute increases in the amounts of the branched $C_4$ products compared to their amounts during CO hydrogenation in the absence of the trapping agent.

During the first few minutes of trapping, the $CH_3I$ in the feed stream was consumed in large quantities by the catalyst, with as much as 80% of the entering $CH_3I$ remaining on the surface in the first few minutes of trapping. Carbon deposition on the catalyst surface by $CH_3I$ might account for the decrease in CO conversion observed during trapping.

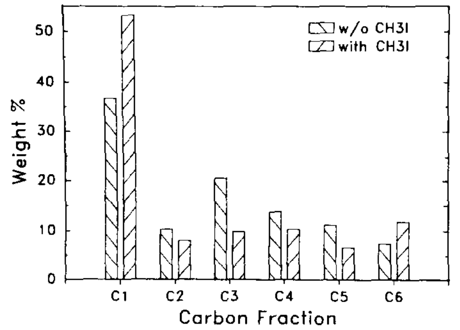

FIG. 3. Ru(KK) catalyst. Comparison of the total hydrocarbon product distributions from $CO/H_2$ reaction in the absence and in the presence of $CH_3I$, a chemical trapping agent.

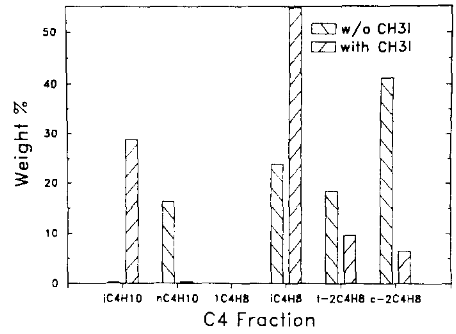

FIG. 4. Ru(K) catalyst. Composition of $C_4$ products in the absence and in the presence of $CH_3I$, a chemical trapping agent. iC4H10, isobutane; nC4H10, *n*-butane; 1C4H8, 1-butene*; iC4H8, 1-butene and isobutene; t-2C4H8, *trans*-2-butene; c-2C4H8, *cis*-2-butene. **Note*: 1-Butene and isobutene were not separated in this product analysis. The C4 fraction labeled iC4H8 is actually the combination of i- and 1-butene.

Table 2 summarizes the sequence of reaction steps employed in these studies. Each step was bracketed by a 40-min purge in $H_2$ at reaction temperature. When the addition of $CH_3I$ was stopped, the activity of the catalyst for the conversion of CO was reduced by nearly an order of magnitude. For Ru(K), the olefin/paraffin ratio increased after exposure to $CH_3I$, suggesting that the hydrogenation ability of the catalyst was partially poisoned. It was also found that further addition of $CH_3I$ to the

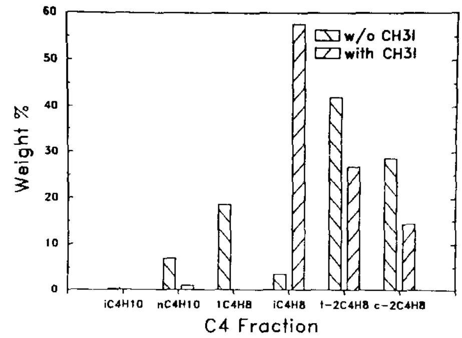

FIG. 5. Ru(KK) catalyst. Composition of $C_4$ products in the absence and in the presence of $CH_3I$, a chemical trapping agent. iC4H10, isobutane; nC4H10, *n*-butane; 1C4H8, 1-butene; iC4H8, isobutene; t-2C4H8, *trans*-2-butene; c-2C4H8, *cis*-2-butene.

TABLE 2

Summary of the Experimental Sequence in the Study of Chemical Trapping of $CO/H_2$ Surface Species over Ru(K) and Ru(KK)

| Step | Feed | Products |
|---|---|---|
| 1 | $CO + H_2$ | Typical $C_1$–$C_6$ F–T hydrocarbons |
| 2 | $CO + H_2 + CH_3I$ | Shift in $C_4$ fraction to more branched products |
| 2 | $CO + H_2$ | $C_1$–$C_6$ hydrocarbons; lower conversion |
| 4 | $CO + H_2 + CH_3I$ | Same distribution as Step 2; lower conversion |
| 5 | $He + H_2 + CH_3I$ | Small amount of $CH_4$; trace $C_2$, $C_3$ |

*Note.* Each step was bracketed by a 40-min purge in pure $H_2$ at the reaction temperature.

reaction mixture yielded the same product distribution obtained with the first $CH_3I$ addition, albeit with lower activity.

In the last step in the reaction sequence, the CO in the reaction mixture was replaced with helium. Only a small percentage of the $CH_3I$ reacted in the absence of CO, forming mostly methane and traces of ethane and propane. This same step was also carried out on a catalyst sample which had not been contacted with $CH_3I$, with very similar results. This indicates that the reactions observed did not stem merely from interactions between the trapping agent and the zeolite support, but that the presence of CO was required to obtain a product distribution characterized by significant amounts of branched $C_4$ hydrocarbons.

All of the reaction steps discussed above were also carried out with Ru(KK) using $^{13}C$-labeled $CH_3I$ as a trapping agent. Because of the significant drop in CO conversion which occurred during trapping, the concentrations of products were very low and the MS signals observed were quite weak and noisy, especially as the time of trapping increased. However, the spectra obtained at 3 min trapping time clearly show that $^{13}C$ was selectively incorporated into isobutene *alone* of the major products.

Figure 6 shows MS results for four of the hydrocarbon products from CO hydrogenation reactions both without $CH_3I$ and with $^{13}C$-labeled $CH_3I$. For the spectra of propylene, 1-butene, and *cis*-2-butene, the only influence of the trapping agent was an overall decrease in the signal intensity, indicating a decrease in the amount of product formed. The spectrum of isobutene provides a very different picture. Significant signal intensity was observed at ion fragment numbers different from those of [$^{12}C$]isobutene, indicating incorporation of $^{13}C$ into the branched product. There was no evidence for the incorporation of $^{13}C$ into $C_3$ products, into $C_4$ products other than isobutene, or into $C_5$ products. MS analysis of the $C_1$ and $C_2$ products was hampered by the large CO background signal resulting from the similar retention times of these compounds in the chromatographic column.

1-Butene isomerization experiments were performed over both Ru(K) and Ru(KK) catalysts. The fresh catalysts showed only *cis–trans* isomerization and no significant structural isomerization. This activity was unchanged for the Ru(KK) after exposure to $CH_3I$, but the Ru(K) catalyst exhibited some activity for the structural isomerization of 1-butene after reaction with $CH_3I$.

## DISCUSSION

Addition of $CH_3I$ as a trapping agent to the reactant stream during F–T synthesis caused changes in both the activity and the selectivity of the catalysts. The increase in isobutane for Ru(K) and isobutene for

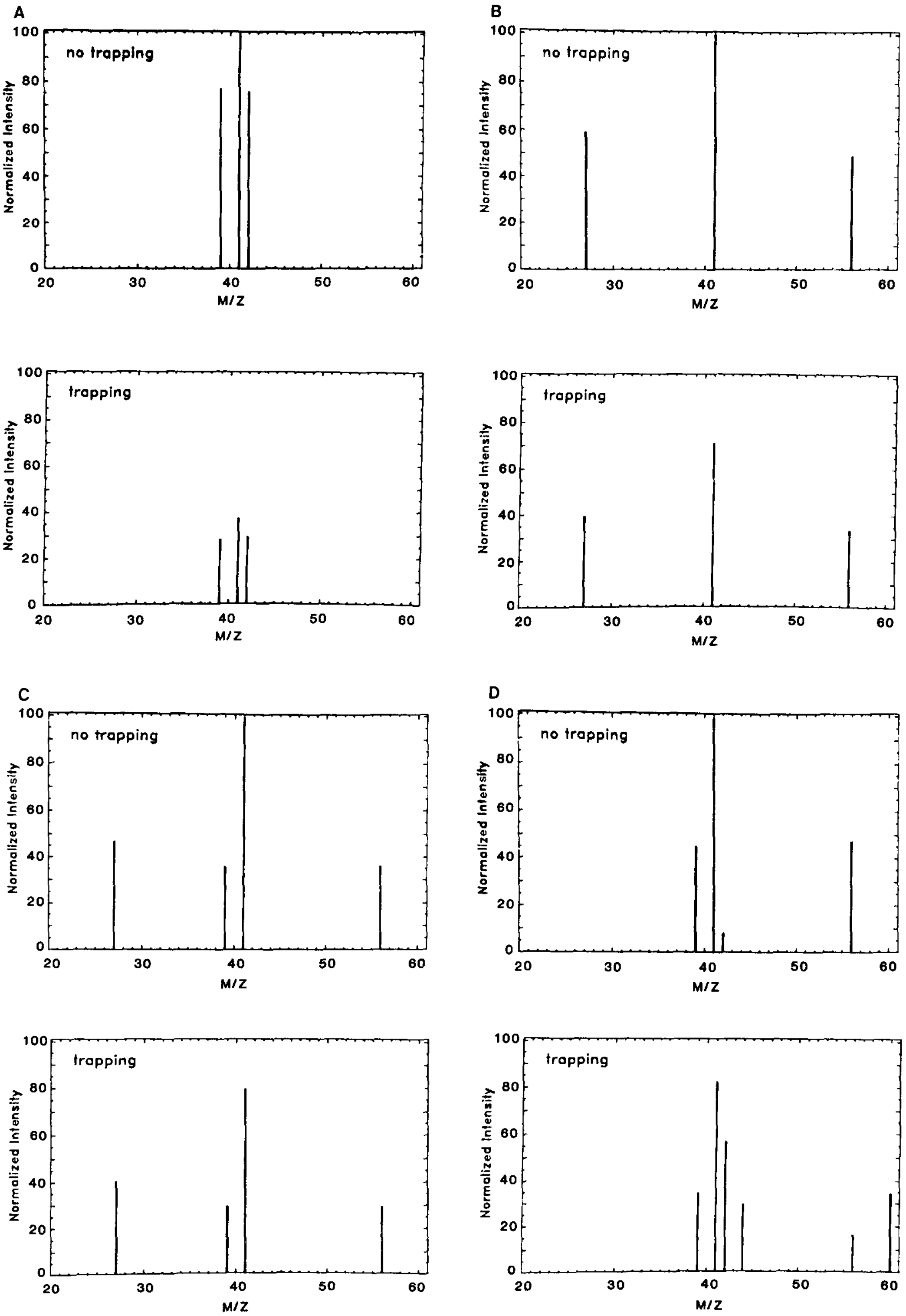

FIG. 6. Mass spectra of CO hydrogenation products during trapping without and with $^{13}CH_3I$ in the reactant stream. (A) Propylene; (B) *cis*-2-butene; (C) 1-butene; (D) isobutene. Signals are normalized to that of the most intense fragment from reaction without $^{13}CH_3I$ (i.e., for each product shown, ion fragment 41 = 100% for reaction without $^{13}CH_3I$).

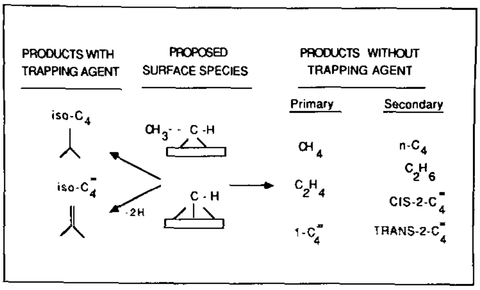

FIG. 7. Proposed surface species which may explain the product distributions found from CO/$H_2$ reactions over Ru(K) and Ru(KK) in the presence and in the absence of a chemical trapping agent $CH_3I$.

Ru(KK)—branched hydrocarbon products not normally produced during F–T reactions on nonacidic catalysts—indicates that the trapping agent caused significant perturbations in the dynamics of the reaction system. Our task then is to discern whether these perturbations can be explained by the trapping hypothesis as discussed by Deluzarche *et al.* (*1*). A reaction scheme which incorporates the action of the trapping agent into a dynamic F–T reaction network is proposed in Fig. 7. $C_xH_y$ surface species such as those shown have been hypothesized (*15, 16*) to explain commonly accepted F–T pathways to olefinic and paraffinic products.

The left side of Fig. 7 shows that these proposed surface species can also correctly predict the products observed in the presence of $CH_3I$ acting according to the scheme proposed by Deluzarche and coworkers (*1, 2*). If $CH_3I$ is introduced to a catalyst surface undergoing normal F–T reaction, surface intermediates responsible for the normal secondary products might be "derailed" from their usual pathway by instead interacting with $CH_3I$. Either of the two proposed surface species can explain the increase in isobutane for Ru(K) (or isobutene for Ru(KK)) as well as the decrease in the normal secondary-reaction products upon addition of $CH_3I$. Hence for this example the chemical trapping technique gives a reasonable prediction of the type of reactive surface species in good agreement with what has been suggested from studies using other techniques (*9, 15–18*). Its value as a probe of surface species stems from the fact that it appears to "tag" the former surface species by producing from it products not normally found in CO hydrogenation reactions over these catalysts.

The decrease in activity for normal CO hydrogenation suggests that the trapping agent poisons sites on the surface necessary for F–T reaction. Carbon deposition on the surface from the trapping agent may account for a large nonselective decrease in activity due to site blockage. The increase in the olefin/paraffin ratio observed for both Ru(K) and Ru(KK) after the surface has been contacted with $CH_3I$ indicates loss of hydrogenation ability. This might be related to the iodine introduced to the system as $CH_3I$. The effect of halogens on the chemisorptive and catalytic properties of supported transition metals has been studied (*23–26*). It has been reported that residual chlorine from reduction of precursor metal chlorides is partitioned between the metal and the support (*23, 24*), and that it may in some cases inhibit chemisorption (*25, 26*). Halogens might act to poison hydrogen adsorption on the surface much faster than sites for CO and growing hydrocarbon chains are perturbed (*26*).

Butene isomerization experiments were performed over both Ru(K) and Ru(KK) catalysts to detect the possible presence of acidic sites. The fresh catalysts showed only *cis–trans* isomerization. Lack of significant structural isomerization indicated the lack of strong acid sites on the surface of either catalyst. This activity was unchanged for the Ru(KK) after exposure to $CH_3I$, but the Ru(K) catalyst exhibited some activity for the structural isomerization of butene after reaction with $CH_3I$.

The fact that the Ru(K) catalyst showed activity in structural isomerization *after* exposure to methyl iodide indicates that irreversible changes in the surface chemistry had taken place. The KY support in Ru(K) was less extensively exchanged with K and had some protons or Na cations remaining in the structure. The protons might interact with halogen ions to create strong acid sites where there were none initially. In the case of $Al_2O_3$ (*27*) and $Pt/Al_2O_3$ reforming catalysts (*28, 29*), it is well known that the addition of HCl or other Cl-containing compounds increases the acidity of the support. The results from the CO hydrogenation reactions in the presence of $CH_3I$ might then be reinterpreted: reactions taking place with surface species on acid sites on the support could perhaps explain the appearance of branched $C_4$ products without invoking the scheme involving the trapping of surface species on metal sites. However, a number of other observations discussed below preclude the conclusion that formation of acid sites might account for the changes in surface chemistry of these catalysts.

Methylating agents have been shown to react over materials such as ZSM-5 to give hydrocarbons (*30–32*). However,, it has been demonstrated (*30*) that $CH_3I$ is an order of magnitude less active for methylation on ZSM-5 than are other agents such as dimethyl sulfate. The interaction between $CH_3I$ and the support alone is unlikely to be sufficient to produce the significant changes observed here.

It has also been observed (*22*) that F–T reactions on metal catalysts with acidic supports produce, in addition to an increase in branched products, *lower* olefin/paraffin ratios than nonacidic catalysts, not *higher* ratios as were found in the present study. It also appears that any acid sites present on the support cannot be responsible for all of the surface chemistry occurring on the Ru(K) or the Ru(KK) catalyst. If this were true, the reaction of $CH_3I$ ought to be able to proceed in the absence of CO, which it does not. It is unlikely that the formation of acid sites can fully explain the results observed in the present study.

The formation of hydrocarbon chains from alkyl halogen molecules on *metal* surfaces has been reported by van Barneveld and Ponec (*14*) and by Fung and Sinfelt (*33*). The former group postulated that $CH_x Cl_{4-x}$ ($x$ = 1–3) reactants formed ($-CH_x-$) intermediates on metal surfaces which led to growing hydrocarbon chains even in the absence of CO. This scheme is essentially similar to the chemical trapping scheme postulated by Deluzarche and co-workers (*1, 2*); here, however, the alkyl halogen molecule acts (in place of CO) as the entity which *generates* surface species as well as the entity which traps them. In addition, in these authors' scheme, the alkylating agent is postulated as being able to sequentially insert numerous ($-CH_x-$) fragments into a growing hydrocarbon chain on the surface. In the chemical trapping scheme, the trapping agent is thought to perform only one alkylation on each surface–carbon bond.

Van Barneveld and Ponec (*14*) found that chloromethane ($CH_3Cl$) was quite inactive for chain growth compared to doubly or triply chlorinated carbon. The authors concluded that hydrocarbon chains had a better chance of growing from more highly substituted chlorinated methane species. Perhaps the singly substituted $CH_3I$ used in the present study was able to perform only a single alkylation on a surface species. The surface species might then have desorbed without further addition of alkyl groups.

In earlier work, Brady and Pettit (*12*) added $CH_2N_2$ in CO hydrogenation reactions. They observed an increase in the chain growth probability but the distribution of products was still that predicted by the Anderson–Schulz–Flory polymerization model, indicating the ease of $CH_2$ insertion into normal F–T chain growth. Comparison of these results with our own findings strongly suggests that $CH_3$ groups from $CH_3I$ do not insert into the growing chain but rather terminate it in a way that causes branched hydrocarbon products to form. The "single alkylation" of van Barneveld and Ponec (*14*) might then in fact be synonymous with the "chemical trapping" of Deluzarche and co-workers (*1*, *2*). This suggestion represents the first attempt since the beginning of work on this "chemical trapping" technique to explain the mechanism by which the chemical trapping reaction occurs.

Fung and Sinfelt (*33*) have also studied the reaction of alkyl halides on supported metal catalysts. They compared the hydrogenolysis of C–C bonds with C–Cl bonds on transition metals. Experiments with $CH_3I$ as the only carbon-containing entity (step 5 in the sequence) indicate that on a clean catalyst surface the hydrogenolysis of $CH_3I$ cannot account for the increase in the absolute amount of branched $C_4$ products formed during the trapping steps of the reaction cycle. Again, the lack of significant activity of the $CH_3I$ in the absence of CO rules out this pathway as the major route to the products obtained during the *in situ* trapping reactions described in the present study.

These studies lend support to the idea that a molecule such as $CH_3I$ may be used as an alkylating agent which can then be traced in product molecules to help deduce the nature of certain surface species. $CH_3I$ may be active enough to perform a single alkylation on the metal surface without being so active as to aid in further hydrocarbon chain growth. $CH_3I$ may also be active enough to create acid sites on the support and to lay down carbonaceous species on the metal, but not so active as to promote significant hydrocarbon formation in the absence of CO. The actual reaction scheme could involve interactions between $CO/H_2$ surface species and $CH_3I$ on both metal and support sites.

The labeled trapping studies on Ru(KK) showed that the carbon group from the trapping agent was selectively incorporated in isobutene, confirming that this trapping agent was indeed involved in the formation of branched products. The fact that this branched $C_4$ product contained some $^{12}C$ and some $^{13}C$ supports the suggestion that the trapping agent participates in some sort of alkylation reaction that occurs on a surface hydrocarbon entity which was produced from the original CO and $H_2$ reactants, as envisioned in the trapping reaction scheme. This mixture of isotopes is also further evidence for the assertion that the increase in the production of isobutene is not due simply to the self-reaction between $CH_3I$ molecules.

These isotopic labeling studies show that initially the trapping reaction over Ru(KK) is quite specific for $(-C_xH_y)$ species where $x$ may be 1, 2, or 3. Under CO hydrogenation conditions, the catalyst surface is covered with a variety of species including CO, $H_{ads}$, and perhaps other C–H–O species. $CH_3I$ selectively attacks partially hydrogenated adsorbed carbon species and growing carbon chains. This important finding is the first real evidence that this chemical trapping technique can indeed provide information about *active* surface species.

At reaction times longer than 3 min, it appeared that $^{13}C$ might be incorporated in products other than isobutene, but weak signals prohibited quantitative confirmation of this. The possibility of gaining further information from the mass spectra about the nature of the surface species trapped by $^{13}CH_3I$ (including the position of the $^{13}C$ atom(s) in the isobutene molecule) was ruled out both because of the small ion current obtained in the experiment and because of the randomization of hydrogen and carbon which occurs prior to fragmentation of the isobutene molecular ion in the mass spectrometer (*34*).

Suggestions that $CH_3I$ may be involved in more extensive reaction as trapping progresses indicate that interactions other than the trapping or alkylation reaction may take place between $CH_3I$ and other species adsorbed on the surface. Competition between the various processes occurring on the surface may lead to an extremely complicated reaction network in which reactions involving $CH_3I$ (including trapping and deactivation reactions) are overlaid onto the existing F–T reaction scheme.

While these results are intriguing, they demonstrate that the action of the trapping agent is much more complex than had previously been suggested. There is a need for a better understanding of how the trapping agent reacts with the surface, how certain sites may be deactivated by contact with the agent, and how the kinetics of competing reaction processes may be altered by the action of the agent. In addition, preliminary work by our group (*35*) has indicated that parameters such as the type of trapping agent, its concentration in the feed stream, and the time of exposure of the catalyst have significant effects on the trapping reaction which need to be further explored. Sorting out these processes is a crucial step which must precede further investigation of the usefulness of the trapping technique for identification of catalytically important surface species.

## CONCLUSIONS

A novel technique which had been proposed for use in identifying surface species was employed for the first time under dynamic CO hydrogenation reaction conditions over Ru catalysts. The results indicate that the surface chemistry of this chemical trapping reaction is more complex than had been previously suggested. The most significant observation was a change in the selectivity of products obtained in the $C_4$ fraction upon addition of $CH_3I$ to the reactant mixture. This shift toward branched products could be predicted quite well by the trapping mechanism proposed by Deluzarche and co-workers (*1*, *2*). Results from studies using isotopically labeled $CH_3I$ provide the first evidence that chemical trapping may indeed be selective for catalytically *active* surface species.

A number of other significant changes in the reaction system occurred which indicate that the addition of the trapping agent irreversibly perturbs some aspects of the reaction scheme. These processes resulted in a decrease in the overall conversion of CO and a suppression of hydrogen adsorption.

These investigations suggest that $CH_3I$ acts on adsorbed species as an alkylating agent and that the identity of these adsorbed species may indeed be inferred from the products of the alkylation reaction. The chemistry of this trapping agent (including alkylation and deactivation) is overlaid onto the already complex CO hydrogenation reaction network of the Ru catalysts. The relative magnitude of the competing processes of hydrogenation, chain growth, carbon deposition, acid site chemistry, and chemical trapping of surface species must be deconvoluted before the value of the trapping technique in predicting surface species may be fully assessed.

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## REFERENCES

*1*. Hindermann, J. P., Thesis, University of Strasbourg, 1981.

*2*. Deluzarche, A., Hindermann, J. P., Kiennemann, A., and Kieffer, R., *J. Mol. Catal.* **31,** 225 (1985).

*3*. Kummer, J. T., Dewitt, T. W., and Emmett, P. H., *J. Amer. Chem. Soc.* **70,** 3632 (1948).

*4*. Emmett, P. H., *Catal. Rev.* **7,** 1 (1973).

*5*. Pichler, H. "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Eds.), Vol. 4, p. 271. Academic Press, San Diego, 1952.

*6*. Hall, W. K., Kokes, R. J., and Emmett, P. H., *J. Amer. Chem. Soc.* **79,** 2983 (1957).

*7*. Eidus, Y. T., *Russ. Chem. Rev.* **36,** 338 (1967).

*8*. Takeuchi, J. T., and Katzer, J. R., *J. Phys. Chem.* **86,** 2438 (1983).

*9*. Chuang, S. C., Goodwin, J. G., Jr., and Wender, I., *J. Catal.* **96,** 396 (1985).

*10*. Blyholder, G., and Emmett, P. H., *J. Phys. Chem.* **63,** 962 (1959).

*11*. Brady, R. C., and Pettit, R. J., *J. Amer. Chem. Soc.* **102,** 6181 (1980).

*12*. Brady, R. C., and Pettit, R. J., *J. Amer. Chem. Soc.* **103,** 1287 (1981).

*13*. Van Barneveld, W. A. A., and Ponec, V., *J. Catal.* **53,** 382 (1978).

*14.* Van Barneveld, W. A. A., and Ponec, V., *J. Catal.* **88,** 382 (1984).

*15.* Biloen, P., Helle, J. N., van den Berg, F. G. A., and Sachtler, W. M. H., *J. Catal.* **81,** 450 (1983).

*16.* Happel, J., Cheh, H., Otarod, M., Ozawa, S., Severidia, A. J., Yoshida, T., and Fthenakis, V., *J. Catal.* **75,** 314 (1982).

*17.* Winslow, P., and Bell, A. T., *J. Catal.* **86,** 158 (1984).

*18.* Ekerdt, J. G., and Bell, A. T., *J. Catal.* **62,** 19 (1980).

*19.* Wang, C. J., and Ekerdt, J. G., *J. Catal.* **80,** 172 (1980).

*20.* Oukaci, R., Ph.D. thesis, University of Pittsburgh, 1986.

*21.* Chen, Y. W., Wang, H. T., and Goodwin, J. G., Jr., *J. Catal.* **85,** 499 (1984).

*22.* Oukaci, R., Sayari, A., and Goodwin, J. G., Jr., *J. Catal.* **102,** 126 (1986).

*23.* Bond, G. C., and Xu, Y., *J. Chem. Soc. Faraday Trans. 1* **80,** 3103 (1984).

*24.* Bond, G. C., Rajaram, R., and Burch, R., *Appl. Catal.* **27,** 379 (1986).

*25.* Marques da Cruz, G., Djega-Mariadassou, G., and Bugli, G., *Appl. Catal.* **17,** 205 (1985).

*26.* Narita, T., Miura, H., Sugiyama, K., Matsuda, T., and Gonzalez, R. D., *J. Catal.* **103,** 492 (1987).

*27.* Melchor, A., Garbowski, E., Mathieu, M. V., and Primet, M., *J. Chem. Soc. Faraday Trans. 1* **82,** 1893 (1986).

*28.* Marczewski, M., Derewinski, M., and Malinowski, S., *Canad. J. Chem. Eng.* **61,** 93 (1983).

*29.* Menon, P. G., DePauw, R. P., and Froment, G. F., *Ind. Eng. Chem. Prod. Res. Dev.* **18,** 110 (1979).

*30.* Hunter, R., and Hutchings, G. J., *J. Chem. Soc. Chem. Commun.*, 1643 (1985).

*31.* Chang,, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).

*32.* Lee, C. S., and Wu, M. M., *J. Chem. Soc. Chem. Commun.*, 250 (1985).

*33.* Fung, S. C., and Sinfelt, J. H., *J. Catal.* **103,** 220 (1987).

*34.* Lin, M. S.-H., and Harrison, A. G., *Canad. J. Chem.* **52,** 1813 (1974).

*35.* Cavalcanti, F. A. P., Wender, I., and Blackmond, D. G., unpublished results.