JOURNAL OF CATALYSIS 96, 23–31 (1985)

Support Effects in the Ruthenium-Catalyzed Hydrogenation of Carbon Monoxide: Ethene and Propene Addition

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Received February 10, 1984; revised March 27, 1985

CO hydrogenation catalyzed at about 500 K by 2.6% Ru/silica (I), 1.5% Ru/13X-zeolite (II), 17% Ru/titania (III), and 5% Ru/magnesia (IV) gave methane and 1-alkenes as primary products. 1-Alkene isomerization and hydrogenation gave internal alkenes and alkanes as secondary products. Specific activity varied in the sequence III ≫ II > I > IV whereas selectivity for methane formation, as opposed to higher hydrocarbon formation, varied in the sequence I > II > III > IV. Comparison of one catalyst with another showed that when the methane yield was high the fraction of higher hydrocarbon appearing as alkane at moderate conversions was also high, and vice versa. Ethene addition to CO hydrogenation over (I) and (II) at low conversions (2 to 15%) markedly increased the rate of higher hydrocarbon formation without greatly influencing the methanation rate, whereas ethene addition over (III) and (IV) enhanced the rate of higher hydrocarbon formation by a factor of less than 2 and reduced the methanation rate. Propene addition to CO hydrogenation over (I) increased the rates both of higher hydrocarbon formation and of C_2-hydrocarbon formation, again without markedly affecting the methanation rate. The single most important factor in the determination of the total product distribution is the availability of adsorbed hydrogen which varies from catalyst to catalyst in the sequence I > II > III > IV. The activity sequence is ascribed to various metal–support effects.

INTRODUCTION

CO hydrogenation over supported ruthenium is a reaction in which activity and selectivity are principally determined by the choice of the support (*1*). Selectivity for methane formation or for the formation of higher hydrocarbons is virtually independent of the source of the metal, the dispersion of the metal in the range 5 to 55%, support acidity, and (in the case of Ru/titania) the presence or otherwise of a strong metal–support interaction (SMSI) (*1*).

In this paper we report experiments in which ethene has been added to CO hydrogenation over four supported ruthenium catalysts which, in the absence of added ethene, exhibit very different activities and selectivities. These catalysts have been selected from the 17 formulations characterized in our previous publication (*1*).

Alkene additions to CO hydrogenation have been the subject of many studies concerned primarily with the determination of reaction intermediates. As early as 1930 it was noted that the product yields from a cobalt-catalyzed reaction were increased substantially by the addition of ethene at concentrations in the range 10 to 30% (*2*). This increase was most noticeable in the alkene and alcohol fractions but the methane yield remained unchanged. Later work showed that lower concentrations of ethene, of less than 2%, were incorporated into higher hydrocarbons synthesized over a cobalt catalyst (*3*, *4*). The use of ^{14}C-labeled ethene demonstrated that the additive participated in the initiation rather than the propagation of hydrocarbon chains. At slightly higher concentrations of about 5%, ethene also participated in propagation (*4*). A mechanism involving

0021-9517/85 $3.00

alkylidene intermediates was proposed. Later, Schulz and co-workers showed that ethene, propene, 1-butene, and 1-hexadecene could each act as additional initiators for chain growth, although the extent of incorporation decreased markedly with increasing molecular weight of the additive (*5*). By contrast, alkanes added to the reaction could be recovered in nearly 100% yields. This indicated that hydrocracking and structural isomerization play a negligible role in the determination of the final products.

Dwyer and Somorjai demonstrated that 1-alkene produced as an initial product could undergo readsorption in competition with CO and hydrogen, and that such alkene then contributed significantly to the synthesis of high-molecular-weight hydrocarbons (*6*). Under their conditions of 6 atm pressure and 573 K, an Fe(111) single-crystal catalyst produced predominantly methane. Addition of ethene or propene resulted in significantly higher yields of higher hydrocarbons. The rate of methanation was only slightly affected by the presence of the added alkene. It was noted that the product distribution was very similar to that obtained over an industrial iron catalyst operated under similar conditions but at substantially higher conversions. This led to the suggestion that the readsorption and incorporation of initially produced alkenes contributed significantly to the synthesis of higher-molecular-weight hydrocarbons. Kellner and Bell have also investigated the role of ethene readsorption over a Ru/Al_2O_3 catalyst (*7*). When added in levels similar to those produced by the CO/H_2 reaction itself no ethene incorporation was observed. Higher concentrations (>1%) produced some enhancement in the rates of C_3 and C_4 formation but the synthesis of C_{6+} hydrocarbons was suppressed.

Experiments using labeled alkenes have shown that bond fission can occur especially at the carbon–carbon double bond. Pichler and Schulz (*8*) found that the α-carbon atom of 1-hexadecene underwent exchange with an adsorbed C_1 species. Lower-molecular-weight hydrocarbons showed a linearly increasing molar radioactivity which indicated that the exchanged group was participating in the propagation steps which gave rise to these products. Tamaru and co-workers have examined the effects of ethene, propene, and 4-octene as additives (*9*). When ^{12}C-labeled alkenes were added to ^{13}CO hydrogenation, the isotopic distribution of products showed that the carbon from the additives was incorporated randomly in the products; even 4-octene was found to be capable of contributing carbon, and this suggested that bond fission and formation occurred simultaneously during reaction.

Barrault and co-workers have also found that the addition of ethene significantly enhanced the formation of methane and C_3–C_4 hydrocarbons from CO and H_2 over Fe/Al_2O_3 catalysts (*10*). The results suggested that chain growth occurred by a carbene–olefin mechanism. Clearly, alkene addition to CO hydrogenation may influence both the initiation of higher hydrocarbon formation and the propagation of this process. It is generally agreed that surface carbon and partially hydrogenated carbon species such as $CH\equiv$, $CH_2=$, and CH_3- are the main intermediates in CO hydrogenation (*11*). After adsorption, an alkene additive may initiate hydrocarbon chain growth by reacting with these species. Alternatively, bond fission may occur, thus increasing the concentration of the basic C_1 "building" units. The alkene additive would therefore assist chain propagation.

On catalysts which exhibit widely different activities and selectivities for hydrocarbon formation one would expect variations in the mode and extent of alkene incorporation. In this work we have studied alkene addition to a system in which the selectivity is controlled simply by the choice of support. It was hoped that these experiments would improve our understanding of the origins of selectivity and of the support effects.

TABLE 1

Product Distributions and Activities in CO Hydrogenation under Standard Conditions[a]

Catalyst	Product distribution (%)							% Propene in C_3	Specific activity[b]
	C_1	C_2	C_3	C_4	C_5	C_6	C_7		
2.6% Ru/silica	91.9	4.2	2.6	1.3	tr[c]	tr[c]	tr[c,d]	8	4
1.5% Ru/13X-zeolite	54.5	5.0	16.5	12.5	7.0	3.5	1.0[d]	75	7
17% Ru/titania	47.5	6.5	18.0	13.0	7.5	4.5	3.0[d]	82	59
5% Ru/magnesia	26.5	3.5	23.0	20.0	12.0	9.0	6.0[d]	90	2

[a] $H_2:CO = 3:1$; total pressure = 1 atm; temperature = 493 K; conversion = 10%.

[b] Units = (CO molecules converted per site per second) × 10^{-3}. Site concentrations determined from CO adsorption isotherms on used samples; closely similar values were determined from H_2 adsorption isotherms.

[c] tr = trace = <0.5%.

[d] Higher hydrocarbons were not analyzed.

EXPERIMENTAL

Catalysts, typically 0.3–0.4 g, were studied in a down-flow fixed-bed microreactor which could be isolated and pumped to better than 10^{-5} Torr (1 Torr = 133.3 N m^{-2}) and thereafter used for *in situ* adsorption measurements. Samples were characterized by measurements of isotherms for the chemisorption of hydrogen and of carbon monoxide at room temperature both before and after use (*1*). Measurements on used samples were employed in the calculation of specific activities.

CO hydrogenation was studied using a 3 : 1 mixture of hydrogen and carbon monoxide at a total pressure of 1 atm with flow rates adjusted to restrict conversion to the range 2 to 15%. The effect of ethene or propene addition was examined using alkene concentrations which constituted 2.5 to 15% of the total reactant flow. Steady-state operation was achieved by allowing the feed stream to flow over the catalyst for 20 min before a product analysis was made; between such runs a flow of hydrogen was maintained over the sample and this regenerated a reproducible metal surface and avoided significant permanent deactivation (the Vannice procedure (*12*)).

Products were analyzed by use of a Perkin–Elmer Sigma 1 gas chromatograph fitted with a thermal conductivity detector. Separation of C_2 to C_7 hydrocarbons and CO_2 was achieved by use of a Chromosorb P column with stationary phases of bis-2-methoxy-ethyl adipate (13.5%) and diethylhexyl sebacate (6.5%). Hydrogen, carbon monoxide, and methane were separated by a column containing partially activated 13X molecular sieve.

Details concerning ruthenium compounds and methods used in catalyst preparation have been described (*1*). Ru/13X-zeolite was the gift of Professor G. C. Bond and was prepared by an ion-exchange method using $Ru(NH_3)_6Br_3$. Before adsorption measurements were made, catalysts were reduced or rereduced overnight in flowing hydrogen at 623 K.

RESULTS

Four catalysts were used: 2.6% Ru/silica, 1.5% Ru/13X-zeolite, 17% Ru/titania, and 5% Ru/magnesia. In the absence of added ethene these catalysts showed considerable differences in both their activities and selectivities in CO hydrogenation (Table 1). Ru/titania was about 10 times as active as Ru/silica or Ru/zeolite and nearly 30 times as active as Ru/magnesia. Ru/silica was highly selective for methane formation, whereas Ru/magnesia favored the formation of higher hydrocarbons. Over each catalyst, and at all temperatures studied in the

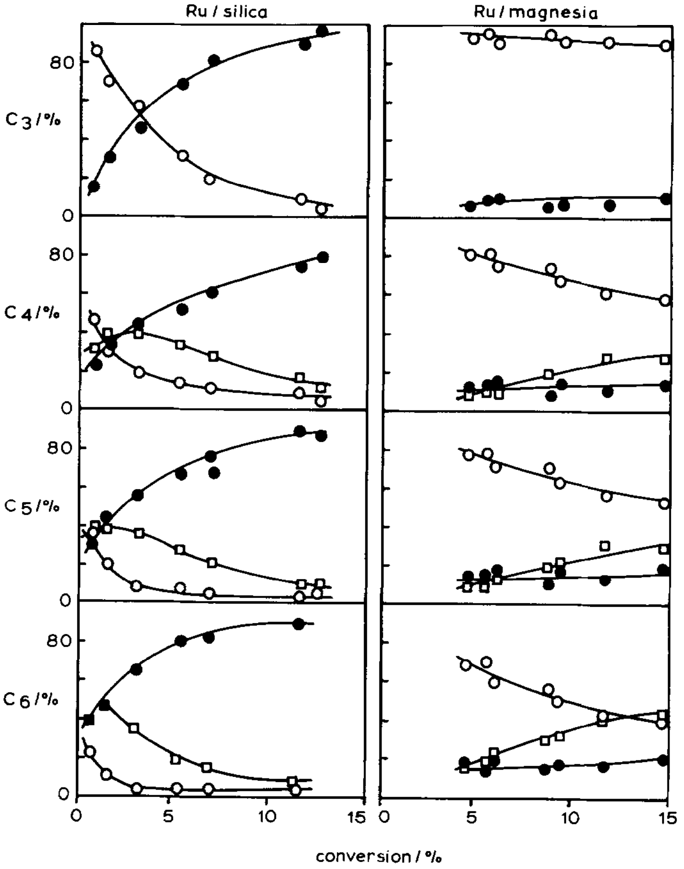

FIG. 1. CO hydrogenation over Ru/silica and over Ru/magnesia; variation with conversion of the yields of 1-alkene (open circles), total 2- and 3-alkene (squares), and alkane (filled circles). Conditions: H_2:CO = 3:1, total pressure = 1 atm.

range 450 to 575 K, the primary products of higher hydrocarbon formation were 1-alkenes (Fig. 1). Over Ru/silica preferential formation of 1-alkene was observed only at conversions below about 1%, and the rate of subsequent hydrogenation to alkane increased with increasing carbon number. At the other extreme, over Ru/magnesia, 1-alkene was the major product of higher hydrocarbon formation over the whole range of conversion studied. Moreover, the yields of the internal alkenes, like those of the alkanes, approached zero at very low conversions, indicating that they also were secondary products.

The selectivity of Ru/13X-zeolite and of Ru/titania was always intermediate between that of Ru/silica and that of Ru/magnesia.

Addition of ethene to CO hydrogenation modified the product composition. The variation of the overall product distributions, classed by carbon number, with the percentage of ethene added to the reactant flow is shown in Fig. 2. C_2 products are not included because synthesis of these is masked by the large quantities of ethene present in the reactant mixture. However, C_2 production was assumed to have continued at the rate observed under normal conditions and allowance has been made for this. An analogous procedure was adopted for those experiments in which propene was added to the (CO + H_2) mixture (Table

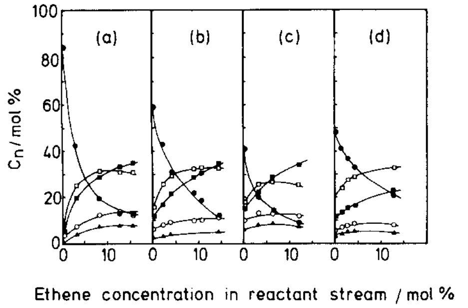

FIG. 2. CO hydrogenation. Variation of the product composition, C_n, with the concentration of added ethene over (a) Ru/silica at 489 K, (b) Ru/13X-zeolite at 505 K, (c) Ru/titania at 478 K, and (d) Ru/magnesia at 559 K. Conditions: $H_2 : CO = 3:1$; total pressure ($H_2 + CO + C_2H_4$) = 1 atm. Filled circles = C_1; open squares = C_3; filled squares = C_4; open circles = C_5; and filled triangles = C_6.

TABLE 3

Rate Enhancements Observed When Ethene or Propene at a Concentration of 5% Was Added to CO Hydrogenation[a]

Catalyst	Additive	Rate enhancement factor					
		C_1	C_2	C_3	C_4	C_5	C_6
2.6% Ru/silica	Ethene	1.2		13	24	22	30
1.5% Ru/13X-zeolite	Ethene	1.8		7.2	8.0	4.4	4.5
17% Ru/titania	Ethene	0.2		1.6	1.9	1.7	1.6
5% Ru/magnesia	Ethene	0.6		1.5	1.4	1.3	1.2
2.6% Ru/silica	Propene	1.4	11.0		14.0	15.0	16.7

[a] Experimental conditions are described in Fig. 2.

2). Rate enhancements caused by ethene and propene additions are shown in Table 3.

Over all four catalysts, ethene addition caused an increase in the yields of higher hydrocarbons. C_4 production was most noticeably increased (Fig. 2), but this was due in part to a considerable increase in the rate of *cis*-2-butene formation. There was also a particularly marked increased in the yield of one of the internal hexenes, probably 3-hexene; this product amounted to one-half of the C_6 yield over Ru/silica (Fig. 2a). Since these alkenes are not important primary products of CO hydrogenation in the absence of added ethene, they must have been formed by a process which is an alternative to normal chain growth, i.e., specific dimerization and trimerization. Similar behavior has been observed by other workers (*10*). This reaction is remarkable for its specificity but it is not important for our present study of support effects.

The titania-supported catalyst, notable for its high activity, showed only a slight tendency to involve ethene in further chain growth. Methane formation was suppressed by the presence of added ethene (Table 3), and this was the main reason for the enhanced selectivity for the formation of higher hydrocarbons (Fig. 2). Similar results were obtained for the magnesia-supported sample which was highly selective for higher hydrocarbon formation even under normal operating conditions.

Over Ru/silica and Ru/zeolite ethene was involved in chain growth to a considerably greater extent and higher hydrocarbon production increased by at least one order of magnitude. The change in catalytic behavior was most remarkable in the case of Ru/silica. Under normal operating conditions this sample provided low yields of higher hydrocarbon, and methane was the predominant product. When small concentrations of ethene were introduced into the feed stream the rate of chain growth increased dramatically. This demonstrates that catalysts which strongly favor methanation are in fact capable of higher hydrocarbon formation, but chain growth is inhibited before

TABLE 2

CO Hydrogenation in the Presence of Added Propene over 2.6% Ru/silica at 483 K

Added propene (%)	Yields of hydrocarbon products (%)[a]				
	C_1	C_2	C_4	C_5	C_6
0	88.5	4.2	3.9	2.9	0.5
4.5	48.4	16.7	20.8	9.5	4.6
12.0	32.5	17.1	28.4	14.3	7.7

[a] The total C_3 yield, which cannot be measured for Experiments 2 and 3, has been extracted from the observed product distribution for Experiment 1.

the formation of an adsorbed C_2 unit. When this step is bypassed by the addition of ethene, chain growth can proceed at a rate comparable with that of the most active catalysts studied. A carbon mass balance indicated that as many as 90% of the carbon atoms present in the products originated from the ethene additive, when the additive was present at a concentration of 15% in the reactant flow. Surprisingly, the rate of CO consumption remained unaffected by the presence of ethene in the feed stream.

The ethene addition experiments described above did not provide information concerning the relative rates of hydrogenation and incorporation of ethene because the chromatograph did not separate ethene and ethane. Consequently, a few experiments were performed in which propene was added to CO hydrogenation. The chromatograph separated propene and propane, and hence it was possible to determine the relative rates of hydrogenation and incorporation of propene and to examine whether the characteristics of propene incorporation were similar to those of ethene. A large increase in selectivity for higher hydrocarbon formation was again observed (Table 2), but no evidence for propene dimerization was obtained; the yield of C_2 product was greatly increased, but once again methane formation was unaffected. When the propene concentration was 5%, 25% of the propene was hydrogenated and 6% was incorporated into higher hydrocarbons; on the same catalyst under identical conditions 25% of added ethene was incorporated into higher hydrocarbons.

DISCUSSION

We have argued previously that the support plays the dominant role in determining activity and selectivity of CO hydrogenation over ruthenium catalysts (*1*). These aspects of catalytic behavior were only slightly dependent on metal dispersion in the range 5 to 55%. The unusual behavior of titania-supported catalysts could not be attributed to the strong metal–support interaction because activity and selectivity showed little variation with reduction temperature (*1*). The use of highly acidic supports resulted in secondary reactions of initial products such as isomerization but did not strongly influence the synthesis rate or selectivity. Magnesia, which is a basic support, had a more profound effect on the catalytic behavior of ruthenium but activity and selectivity were sensitive to the presence of chloride impurity. Chloride-free samples, such as the Ru/magnesia used here, showed low activity but favored higher hydrocarbon production.

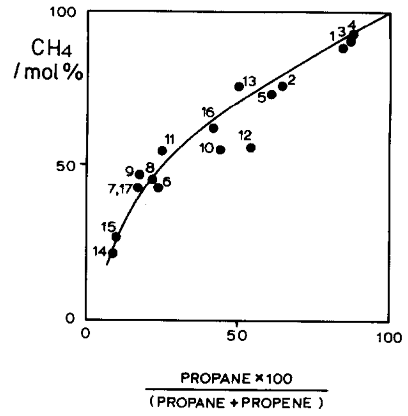

FIG. 3. Correlation of methane yield with the fraction of higher hydrocarbon that appeared as alkane, as typified by the proportion of propane in the C_3 yield. The 17 points plotted represent the behavior of the 17 catalysts listed in Table 2 of Ref. (*1*) and are numbered accordingly. The four catalysts studied further in this paper are numbered 4 (Ru/silica), 9 (Ru/titania), 11 (Ru/13X-zeolite), and 15 (Ru/magnesia). Conditions: $H_2:CO = 3:1$; temperature = 493 K; total pressure = 1 atm; conversion = 10%.

Throughout our studies we have noted a strong correlation between the overall selectivity of a catalyst and the proportion of alkane in the products. A similar observation has been made by King (*13*). When methane production is favored, a high proportion of the higher hydrocarbon is alkane. Conversely, conditions which favor higher hydrocarbon synthesis provide predominantly alkenes. This is demonstrated in Fig. 3, where a clear relationship can be

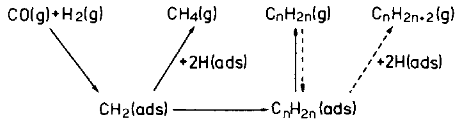

FIG. 4. Formal representation of a mechanism which shows (i) methane and alkene as primary products and (ii) a common dependence of methane yield and of higher alkane yield on hydrogen availability.

seen between methane selectivity and the percentage of propane present in the C_3 fraction.

This correlation suggests that the availability of hydrogen adsorbed at the catalyst surface is the most important factor in determining selectivity. A high surface concentration of hydrogen leads to hydrogenation of monocarbon species rather than their polymerization and also increases the probability that long-chain intermediates become fully hydrogenated (Fig. 4). A catalyst providing this surface condition will therefore be most active in methanation and there will be a high probability that 1-alkene formed as a primary product can be hydrogenated to alkane on readsorption. Conversely, a low surface concentration of hydrogen produces conditions under which the catalyst is selective for alkene formation, and the probability of alkane formation, including methanation, is minimized.

This interpretation of the results can be summarized in the statement that both the availability of adsorbed hydrogen and the extent of alkene incorporation varies, from catalyst to catalyst, in the sequence

$$\text{Ru/silica} > \text{Ru/zeolite} > \text{Ru/titania} > \text{Ru/magnesia}.$$

It is likely that alkene regains access to the catalyst surface by competing for adsorption sites with hydrogen.

Since CO hydrogenation exhibits a positive order with respect to hydrogen (*11*), the availability of adsorbed hydrogen would be expected to influence activity. However, for the range of catalysts studied no clear correlation was found between activity and selectivity, and so other factors such as site density must be primarily responsible for the observed activities.

During propene insertion the formation of C_2 products was increased in a manner similar to that of the higher hydrocarbons but methane formation was unaffected. This suggests that propene was converted into C_2 and/or C_1 fragments from which chain growth occurred. It might appear that an increase in the concentration of such species would lead to an increased rate of methane formation. However, most added alkene is simply hydrogenated and the additive also displaces hydrogen from the surface. Thus, an increased concentration of C_1 species is counterbalanced by a decrease in the surface hydrogen concentration; these two effects apparently cancel, so that the rate of methanation is not, in practice, influenced by alkene addition.

The titania- and magnesia-supported catalysts, although of similarly high selectivity for higher hydrocarbon formation, differed markedly in activity, Ru/titania being the more active. This concurs with many recent reports which have shown that titania can induce high CO hydrogenation activity in Ni (*14–16*), Ru (*17*), Rh (*18, 19*), and Pd (*20, 21*). Magnesia-supported catalysts, on the other hand, were the least active samples studied. These differences in behavior are attributed to metal–support interactions.

Interactions between a metal and support or promoter can be structural or electronic in nature (*22*). The two types of interaction can be distinguished because structural effects of supports tend to modify site concentrations leaving the apparent activation energy of reactions unaltered, whereas electronic effects of supports may cause a modification in apparent activation energy.

In most cases, the activation energies for methanation and for overall CO consumption were not affected by the choice of support (*1*). Titania-supported catalysts exhibited activation energies almost identical to those of unsupported ruthenium powder. If an electronic interaction was directly responsible for their higher activity and their selectivity toward higher hydrocarbon formation, then considerably lower activation energies would have been expected. Unusual behavior of titania-supported catalysts has often been linked with the so-called strong metal–support interaction (SMSI) which may be electronic in nature (*23*). Recently it has been shown that titania-supported catalysts sometimes exhibit a behavior after low-temperature reduction (where SMSI is absent) which is the same as that observed after high-temperature reduction (where SMSI is present) (*18–20*). For example, in this laboratory it has been found that the activity and selectivity of Ru/titania (*1*) and of Rh/titania (*24*) in CO hydrogenation is independent of the temperature of pretreatment. Indeed, adsorbed oxygen produced during CO hydrogenation actually removes the strong metal–support interaction before its effects can be observed. This suggests that the very high activity of Ru/titania recorded here arises from an interaction which is structural rather than electronic in nature and which produces a higher concentration of active sites.

However, Ru/magnesia free of chloride exhibited a behavior which was characteristic of a strong electronic interaction. Compared with unsupported ruthenium, the activity of the catalyst was markedly lower, while the apparent activation energy for methanation was considerably greater (*1*) and the reaction itself was highly selective for the production of alkenes. It has been noted that the support effects of chloride-free magnesia are strikingly similar to the promotional effects of potassium, and this suggests that a similar mechanism may be responsible (*1*). Alkali metal promotion is generally thought (*25*) to involve charge transfer to the metal and a similar transfer may occur between magnesia and ruthenium particles. This would lead to an increase in the back-donation of electrons to the antibonding π orbitals of adsorbed CO, and thus to a strengthening of the metal–carbon bond and a weakening of the carbon–oxygen bond. Thus, CO chemisorption is strengthened and dissociation is assisted by an increase in electron density at the metal. The access of hydrogen to the surface would be reduced by such an increased strength of CO adsorption and this would lead to a lower activity. Selectivity would also be shifted in favor of higher hydrocarbon production because of the reduced availability of hydrogen.

ACKNOWLEDGMENTS

S.R.M. thanks the Science and Engineering Research Council for the award of a CASE Studentship; the collaborating body was ICI plc New Science Group.

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