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A Comparative Evaluation of Cobalt Chromium Oxide, Cobalt Manganese Oxide, and Copper Manganese Oxide as Catalysts for the Water–Gas Shift Reaction

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Cobalt chromium oxide, cobalt manganese oxide, and copper manganese oxide have been compared as catalysts for the water–gas shift reaction. Cobalt chromium oxide and cobalt manganese oxide catalysts can give both high activity and long lifetimes for this reaction. Cobalt chromium oxide catalysts display higher activity compared to the other catalyst systems and this is shown to be mainly due to the stable high surface areas achieved with this catalyst. Studies have shown that both the cobalt chromium oxide and the cobalt manganese oxide catalysts are not sensitive to the presence of up to 240 ppm feedstock sulphur impurities (H_2S and COS) and high catalyst activity can be maintained either in the presence or in the absence of feedstock sulphur. The copper manganese oxide catalysts are demonstrated to be particularly sensitive to feedstock sulphur, being significantly poisoned at levels as low as 1 ppm H_2S. An investigation of the mechanism of the water–gas shift mechanism over the three catalyst systems is also described using both kinetic and model reagent studies. Based on these studies, a mechanism is proposed for the cobalt- and copper-containing catalyst systems involving the formation of a surface formate intermediate.

INTRODUCTION

The chemical industry utilises considerable quantities of hydrogen in the production of chemical products and intermediates, e.g., ammonia synthesis from the reaction of nitrogen with hydrogen or methanol synthesis from carbon monoxide hydrogenation. The hydrogen is primarily obtained, in most locations, by the steam reforming of methane or higher hydrocarbons, a reaction which produces CO and H_2 as the principal products. For most applications the hydrogen concentration of the product gases is insufficient and in this case, the water–gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is extensively used either to adjust the CO/H_2 ratio for the subsequent synthesis of methanol or to produce hydrogen for ammonia synthesis. In view of its industrial importance, the water–gas shift reaction has been the subject of numerous theoretical and mechanistic studies (*1–4*). At present when the production of high-purity hydrogen is required the water–gas shift reaction is carried out in two distinct stages, using catalysts that have been specifically designed for each stage. The first step involves a high-temperature conversion (300–400°C) using an iron–chromium spinel catalyst (*3, 5*), which decreases the CO concentration from an initial value of ca. 35–40

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mol% to ca. 3 mol%. Conversion of the remaining carbon monoxide is carried out in a lower-temperature process stage (200–250°C) since the equilibrium CO concentration decreases with decreasing reaction temperature. The catalyst used in this second step is a high-activity copper–zinc oxide (*6, 7*). The formulations of both these catalysts have been optimised for the conversion of CO/H_2 feedstocks, derived from hydrocarbon steam reforming, which are relatively free from sulphur impurities. The iron–chromium oxide catalysts were originally formulated for use with coal-derived CO/H_2 and in the sulphided form this catalyst retains about half the activity of the nonsulphided material (*8*). Previous attempts to design a high-activity catalyst suitable for use with sulphur-containing feedstocks have identified that cobalt molybdenum oxide catalysts are more active than the iron chromium oxide or copper–zinc oxide catalysts. However, stable high activity is only achieved when these cobalt catalysts are fully sulphided (*9*), which requires that sulphur compounds are continuously fed to the reactor in significant concentration. There is therefore a need to identify a catalyst that retains high activity, both in the presence and in the absence of feedstock sulphur. We have previously shown that cobalt in an alternative oxide matrix, namely cobalt manganese oxide, can also be more active than the present high-temperature iron chromium oxide catalyst in the temperature range 350–400°C (*10–13*).

The cobalt manganese oxide catalysts have been found to be particularly effective for the conversion of high inlet carbon monoxide concentrations and, hence, may be more useful for the conversion of coal-derived CO/H_2. In this paper we extend our study of cobalt-based water–gas shift catalysts and investigate cobalt chromium oxide catalysts which are demonstrated to be most active when compared with iron chromium oxide, cobalt manganese oxide, and copper manganese oxide catalysts. In addition, the sulphur sensitivity of these catalysts is investigated, and we also discuss the mechanism of the water–gas shift reaction over cobalt and copper-based catalyst formulations using both kinetic and model reagent studies.

EXPERIMENTAL

Cobalt manganese oxide catalyst precursors were prepared by coprecipitation from a mixed aqueous solution of cobalt nitrate (0.75 mol liter^{-1}, Aldrich, 99%) and manganese nitrate (0.75 mol liter^{-1}, Aldrich, 99.99%) at 70°C and pH 8.3 ± 0.01 using aqueous ammonia (30% by volume) as precipitant. Copper manganese oxide catalyst precursors were similarly prepared by coprecipitation from a mixed aqueous solution of copper nitrate (0.75 mol liter^{-1}, Aldrich, 98%) and manganese nitrate (0.75 mol liter^{-1}, Aldrich, 99.99%) at 25°C and pH 8.7 ± 0.01 using aqueous sodium carbonate (1 mol liter^{-1}) as precipitant. Cobalt chromium oxide catalyst precursors were prepared by coprecipitation from a mixed aqueous solution of chromium nitrate (0.75 mol liter^{-1}, Aldrich, 99%) and cobalt nitrate (0.75 mol liter^{-1}, Aldrich, 99%) at 70°C and pH 9.3 ± 0.01 using aqueous ammonia (30% by volume) as precipitant. The catalyst precursors were recovered by filtration, washed with deionised water, and dried in air (110°C, 5 kPa, 16 h). Prior to use, catalyst precursors were pelleted and sieved (particle size 0.5–1.2 mm), calcined (500°C, 24 h), and reduced *in situ* in the catalytic reactor with hydrogen and evaluated for the water-gas shift reaction at a pressure 0.82 atm using a laboratory microreactor, described previously (*10, 14, 15*). Alkali-promoted catalysts were prepared by impregnation of the catalyst precursor following calcination with aqueous potassium carbonate solution using an incipient wetness technique. Analysis of catalyst precursors by atomic absorption spectroscopy did not indicate the presence of any significant impurities in the catalyst sample.

Catalysts were evaluated for the reaction of predried model reagents using an all-glass microreactor (i.d. 14 mm) and the reagents were fed to this reactor using controlled vaporisation in a nitrogen carrier gas. All water–gas shift and model reagent reaction products were analysed by gas chromatography. The experimental accuracy of the selectivity and conversion data quoted in this paper is ±0.5%.

The effect of sulphur-containing feedstocks on catalyst performance was evaluated by adding known quantities of sulphur, as H_2S, to a desulphurised CO/H_2 gas mixture. The desulphurised CO/H_2 gas was derived from a coal feedstock and obtained from a coal-based ammonia synthesis plant operated by AECI Ltd (Modderfontein, South Africa).

RESULTS

Cobalt Chromium Oxide Water–Gas Shift Catalysts

Cobalt chromium oxides have been studied previously as catalysts for a broad range of reactions including ammonia oxidation (*16*), hydrocarbon oxidation (*17–19*), and automobile exhaust pollution control (*20–22*). Our interest in the use of cobalt chromium oxides as catalysts for the water–gas shift reaction was prompted by the recent observation that these oxides were active for the oxidation of carbon monoxide (*23, 24*) and the previous observation by Kadenatsi *et al.* (*25*) that at 390–400°C CO could be completely oxidised over a Co Cr_2O_4 spinel catalyst. In addition, cobalt has been used as a promoter for iron chromium oxide water–gas shift catalysts (*26*). However, to date no definitive study of cobalt chromium oxides as water–gas shift catalysts has been reported.

The results from the reaction of CO/H_2O in the presence of N_2 as diluent over a range of cobalt chromium oxide catalysts (Co : Cr = 10 : 1, 3 : 1, 1 : 1, 1 : 10) are shown in Fig. 1. The data presented are for the conversion of CO to CO_2, but identical trends were also observed for the production of H_2 from H_2O. It is apparent that cobalt chromium oxides can be highly effective as catalysts for the water–gas shift reaction, and the ratio of Co to Cr is of crucial importance in determining catalyst activity, with the catalyst activity increasing in line with increasing Co content. At 300°C the highest activity was obtained from the Co : Cr = 3 : 1 catalyst. The Co : Cr ratio was also found to affect the lifetime of the catalysts significantly and typical results are given in Fig. 2 for extended reactions at 400°C. The Co : Cr = 3 : 1 catalyst is found to be particularly stable and no loss in activity was observed for reaction times of ca. 650 h, whereas other Co : Cr catalysts demonstrate a steady loss of catalyst activity with increased reaction

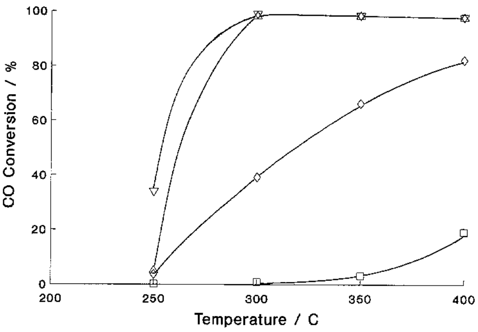

FIG. 1. Effect of temperature on CO conversion for cobalt chromium oxide catalysts, CO GHSV = 510 h^{-1}, $CO:N_2:H_2O$ = 1 : 1 : 4.5; (□) Co : Cr = 1 : 10; (◇) Co : Cr = 1 : 1; (▽) Co : Cr = 3 : 1; (△) Co : Cr = 10 : 1.

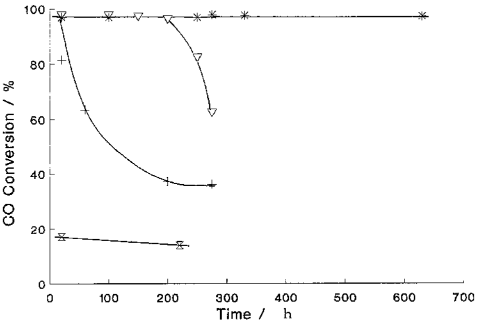

FIG. 2. Stability of cobalt chromium oxide catalysts at 400°C, CO GHSV = 510 h^{-1}, $CO:N_2:H_2O$ = 1 : 1 : 4.5; (⧖) Co : Cr = 1 : 10; (+) Co : Cr = 1 : 1; (*) Co : Cr = 3 : 1; (▽) Co : Cr = 10 : 1.

TABLE 1

Pseudo-First-Order Rate Constants[a]

Temperature (°C)	10^{-7} k_1 (mol g^{-1} atm^{-1} s^{-1})[b]			
	Co : Cr = 3 : 1	Co : Mn = 3 : 1	Cu : Mn = 1 : 3	Fe : Cr[c]
250	33	4.9	4.6	—
300	367	184	101	31

[a] CO GHSV = 510 h^{-1}, CO : N_2 : H_2O = 1 : 1 : 4.5.

[b] $k_1 = (F/mP) \cdot \ln(1/(1 - x_A))$, where F is the molar flow rate of carbon monoxide, m is the mass of catalyst, P is the pressure (1 atm = 101.325 kPa), x_A is the fraction conversion of carbon monoxide.

[c] Commercial iron chromium oxide high-temperature water–gas shift catalyst.

time. In a previous study (*11*) a steady loss of catalyst activity with increased reaction time has also been observed for the cobalt catalyst under these reaction conditions. The loss of activity can be attributed to sintering of the catalyst by the presence of high-temperature steam, and surface area determinations, using the BET method, confirmed this to be the case.

Cobalt chromium oxide catalyst demonstrated very little catalytic activity below 250°C, and in general, catalytic activity increased markedly between 250 and 350°C. In view of this, the cobalt chromium oxides are therefore classified as high-temperature shift catalysts.

Comparison of Catalyst Activity of Co/Cr, Co/Mn, Cu/Mn, and Fe/Cr

In view of the high activity of Co : Cr catalysts for the water–gas shift reactions, it is necessary to compare their catalytic activity with that of the commercial iron chromium high-temperature water–gas shift catalyst, as well as the cobalt manganese oxide (Co : Mn = 3 : 1) and copper manganese oxide (Cu : Mn = 1 : 3) identified as high-activity catalysts in our previous studies (*10, 11*). A comparison of catalyst activity at 250 and 300°C in the form of pseudo-first-order rate constants is shown in Table 1. It can be concluded that the cobalt chromium oxide (Co : Cr = 3 : 1) gives the highest CO conversion for these catalysts and is considerably more active than the current commercial iron chromium oxide high-temperature water–gas shift catalyst. This difference in activity for Co and Fe in the same oxide matrix is in line with previous studies for these metals (*27*).

Surface areas were determined for cobalt chromium catalysts before and after use and the data demonstrated that these catalysts increased in surface area significantly on reduction and use (e.g., Co : Cr = 1 : 1, calcined 28 m^2 g^{-1}, after use for 600 h 86 m^2 g^{-1}). The surface areas of cobalt chromium catalysts were markedly higher than those for cobalt manganese oxide or copper manganese oxide after use (e.g., Co : Mn = 1 : 1, after use for 600 h, 45 m^2 g^{-1}; Cu : Mn = 1 : 1 after use for 600 h, 6 m^2 g^{-1}). It is therefore apparent that the order of catalytic activity observed for these oxides is directly related to the magnitude of the stable surface area achieved under reaction conditions. When catalyst activity is corrected for surface area the Cu : Mn = 1 : 1, Co : Mn = 1 : 1, and Co : Cr = 1 : 1 catalysts give specific activities of 41.6×10^{-4}, 8.68×10^{-4}, and 1.78×10^{-4} mol CO converted m^{-2} h^{-1} (temperature 350°C, CO GHSV = 510 h^{-1}, CO : N_2 : H_2O = 1 : 1 : 4.5). On the basis of this specific activity comparison the manganese oxide matrix can be considered to be superior to the chromium oxide matrix for cobalt as an active metal for the water–gas shift reaction. However, it should be noted

TABLE 2

Temperature Dependence of Equilibrium CO Conversion

Temperature (°C)	CO conversion (%)		
	At equilibrium[a]	Co : Cr = 3 : 1[b]	Co : Mn = 3 : 1[b]
250	99.70	33.9	—
300	99.45	99.0	90.0
350	99.18	98.4	98.7
400	98.28	—	98.3

[a] Calculated using the equilibrium constant for each temperature, CO GHSV = 510 h^{-1}, $CO:H_2O$ = 1:4.5

[b] 2 g catalyst.

that both the Co : Mn = 3 : 1 and the Co : Cr = 3 : 1 catalysts demonstrate high catalytic activity and this activity can be maintained without loss for at least 600 h.

The temperature dependence of the equilibrium constant for the water–gas shift catalyst has been well studied (*8*) and the CO conversion that can be achieved at equilibrium decreases with increasing temperature. The equilibrium CO conversion levels for the reaction conditions utilised in this study are shown in Table 2 and are compared with the conversions achieved for the Co : Cr = 3 : 1 and Co : Mn = 3 : 1 catalysts. It is apparent that the CO conversion of the Co : Cr = 3 : 1 catalyst is very close to the equilibrium value at 300°C and that this is only achieved for the Co : Mn catalyst at higher temperatures. Hence, although the catalyst formulations are yet to be fully optimised, it can be concluded that cobalt chromium oxide catalysts are highly effective for the water–gas shift reaction.

Formation of By-product Methane

Previous studies (*10, 11*) have shown that the commercial iron chromium oxide catalyst and the copper manganese catalyst do not produce any by-product methane via the hydrogenation of CO. However, the introduction of cobalt as a catalytic component causes an increase in the production of by-product methane and the effect of reaction temperature on methane production for Co : Cr and Co : Mn catalysts is shown in Figs. 3 and 4, respectively. Methane is the

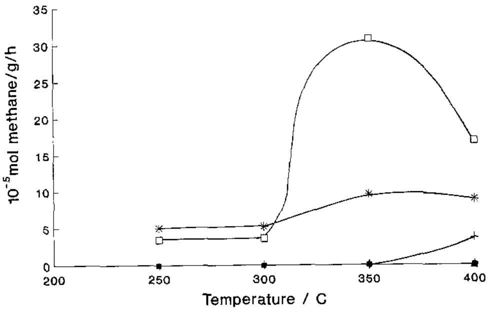

FIG. 3. Methane by-product formation over cobalt chromium oxide catalysts, CO GHSV = 510 h^{-1}, $CO:N_2:H_2O$ = 1 : 1 : 4.5; (■) Co : Cr = 1 : 10; (+) Co : Cr = 1 : 1; (*) Co : Cr = 3 : 1; (□) Co : Cr = 10 : 1.

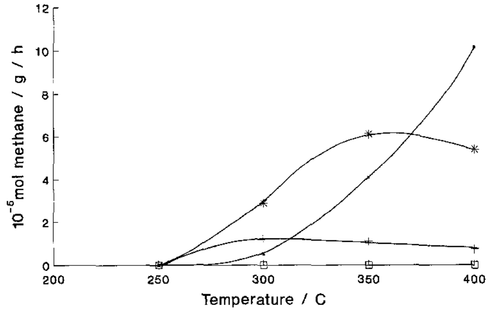

FIG. 4. Methane by-product formation over cobalt manganese oxide catalysts, CO GHSV = 510 h^{-1}, $CO:N_2:H_2O$ = 1 : 1 : 4.5; (■) Co; (+) Co : Mn = 3 : 1; (*) Co : Mn = 1 : 1; (□) Co : Mn = 1 : 3.

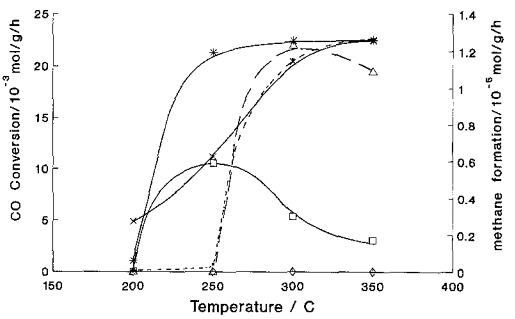

FIG. 5. Effect of potassium addition on rate of carbon monoxide conversion and methane formation for Co : Mn = 3 : 1 at CO GHSV = 510 h^{-1}, CO : N_2 : H_2O = 1 : 1 : 4.5. CO conversion: (□) 0% K^+, (×) 1% K^+, (*) 2% K^+; CH_4 formation: (△) 0% K^+, (□) 1% K^+, (◇) 2% K^+.

only hydrocarbon product observed for Co : Cr or Co : Mn catalysts and its formation is considered to be deleterious for two reasons. First, the CO hydrogenation reaction is highly exothermic and hence could cause the temperature to rise significantly, which could result in damage to the catalyst, e.g., loss of surface area by sintering. Second, methane formation uses some of the desired hydrogen product which gives rise to yield losses in an industrial process.

The addition of alkali metal compounds to CO hydrogenation catalysts is known to significantly affect both the catalytic activity and the product selectivity (*28*). The effect of alkali promotion in the optimal catalyst formulations (i.e., Co : Cr = 3 : 1, Co : Mn = 3 : 1) was investigated by the addition of potassium carbonate via impregnation using an incipient wetness technique followed by the usual calcination step. The effect of the alkali addition on the two catalysts was found to be markedly different (Figs. 5 and 6). For the cobalt manganese oxide catalyst (Fig. 5) the addition of potassium carbonate significantly enhanced the catalytic activity, particularly at temperature <350°C, and additionally resulted in a marked decrease in the formation of by-product methane. In particular, the Co : Mn = 3 : 1 formulation promoted with 1% K_2CO_3 gave 98% CO conversion at 300° with 0.03% methane selectivity. For the cobalt chromium oxide catalyst (Fig. 6), although the addition of potassium carbonate leads to a decrease in the formation of by-product methane, it also causes significant deactivation of the catalyst, particularly at temperatures <350°C.

Effect of Feedstock Sulphur Impurities on Catalyst Activity

The sulphur sensitivity of the cobalt chromium oxide (Co : Cr = 3 : 1), cobalt manganese oxide (Co : Mn = 3 : 1), and copper manganese oxide (Cu : Mn = 1 : 3) was investigated. The reactant gas for these experiments was derived from the desulphurised feed gas for the water–gas shift reaction of a coal-derived ammonia plant to which small amounts of H_2S were added. It is expected that some H_2S subsequently reacted with CO present in the reactant gas and consequently the feed gas was analysed for total sulphur (COS + H_2S) prior to reaction. Two experiments were conducted using different levels of total sulphur. The first experiment utilised a feed gas with composition: CO 56.8 mol%, CO_2 8.4 mol%, H_2 30.6 mol%, N_2 4.2 mol%, total S 1 ppm, and the results are shown in Fig. 7. The subsequent experiment utilised a feed gas containing CO 57.9 mol%, CO_2 6.7 mol%, H_2 31.5 mol%, N_2 3.8

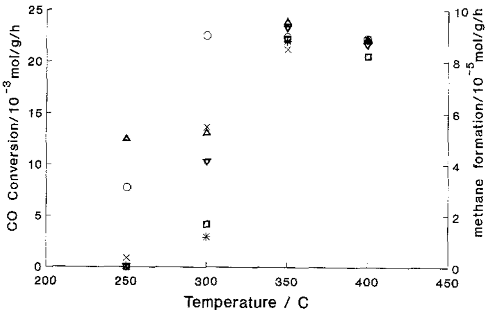

FIG. 6. Effect of potassium addition on rate of carbon monoxide conversion and methane formation for Co : Cr = 3 : 1 at CO GHSV = 510 h^{-1}, CO : N_2 : H_2O = 1 : 1 : 4.5. CO conversion: (○) 0% K^+, (*) 1% K^+, (×) 2% K; CH_4 formation: (△) 0% K, (□) 1% K, (◇) 2% K.

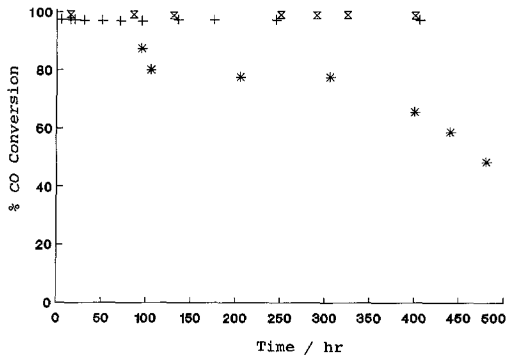

FIG. 7. Stability of catalysts using coal-derived feed gas containing 1 ppm sulphur. CO GHSV = 510 h^{-1}. (⧖) Co : Cr = 3 : 1, 350°C; (+) Co : Mn = 3 : 1, 350°C; (*) Cu : Mn = 1 : 3, 400°C.

mol%, total S 240 ppm, and the results are shown in Fig. 8. These two levels of sulphur were selected to examine the effect of both minor contaminant levels of S (i.e., 1 ppm), which are known to rapidly poison the Cu/ZnO low-temperature shift catalyst, as well as larger levels of S (i.e., 240 ppm) that could be expected from incomplete removal of S from coal-derived synthesis gas.

The results indicate that both the cobalt chromium oxide and the cobalt manganese oxide catalysts not only continue to demonstrate very high activity for the water–gas shift reaction, but that this high activity was maintained in the presence of both levels of sulphur for the duration of the experiment. It can therefore be concluded that both catalysts are insensitive to the presence of feedstock S compounds. Following reaction, the catalysts were cooled in dry nitrogen prior to analysis by X-ray diffractometry and no detectable differences were observed in the diffractograms of catalysts following reaction in the absence of sulphur. While it is possible that any cobalt sulphide phases present could be oxidised by air prior to the X-ray analysis, all care was taken to minimise this possibility. The amount of sulphur passed through the catalyst bed in these experiments corresponded to ca. 14% of the catalyst mass. Since no bulk structural changes were observed to occur, it is considered that the Cr_2O_3 matrix contained sulphides only at the surface. These results are in contrast to the findings for cobalt molybdate catalysts which only function when fully sulphided (*9*). In addition, these findings demonstrate the flexibility of the cobalt chromium oxide and cobalt manganese oxide catalysts towards the presence of feedstock sulphur compounds, since high activity can be maintained either in the presence or in the absence of H_2S and COS.

In contrast to the sulphur insensitivity of the two cobalt formulations, the copper manganese oxide catalyst rapidly deactivated in the presence of both 1 and 240 ppm total feedstock sulphur. This is in agreement with previous observations for the sulphur sensitivity of other copper catalysts (*8*).

Structural Studies

A detailed study of the bulk structure of Co : Cr catalysts was carried out using X-ray diffractometry and the fresh uncalcined catalysts were found to be totally amorphous. Calcination of this material at 500°C leads to the formation of a crystalline spinel $Co_{3-x}Cr_xO_4$ in which the chromium atoms exclusively occupy the octahedral sites. Following reduction in hydrogen at 400°C, the spinel phase is observed to become more crystalline and traces of Co metal were also observed. After reaction for 600 h under the

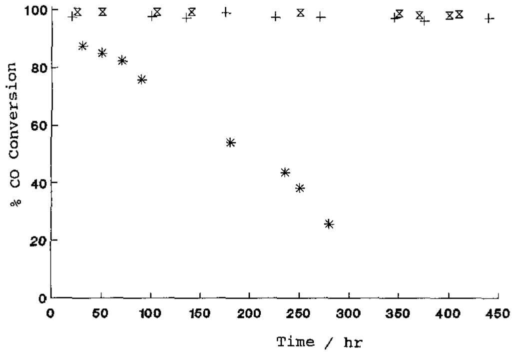

FIG. 8. Stability of catalysts using coal-derived feed gas containing 240 ppm sulphur. CO GHSV = 510 h^{-1}, symbols as in Fig. 7.

standard water–gas shift reaction conditions adopted in this study (350°C, CO GHSV = 510 h^{-1}, $CO:N_2:H_2O$ = 1 : 1 : 4.5) the catalyst was observed to comprise only the spinel phase and no cobalt metal was present in used catalysts.

Kinetic Studies

A study of the kinetics of a reaction can often prove to be a useful probe into the reaction mechanism. However, it is necessary that kinetic results for this purpose are obtained under reaction conditions where diffusion limitations or high reactant conversions are not present. The existence of diffusion limitations can be elucidated by consideration of the apparent activation energy (E_a). For temperatures ≤300°C, E_a for the Co : Cr = 3 : 1, Co : Mn = 1 : 1, and Cu : Mn = 1 : 1 catalysts was 168, 89, and 55 kJ mol^{-1}, respectively. Values of this magnitude are indicative that diffusion limitations are not evident. To confirm this a further series of tests was conducted (*29*). In particular, the rate of product formation was linearly dependent on the reactant feedrate and a plot of rate versus $T^{1/2}$ was found to be nonlinear. At temperatures >300°C, E_a was found to be considerably lower and typically <15 kJ mol^{-1} and the rate was now proportional to $T^{1/2}$; hence, it was concluded that at temperatures >300°C diffusion limitations were present. Consequently, all subsequent kinetic and model reagent studies were carried out at temperatures ≤300°C.

The effect of the partial pressure of H_2O on the rate of H_2O conversion was investigated for Co : Cr = 3 : 1 at 261°C, Co : Mn = 1 : 1 at 275°C, and Cu : Mn = 1 : 1 at 229°C, and the results are shown in Fig. 9. These experiments were carried out with a constant partial pressure of CO of 28.2 kPa. An inert diluent was utilised to ensure that the total gas flow rate for all experiments was held at a fixed value. The results demonstrate that the rate of H_2O conversion is linearly dependent on the partial pressure of H_2O, indicating that the reaction over all three catalysts is first order in water concentration.

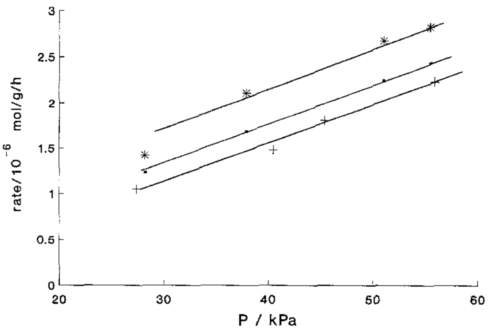

FIG. 9. Rate of H_2O conversion as a function of P_{H_2O} at constant P_{CO}; (*) Cu : Mn = 1 : 1, 229°C; (□) Co : Mn = 1 : 1, 275°C; (+) Co : Cr = 3 : 1, 261°C.

The effect of CO partial pressure on the rate of CO conversion was also investigated using the same reaction temperatures and a fixed water feed rate of 2.72 g H_2O/g catalyst h. From the results presented in Fig. 10 it is apparent that the Cu : Mn = 1 : 1 catalyst exhibits a significantly different relationship between the CO partial pressure and the rate of reaction compared to the other catalyst systems.

Reaction of Model Reagents

The mechanism of the water–gas shift reaction has been well studied for a range of

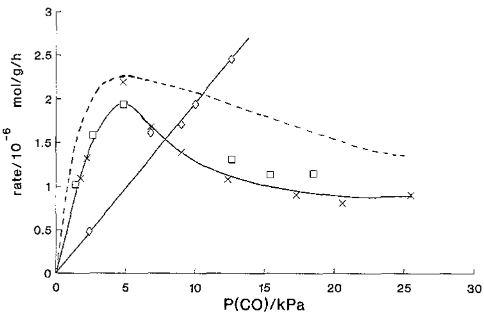

FIG. 10. Rate of CO conversion as a function of P_{CO} at constant P_{H_2O}; (◇) Cu : Mn = 1 : 1, 229°C; (□) Co : Mn = 1 : 1, 275°C; (×) Co : Cr = 3 : 1, 261°C. Solid line, experimental data; dashed line, fit to Eq. 2 with *a* = 1.66 kPa and *b* = 1.82 × 10^3 kPa.

TABLE 3

Reaction of Formic Acid

Catalyst	Time on line (min)[a]	Reaction effluent analysis (% by mass)				
		H_2	CO	CO_2	CH_4	HCOOH
Co : Mn = 1 : 1	10	0.002	—	—	0.057	99.94
	54	0.005	—	—	0.068	99.92
	134	0.003	—	—	0.043	99.95
	260	0.003	—	—	0.025	99.97
Co : Cr = 3 : 1	12	0.004	—	—	0.10	99.89
	32	0.007	—	—	0.15	99.84
	48	0.011	—	—	0.085	99.89
	76	0.005	—	—	0.059	99.94
	129	0.003	—	—	0.046	99.95
Cu : Mn = 1 : 3	60	0.20	—	2.0	0.018	97.65
	105	0.97	—	3.7	0.010	95.37
	120	2.1	—	4.0	0.007	93.86
	180	3.0	—	3.7	—	93.03
	220	3.7	—	4.9	—	91.38
	245	2.7	—	3.7	0.008	93.56

[a] Catalyst temperature = 150°C; —, not detected.

catalysts (*1–4*) and a central intermediate in a number of the mechanisms proposed is a surface formate species. To test this possibility, the decomposition of formic acid was investigated at temperatures below which formic acid thermally decomposes (i.e., <200°C), and the results are given in Table 3. Under all conditions tested formic acid did not react over the Co : Mn = 1 : 1 or Co : Cr = 3 : 1 catalysts to form H_2 and CO_2. In contrast, formic acid did decompose to H_2 and CO_2 over the Cu : Mn = 1 : 3 catalyst.

As an additional probe of the reaction mechanism of the water–gas shift reaction with these catalysts, methanol and ethanol were individually reacted with CO under a range of experimental conditions and the results for methanol are given in Table 4. Ethanol–CO mixtures were not particularly reactive and the only products observed under all conditions tested for the Co : Cr, Co : Mn, and Cu : Mn catalysts were ethene and ethanal. However, for CH_3OH–CO mixtures methyl formate was observed as a significant product for all three catalysts, although only at low conversions. The production of methyl formate was not particularly long lived for the cobalt-containing catalyst, but at reaction times of ca. 1.5 h the Cu : Mn = 1 : 3 catalyst still gave significant amounts of this product.

In addition to methyl formate significant levels of H_2 and CO_2 were observed during the reaction of CH_3OH–CO over the Cu : Mn = 1 : 3 catalyst. The possibility of the water–gas shift reaction occurring during the reaction is discounted, since the methanol was dried prior to reaction. In view of this, it is considered that methanol decomposition to form CO and H_2 could be a probable source of H_2 as product. In addition, direct decomposition of methanol to H_2, CO_2, and C may also be possible. Subsequent catalyst analysis confirmed that significant carbiding of the Cu : Mn = 1 : 3 catalyst occurred during the CH_3OH–CO cofeeding experiment.

DISCUSSION

Comparison of Catalyst Performance

The results of this study indicate that cobalt chromium oxide and cobalt manga-

TABLE 4

Reaction of CH_3OH–CO

Catalyst	Time on line (min)	Selectivity of gaseous organic phase (% by mass)[a]			
		CH_4	CH_3OCH_3	CH_3OH	HCO_2CH_3
Co : Mn = 1 : 1[b]	9	2.68	1.53	81.8	14.0
	24	0.63	4.17	67.7	27.5
	41	0.31	2.22	81.8	15.6
	59	0.67	3.72	95.6	—
	90	0.14	0.61	99.2	—
Co : Cr = 3 : 1[b]	30	2.11	—	97.1	0.82
	40	1.56	—	97.4	1.08
	50	0.60	—	98.1	1.27
	60	0.61	—	97.4	1.97
	70	0.39	—	98.4	1.18
	80	0.47	—	97.9	1.60
Cu : Mn = 1 : 3[c]	20	0.02	—	99.0	0.95
	30	0.31	—	85.7	10.3
	40	0.68	—	84.5	14.9
	50	0.35	—	86.9	12.7
	70	0.40	—	86.8	12.8
	90	0.23	—	92.3	7.5

[a] After 99% of methanol in reactor gaseous effluent collected in trap at 0°C.

[b] Reaction temperature 150°C.

[c] Reaction temperature 200°C.

nese oxide catalysts can give high-activity, long-lived catalysts for the high-temperature water–gas shift condition. Both these catalysts demonstrated significantly higher activity than the commercial iron chromium oxide catalyst under comparable reaction conditions at 250–300°C. For the cobalt chromium oxide catalyst (Co : Cr = 3 : 1) CO conversions approaching equilibrium values were observed at 300°C, whereas for the cobalt manganese oxide (Co : Mn = 3 : 1) this was observed at 350°C, and this difference in activity can be mainly ascribed to surface area differences. Of particular importance is the observation that both these cobalt catalyst systems are not sensitive to the presence of up to 240 ppm feedstock sulphur impurities (H_2S and COS), and high catalyst activity was maintained in the presence or absence of feedstock sulphur. It is known that the commercial iron chromium oxide catalyst does exhibit some sulphur sensitivity, losing ca. 50% of its activity on total sulphiding (*8*). By comparison, the copper manganese oxide catalysts demonstrate lower activity than the cobalt-containing catalysts and also demonstrate significant sensitivity to the presence of feedstock sulphur compounds. Unfortunately, the high-activity cobalt chromium oxide catalysts demonstrate significant CO conversions to methane and further work is required to overcome this disadvantage. However, potassium carbonate-promoted cobalt manganese catalysts exhibit high sustained water–gas shift activity, together with negligible methane formation. It is therefore considered that these high-activity, sulphur-tolerant water–gas shift catalysts could be of value in processing CO–H_2O reactant mixtures derived from the gasification of coal.

Catalyst Structure and Role of K^+ Promoter

Detailed structural studies for the cobalt manganese oxide and copper manganese oxides have been reported by us previously (*10*). For these catalysts spinel phases were also observed to be the major catalyst component following calcination and prior to reduction. For the copper manganese oxide spinel phase, the copper was observed to occupy the tetrahedral sites exclusively, whereas for the cobalt manganese spinel the cobalt and manganese ions did not occupy either the tetrahedral or the octahedral sites exclusively. However, the major difference for these two catalyst systems was observed following reduction in hydrogen and reaction under water–gas shift conditions. Both the cobalt manganese oxide and the copper manganese oxide catalysts were found to comprise either cobalt or copper metal supported on MnO. This is a direct contrast to the cobalt chromium oxide catalyst when no cobalt metal is observed following reaction. This observation can be used to explain the different effects observed for the addition of K_2CO_3 to cobalt chromium oxide and cobalt manganese oxide catalyst. For cobalt manganese oxide catalysts addition of 1% K_2CO_3 increases the catalytic activity and decreases the rate of by-product methane formation (Fig. 5). K^+ increases the rates of both the water–gas shift reaction and the methane-forming reactions; however, at higher temperatures the water–gas shift reaction becomes dominant. This implies that potassium ions selectively poison the methanation active sites due to the greater steric requirement. This is supported by the measured surface areas of the used catalysts: 0% K^+, 64.0 $m^2 g^{-1}$; 1% K^+, 62.7 $m^2 g^{-1}$; 2% K^+, 52.5 m^2 g^{-1}. For the cobalt chromium oxide, addition of 1% K_2CO_3 leads to a decrease in catalytic activity, as well as methane formation (Fig. 6). Cobalt supported on chromia is almost certainly composed of isolated cobalt ions under water–gas shift reaction conditions. (Indeed, extremely high temperatures and severe reducing conditions are required to produce metallic cobalt (*30*)). The steric blocking effect of potassium is therefore much greater on such a catalyst with highly dispersed active centres, whereas islands of metallic cobalt in cobalt manganese oxide will be much less affected.

Kinetic Studies

The kinetic data presented in this paper indicate that the rate of H_2O conversion is linearly dependent on P_{H_2O} for all three catalysts. This indicates that the reaction is first order in water concentration for these catalysts. The rate of CO conversion, r_{CO}, was found to be linearly dependent on the CO partial pressure for the Cu : Mn = 1 : 1 catalyst. Hence, the overall rate of reaction over the copper manganese catalyst is given by the expression

$$r_{CO} = kP_{CO} \cdot P_{H_2O}. \qquad (1)$$

However, for the Co : Cr = 3 : 1 and Co : Mn = 1 : 1 catalysts, the rate of CO conversion initially increases with increasing CO partial pressure, but then declines to a steady value. The observation of a maximum rate with increasing CO partial pressure is possibly indicative of a Langmuir–Hinshelwood reaction mechanism for which the rate-determining step involves the reaction between two surface-adsorbed intermediates derived from gas phase CO and H_2O. At constant H_2O partial pressure, the variation of reaction rate r_{CO} with P_{CO} for such a mechanism is given by the expression

$$r_{CO} = a\,P_{CO}/(1 + bP_{CO})^2. \qquad (2)$$

Although such an expression predicts that a maximum for r_{CO} should be observed, it does not fit the observed rate data particularly well (Fig. 10). The observed variation in r_{CO} with P_{CO} is therefore not wholly consistent with a simple Langmuir–Hinshelwood biomolecular reaction mechanism occurring with the Co : Cr = 3 : 1 and Co : Mn = 1 : 1 catalysts. It is possible that a number of reaction pathways are feasible, the dominance of one particular mechanism being dependent on P_{CO}. For example, the Langmuir–Hinshelwood bimolecular reaction mechanism could occur at low to medium P_{CO} and an alternative mechanism could occur at high P_{CO}.

Initial inspection of these rate data would lead to the conclusion that the different behaviour of r_{CO} with P_{CO} for the copper and cobalt catalysts could imply that different mechanisms were occurring for these catalysts. However, if $b \ll 1$, i.e., CO adsorption is weak, Eq. (2) reduces to a first-order rate expression,

$$r_{CO} = a\,P_{CO}.$$

This is the rate equation observed for copper manganese catalysts at constant P_{H_2O}, and hence the differences in kinetic behaviour observed for the copper and cobalt catalysts could be explained in terms of differences in CO chemisorption.

Reaction of Model Reagents

The reaction of formic acid over the three catalyst systems showed that the copper manganese oxide catalyst demonstrates significantly different behaviour compared to the other two systems. The decomposition of formic acid on the Cu:Mn = 1:3 catalyst is in agreement with previous studies (*31, 32*) for the commercial Cu/ZnO commercial low-temperature shift catalyst. This is consistent with the structural studies of the copper manganese oxide catalyst which have shown that the catalyst comprises copper metal supported on MnO, since copper metal is also known to be a component of the reduced copper zinc oxide catalyst (*6*). It is possible that the difference in the behaviour of the cobalt and copper-containing catalysts may be due to differences in the structure of the surface formate on adsorption of formic acid. However, it is also feasible that a similar species is formed on all three metal catalysts, but that only on the copper surface does decomposition of the surface formate occur to produce CO_2 and H_2. Hence the differences observed can be attributed to differences in the reactivity of the surface formate intermediates.

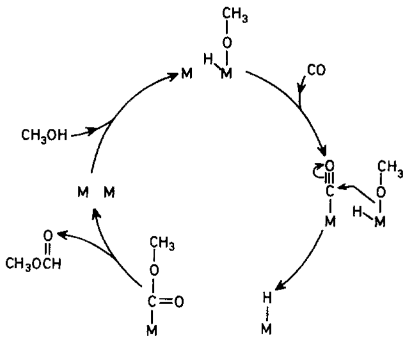

FIG. 11. Mechanism of formation of methyl formate.

The reaction of CH_3OH–CO mixtures resulted in the formation of methyl formate for all three catalysts. The formation of methyl formate from the reaction of CH_3OH–CO is well known for other catalyst systems, particularly at higher reaction pressures (*33, 34*). The product is considered to be formed via an oxidative addition mechanism according to Fig. 11. In this mechanism methanol dissociatively adsorbs at the surface to give a methoxy group. A similar pathway could be available for ethanol adsorption, as shown in Fig. 12, but now β-elimination to yield ethene and oxidation to ethanal are the more facile reaction pathways compared to a subsequent CO insertion, hence accounting for the absence of ethyl formate as a reaction product.

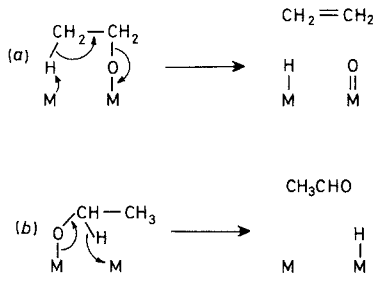

FIG. 12. Mechanism of ethanol conversion.

Reaction Mechanism

A number of previous studies have considered the mechanism of the water–gas shift reaction for the current commercial iron chromium oxide catalyst (*35–37*) and the copper–zinc oxide/alumina catalyst (*38*) and over bulk oxides (*39*). In general there are two mechanisms that have been proposed, namely, a dissociative mechanism proceeding via a lattice or adsorbed oxygen intermediate and associative mechanism which involves an adsorbed formate intermediate. The key difference in these two mechanistic proposals involves the pathway by which water adsorbs onto the surface. In the dissociative mechanism water dissociates to form a surface-adsorbed oxygen species which subsequently reacts with CO to form CO_2.

$$H_2O(g) + * = H_2 + O(a) \tag{3}$$

$$CO(g) + O(a) = CO_2, \tag{4}$$

where * is a vacant surface site. Reaction (3) may occur via a hydroxyl intermediate. For the associative mechanism, adsorbed CO reacts with a surface hydroxyl species to form an adsorbed formate intermediate which subsequently decomposes to CO_2 and H_2. It is considered that the experimental data for the kinetic studies and the use of model reagents can be instructive in elucidating which of these mechanisms occurs with the three catalysts investigated. In particular, the data concerning the reaction of model reagents are considered to be highly significant with respect to the mechanism of the water–gas shift reaction over the catalyst systems investigated. For methanol and ethanol, these reagents of the form ROH can be considered as models for water (HOH) in which an alkyl group replaces hydrogen. For all three catalyst systems with methanol as reagent a major product observed was that from the oxidative addition of a surface methoxy intermediate to a surface CO. For ethanol, elimination of ethene which can be considered to be due mainly to β-elimination from a surface ethoxy group was observed. By analogy with these model studies water would then be expected to be dissociatively adsorbed to give surface OH and H intermediates. By further analogy with the observed reaction of CH_3OH–CO, adsorbed CO could react with the surface OH, leading to the formation of a surface formate. Hence, on this basis an associative mechanism can be considered feasible for all three catalysts. Further experimental evidence concerning the role of formate intermediates comes from the reaction of formic acid over the three catalyst systems. For the copper manganese oxide catalyst, formic acid was found to decompose to CO_2 and H_2, whereas in the temperature range investigated, formic acid did not decompose over the cobalt-containing catalysts. As discussed previously, formic acid can be expected to adsorb on all three catalysts and these results indicate that the intermediate formed is much less stable in the copper catalyst than on the cobalt catalyst systems. Such an observation is in line with the known low-temperature shift behaviour of copper catalysts (*6–8*).

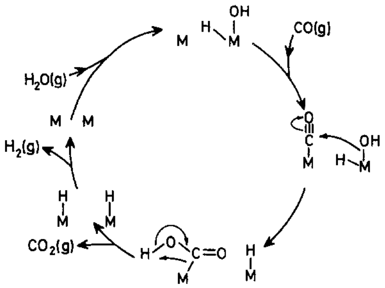

FIG. 13. Proposed mechanism for the water–gas shift reaction for cobalt manganese oxide, cobalt chromium oxide, and copper manganese oxide catalysts.

On the basis of these model studies, we propose a reaction mechanism for the water–gas shift reaction for the cobalt and copper catalysts investigated, which is shown in Fig. 13. It is proposed that water dissociatively adsorbs onto a surface site with subsequent adsorption of CO onto an adjacent site, followed by oxidative addition of the surface bonded OH to CO. The reaction of CH_3OH–CO to form methyl formate is considered to be evidence in support of this proposed step. Subsequent reaction could occur via β-elimination of the surface formate intermediate to give gas phase CO_2 and surface hydride. Combination of the surface hydride would then lead to the formation of hydrogen. The decomposition of such a metallocarboxylic acid to yield CO_2 is well supported in the reaction of numerous organometallic compounds (*40–42*) following its initial demonstration for $IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$ (*43*). For the cobalt manganese oxide and the cobalt chromium oxide the kinetic data support this reaction mechanism, since this is consistent with a bimolecular reaction between adsorbed CO and surface OH. It can be expected that the decomposition of the surface formate intermediate could be the rate-determining step by analogy with the model experiments concerning formic acid decomposition.

The observation for the cobalt-containing catalysts that r_{CO} becomes constant at high P_{CO} when P_{H_2O} is held constant could be due to CO successfully competing with H_2O for adsorption sites, such that the concentration of surface hydroxy groups, a key intermediate, becomes limited. Alternatively, as discussed previously, a different mechanism could occur at high P_{CO}, and it is possible that under these conditions a dissociative mechanism could occur in which the reaction occurs via Eqs. (3) and (4). The reaction rate for such a mechanism would depend on the competition between the H_2O and the CO at the catalytic surface sites. At high P_{CO}, such a mechanism would lead to a constant value for r_{CO}. It is therefore possible that for the two cobalt catalysts at low P_{CO} the proposed surface formate mechanistic pathway is dominant, but at high P_{CO} the dissociative pathway may also operate competitively, or indeed, become dominant.

The differences observed between the reaction over the copper and cobalt-containing catalysts may be indicative that different reaction mechanisms occur for these catalysts. However, it could also be due to a different reaction step being rate controlling. For the copper catalysts, the experiments with formic acid indicate that decomposition of a surface formate may be more facile than for a cobalt catalyst. In addition, the heat of adsorption of CO on Co and Cu are very different (*44*), and for the copper catalyst the adsorption of CO may be the rate-determining step. In this case the proposed mechanism would also be consistent with the observed kinetic data for the copper manganese oxide, since it has previously been discussed that the differences observed in the kinetic data can be accounted for in terms of differences in CO chemisorption.

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REFERENCES

1. Temkin, M. I., *Adv. Catal.* **28,** 263 (1979).
2. Ford, P. C., *Acc. Chem. Res.* **14,** 31 (1981).
3. Newsome, D. S., *Catal. Rev. Sci. Eng.* **21,** 275 (1980).
4. Laine, R. M., and Wilson, R., "Aspects of Homogeneous Catalysis" (R. Ugo, Ed.), Vol. 5, p. 217. Reidel, Dordrecht, 1985.
5. Chinchen, G. C., Logan, R. H., and Spencer, M. S., *Appl. Catal.* **12,** 69, 89, 97 (1984).
6. Chinchen, G. C., Spencer, M. S., Waugh, K. C., and Whan, D. A., *J. Chem. Soc. Faraday Trans. 1* **83,** 2193 (1987).
7. Petrini, G., Montino, F., Bossi, A., and Garbassi, F., "Preparation of Catalysts III" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), p. 835. Elsevier, Amsterdam, 1983.
8. Twigg, M. V., "Catalyst Handbook." Wolfe, Frome, England, 1989.
9. Hou, P., Mecker, D., and Wise, H., *J. Catal.* **80,** 280 (1983).
10. Gottschalk, F. M., and Hutchings, G. J., *Appl. Catal.* **51,** 127 (1989).
11. Gottschalk, F. M., and Hutchings, G. J., *J. Chem. Soc. Chem. Commun.*, 123 (1988).
12. Gottschalk, F. M., Copperthwaite, R. G., van der Riet, M., and Hutchings, G. J., *Appl. Catal.* **38,** 103 (1988).
13. Hutchings, G. J., Gottschalk, F. M., Hunter, R., and Orchard, S. W., *J. Chem. Soc. Faraday Trans. 1* **85,** 363 (1989).

14. van der Riet, M., Hutchings, G. J., and Copperthwaite, R. G., *J. Chem. Soc. Chem. Commun.* 798 (1986).

15. Copperthwaite, R. G., Hutchings, G. J., van der Riet, M., and Woodhouse, J., *Ind. Eng. Chem. Res.* **26,** 869 (1987).

16. Senes, M. P., Pottler, M., and Gourdier, J. F., Ger. Offen. 2329962 (1974).

17. Fattakhova, Z. T., Berman, A. D., and Kadenatsi, B. M., *Kinet. Katal.* **20,** 651 (1979).

18. Kennedy, L. A., *Energy Res.* **8** (1983).

19. Vorob'ev, V. N., Iskandarov, Sh. A., Abidova, M. F., and Talipov, G. Sh., *Kinet. Katal.* **15,** 1045 (1974).

20. Roth, J. F., US Patent 3493325 (1970).

21. Koberstein, E., and Lakatos, E., Ger. Offen. 1283247 (1868).

22. McKinzie, H., Lester, J. E., and Palilla, F. C., US Patent 4147763 (1979).

23. Rajwar, D. P., Ghosh, A. K., and Guha, D., *in* "Proceedings, 7th National Symposium on Catalysis)," (T. P. Rao, Ed.), p. 573. Wiley, New York, 1985.

24. Mekhandzhiev, D., Zhecheva, E., Fattakhova, Z. T., and Berman, A. D., *Kinet. Katal.* **27,** 889 (1986).

25. Kadenatsi, B. M., Spiridonov, K. N., Shibanova, M. D., and Kushnerev, M. Ya., *Kinet. Katal.* **19,** 1259 (1978).

26. Andreev, A. V., Idakiev, V., Mihajlova, D., and Shopov, D., *Appl. Catal.* **22,** 385 (1986).

27. Grenoble, D. C., Estadt, M. M., and Ollis, D. F., *J. Catal.* **67,** 90 (1981).

28. Dry, M. E., "Catalysis—Science and Technology," Vol. 1, p. 159. Springer-Verlag, Berlin, 1981.

29. Bond, G. C., "Heterogeneous Catalysis: Principles and Applications," p. 58. Clarendon Press, Oxford, 1987.

30. Colley, S. E., Copperthwaite, R. G., and Hutchings, G. J., *Catal. Today* **9,** 203 (1991).

31. van Herwijnen, T., and de Jong, W. A., *J. Catal.* **63,** 83 (1980).

32. Van Herwijnen, T., Guczalski, R. T., and de Jong, W. A., *J. Catal.* **63,** 94 (1980).

33. Peltzmann, A., *Oil Gas J.* **79,** 103 (1981).

34. Trimm, D. L., and Wainwright, M., *Catal. Today* **6,** 261 (1990).

35. Kul'kova, N. V., and Temkin, M. I., *Zh. Fiz. Chim.* **23,** 695 (1949).

36. Boreskov, G. K., Yureva, T. M., and Sergeeva, A. S., *Kinet. Katal.* **11,** 1476 (1970).

37. Kubsh, J. E., and Dumesic, J. A., *AIChE J.* **28,** 793 (1982).

38. Chinchen, G. C., and Spencer, M. S., *J. Catal.* **112** 325 (1988).

39. Rethwisch, D. G., and Dumesic, J. A., *Appl. Catal.* **21** 97 (1986).

40. Grice, N., Kao, S. C., and Pettit, R., *J. Am. Chem. Soc.* **101,** 1627 (1979).

41. Catellani, M., and Halpern, J., *J. Inorg. Chem.* **19,** 566 (1980).

42. Sweet, J. R., and Graham, W. A. G., *Organometallics* **1,** 982 (1982).

43. Deeming, A. J., and Shaw, B. L., *J. Chem. Soc. A* **443** (1969).

44. Bowker, M., *in* "Fuel Additives and Extenders" (G. J. Hutchings and M. S. Scurrell, Eds.) Elsevier, Amsterdam, 1992, *Catal. Today,* in press.